Development of a Thermodynamic Model for Zinc, Lead and Cadmium in Saline Solutions

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Remark

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Editorial Remark

This report is an English translation of the revised report ‘Entwicklung eines thermodynamischen Modells für Zink, Blei und Cadmium in salinaren Lösungen‘ GRS-219 rev. Out of practical reasons, some figures were not translated.

Descriptors

Data Basis, Heavy Metals, Modelling, Thermodynamics

Content

Editorial remark

The present document is an edited machine-translated version of German language GRS report 286 (revised edition). Because the original computer programs used to generate many of the diagrams and formula in chapters 2 to 11 was no longer available, it would have required a great deal of effort to recreate these items with English axis titles, legend entries and indices on another platform. Instead, most diagrams and formula were chosen to be left unchanged. To allow the English-speaking reader to understand their content, a list of German terms with English translation is provided below.

Tab. 1.1 German terms used in diagrams and formulas and their English translations

German term	English translation
Anteil	Percentage
Berechnet	Calculated
Diese Arbeit	This work
Eigenvektor	Eigenvector
Intensität	Intensity
Isopiestische Konzentrationen	Isopiestic concentrations
Konzentration	Concentration
Löslichkeitskurve	Solubility curve
Osmotischer Koeffizient	Osmotic coefficient
Signalstärke	Signal strength
Spezies	Species
Wellenzahl	Wavenumber

1 Introduction

1.1 Background and objective

The impact of water on surface and underground waste disposal sites or other contaminated sites such as mining tailings piles etc. can cause a mobilisation of heavy metals and other pollutants. Therefore, groundwater and drinking water resources may be at risk. To assess the risk potential, it is necessary to know as precisely as possible the physical and chemical processes that occur during water inflow. This requires not only qualitative knowledge of reaction and transport phenomena, but rather high-quality data backed up by experiments and qualified estimates that allow a quantitative prediction of pollutant mobilisation. A comprehensive understanding of the system, combined with a reliable prediction model, also provides the tools to develop or optimise strategies to minimise or avoid such releases.

Heavy metals that are easily mobilised include zinc, cadmium, and lead, some of which are present in the waste in quite high concentrations (BRASSER 1991) and occur in many contaminated sites. Leaching can result in solution concentrations that are above various limit or guideline values.

For weakly mineralised solutions with ionic strengths < 0.5 mol/kg, several geochemical prediction models are available, which have already been used successfully for many inorganic pollutants. For higher concentrated solutions, on the other hand, the tools for geochemical modelling of the processes taking place are not yet as well developed. That is mainly due to the incomplete database for solutions containing zinc, cadmium, and lead with high ionic strengths. In particular, the database has gaps in the neutral and basic pH range and in the consideration of complexes with the anions of saline solutions.

The aim of the present project was to create a widely applicable database for geochemical modelling of solutions containing zinc, cadmium, and lead at low to high ionic strengths at 25 °C. It was based on existing databases, which were previously only suitable for the weak acid range. For this purpose, literature data was to be evaluated, and missing data should be determined by experimental investigations. The database should be usable for geologically influenced solutions containing pollutants in the pH range between 2 and 12 and consider the speciation of the metal ions in solution, in particular their pronounced tendency to form chloro and hydroxo complexes. The solubility constants of mineral phases containing the anions chloride, sulphate, hydroxide, and carbonate should be determined based on a critical evaluation of literature and laboratory data. This project should provide a versatile tool for geochemical modelling of contaminated fluids of geogenic origin, with the potential to develop or optimise remediation measures for emission events, if necessary.

1.2 Thermodynamic database for geochemical model calculations in saline solutions

Geochemical model calculations based on equilibrium thermodynamics have been successfully used for many years to interpret and simulate conditions and processes in aquatic systems (GRENTHE and PUIGDOMENECH 1997). For example, they can be used to determine the speciation form of water constituents, whether thermodynamic precipitation or dissolution of certain minerals is possible, or how water composition changes on contact with a solid phase.

For this purpose, the thermodynamic activities of all reaction partners involved must be calculated. The activity of a species is calculated from the product of the respective species concentration and the activity coefficient. This is a correction factor that describes the deviation from the ideal behaviour of a solution, and in turn depends on the solution composition. Ionic solutions deviate strongly from the ideal behaviour due to the electrostatic interactions of the ions. While various general and simple calculation methods based on the total ionic strength exist for dilute solutions (simple and extended Debye-Hückel approaches), the use of models based on specific interactions between the solution components is recommended for ionic strengths > 0.5 mol/kg. Particularly well suited for concentrated salt solutions is the set of semi-empirical formulae developed in the 1970s by Pitzer and co-workers for calculating the activities of the solution constituents (a good summary can be found in PITZER, 1991). In addition to a general Debye-Hückel term, they contain a series of empirical parameters that can be derived from measurement data, the so-called Pitzer coefficients.

The starting point for all further considerations was the database of HARVIE et al. (1984), with which the chemical ratios and physical properties of solution/solid equilibria of the system H - Na - K - Mg - Ca - HCO_3 - CO_3 - Cl - SO_4 - OH - H_2O covering practically all essential ground and surface waters at 25 °C can be described with excellent reliability.

This database has already been extended to include solubility constants and Pitzer ion interaction coefficients for neutral to acidic solutions containing zinc, cadmium, and lead

(HERBERT and MÖNIG 1996; HAGEMANN 1999; HERBERT et al. 1999). Despite significant progress, limitations still exist. In agreement with earlier work (ANSTISS and PITZER 1991), it became apparent that the description of the thermodynamic properties of zinc as well as cadmium in chloride solutions is only possible to a very limited extent without explicit consideration of complexes. Although FILIPPOV et al. (1987, 1991) were able to show, using the example of the system Na, Cd||Cl, SO_4 - H_2O, how the explicit consideration of chloro complexes can be avoided by extending the Pitzer equations, according to the co-author Mr. Rumyantsev[1] a transfer to the analogous system K, Cd||Cl , SO_4-H_2O was only partly possible.

1.3 Procedure

The overarching goal of creating a broadly applicable database mentioned in the previous section can be structured as follows:

1. Development of a database for neutral to acidic saline solutions containing zinc, cadmium, and lead. The initial assumption was that the formation of chloro and sulphato complexes does not need to be explicitly considered. For lead, all the necessary data were already available thanks to HAGEMANN (1999). For zinc and cadmium, specific data gaps were identified in HERBERT and MÖNIG (1996). These are the physicochemical properties of ternary chloride-containing solution systems, knowledge of which is necessary to determine ternary interaction parameters. The previous evaluations had shown that solubility experiments are not useful because of the very high solubility of $ZnCl_2$ and $CdCl_2$, as no conclusions can be drawn for environmentally relevant undersaturated solutions. The investigation of undersaturated solutions can be advantageously achieved with isopiestic measurements. In suitable cases with zinc and cadmium sulphates, solubility tests were also carried out.

2. Investigation of the complex formation of zinc, lead, and cadmium with chloride. A detailed investigation of lead chloro complexes was already conducted by HAGEMANN (1999). It should be examined whether an improvement of the description of chloro complex formation is possible by applying advanced mathematical-statistical methods to UV measurements. Chloro complexes of zinc and cadmium, on the other

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[1] Personal communication

hand, can be better investigated by Raman spectroscopy. The data published in the literature so far were not sufficient for a more in-depth evaluation. Based on this and in combination with the measurement data collected under point 1, an attempt should then be made to develop a parameter set for the interaction of the chloro complexes with the cations of the seawater system

3. Creation of a consistent thermodynamic database for compounds of zinc, lead and cadmium with oxide, hydroxide, carbonate, as well as basic chlorides, sulphates, and carbonates. All solid compounds of this type are sparingly soluble and can therefore already be investigated in dilute solutions, in which the application of the Pitzer formalism is generally not yet necessary.

2 Isopiestic investigation of zinc- and cadmium-containing solutions

2.1 Experimental principles

The aim of isopiestic measurements is to determine the water activity of one or a series of solutions. The basic experimental principle is that in a closed container (e.g., a stainless-steel pot) two or more aqueous solutions in separate cups can be brought into thermodynamic equilibrium by exchanging water and heat between them via the atmosphere and a heat conducting metal body until the partial pressure of water of all solutions and thus their water activity is the same in all cups. If the water activity of one solution is known or can be calculated, this value also applies to all other solutions.

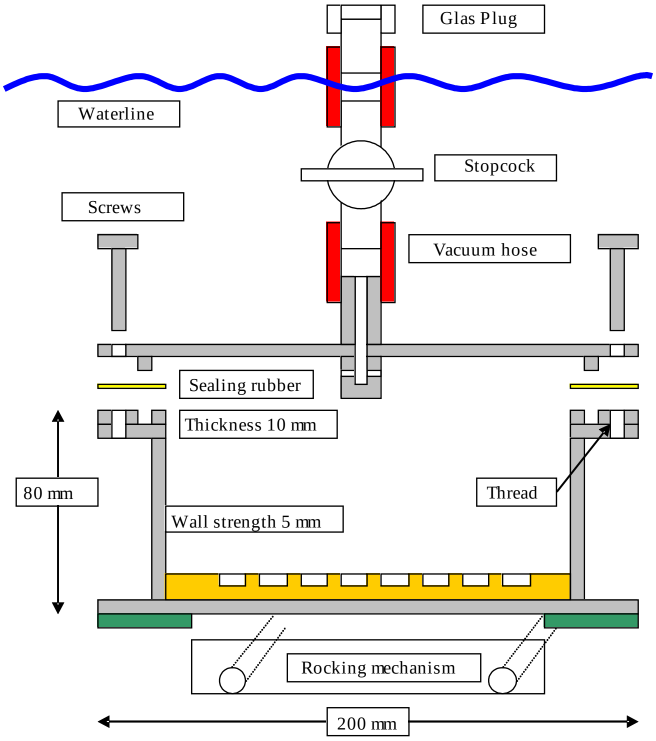

Fig. 2.1 Structure of an isopiestic pot

For the isopiestic measurements in this work, a steel pot that can be closed by a lid was used (Fig. 2.1). Its temperature was controlled at 25.0 °C in a water bath. The pot contained several solution-filled cups made of tantalum. On the one hand, they are very corrosion-resistant even to strongly saline solutions, and on the other hand are sufficiently good heat conductors. To accelerate the equilibrium setting, the entire pot is permanently rocked.

The evaluation of the experiment is done exclusively by weighing. If the composition of the solutions used is known exactly, the composition of the solutions obtained at the end of the experiment can be determined easily and accurately by determining the difference in weight (due to loss or gain of water). The water activity is determined by using reference solutions. For these (NaCl, KCl, $CaCl_2$ or H_2SO_4) very accurate measurement data are already available in the literature. If the concentration of the reference solution is known at the end of the experiment, its water activity can be calculated. If all solutions are in osmotic equilibrium, the water activities of all other solutions are the same.

The isopiestic experiments were carried out in cooperation with the Chemical Institute of the University of St. Petersburg (Russia) by Mr. Rumyantsev. Experimental details, especially on the preparation of the stock solutions used and detailed descriptions of the weighing procedures can be found in the appendix (Appendix: Additional tables, p. 471 ff.).

2.2 Preparation and characterisation of stock solutions

2.2.1 $ZnCl_2$ stock solution

Preparation

The following compounds were used as starting substances:

- ZnO (suprapur, Merck)
- HCl ("special purity"), 10% and 36% aqueous solution
- H_2O (bidest.)

The preparation was based on the method of RARD and MILLER (1984). A slight excess of ZnO (about 100 g) was treated with 10% HCl (about 800 ml) for a few hours at about 60°C and the resulting solution was filtered. Addition of 10-20 ml water resulted in intense precipitation of white zinc hydroxy and oxychlorides. 36% HCl was added dropwise with continued stirring until the solution showed no precipitate. The solution was then heated to 80-90°C in an open beaker until it evaporated to about half its original volume (about 400 ml). The solution was diluted to the old volume by adding water. This procedure (water addition, precipitation test, acidification, evaporation, re-dilution) was repeated (about 20 times) until no more precipitation or turbidity was observed. This process took about two weeks. The yield was about 700 ml of a 20% $ZnCl_2$ solution. The solution was absolutely clear, even after a storage time of more than one year and even then, did not show any turbidity when water was added. It has been shown that the preparation of smaller amounts of stock solution is not practicable.

Chemical analysis (chloride determination)

The chloride analysis was carried out according to WILLIAMS (1979). The following substances were used: $AgNO_3$ (p.a.) as 5% aqueous solution, as well as HNO_3 (suprapur) as 35% and 0.01% aqueous solution.

The analysis consisted of the following steps:

1. Five samples of the stock solution are each placed in a weighing vial. The chloride content of each sample should be about 70 - 200 mg.
2. The weighing vials are closed with a lid and weighed immediately. The weight and mass of the weighed-in solution is calculated.
3. The samples are quantitatively transferred into beakers. 3 ml of HNO_3 (35%) and 100-150 ml of water (bidest.) are added. The same amount of HNO_3 and water is added to a separate beaker for the determination of the blank value.
4. A small excess of $AgNO_3$ solution is slowly added to each preparation at room temperature. From this point on, any direct light contact of the preparation must be avoided (see also: "Special notes").
5. Heat each batch to 90-95 °C and stir for 2-3 minutes (until complete coagulation of the precipitate). After this treatment, allow the solutions to cool and stand in a dark place for no less than 1-2 hours.
6. The precipitates are washed with cold 0.01 % HNO_3, decanted and filtered over previously weighed glass frits. The precipitate transferred to the frits is washed with aqueous, cold 0.01 % HNO_3 until the filtrate no longer shows a positive reaction to Ag^+ (with HCl).
7. The frits are each dried for 3-5 hours at 95- 98 °C and then at 130-180°C.

8. The frits are then left to cool in a desiccator and then weighed. The weight and mass of the AgCl are calculated from the results (the density of the solid AgCl is assumed to be 5.56 g-cm^{-3}).

The concentration of the $ZnCl_2$ stock solution was calculated according to the following formula:

$$C_{ZnCl2} = 100 \cdot (136.296 / (2 \cdot 143.323)) \cdot (M_{AgCl} - M_{blank}) / M_{smp} \qquad (2.1)$$

M_{AgCl}	Mass of AgCl precipitate
M_{blank}	Mass of precipitation in the blind test
M_{smp}	Mass of the stock solution sample
136.296	Molar masses of $ZnCl_2$
143.323	Molar masses of AgCl;
2	stoichimoetric coefficient of Cl in $ZnCl_2$.

The following points should be observed:

1. Each weighing vial should have a tight-fitting lid. The vial must be closed immediately after the sample has been added (procedure, point 1). Neglection of this this rule can cause serious errors.

2. To convert weights into masses (point 2), the solution density is required. This can either be determined directly (e.g., via the sample volume) or taken from suitable tables (e.g., NOVOTNÝ and SÖHNEL, 1988).

3. From the time of precipitation formation (point 6) onwards, all operations should be carried out under darkened conditions. Daylight and especially sunlight must be absolutely excluded. It is highly recommended to carry out the work in soft white light (but not in the light of fluorescent lamps). Neglect of this rule is a frequent cause of serious errors.

4. When transferring the precipitate into the frit (point 6), make sure that no precipitate remains (e.g., as a film) in the beaker. If there is any, it must be removed and transferred to the frit.

5. Before use, the frit must be washed, dried, and weighed under the same conditions as later after transfer of the precipitate (points 7 and 8).

6. Because of the possible colloid formation of the AgCl precipitate, the precipitate should be washed out with cold 0.01% HNO_3. Simple final washing with cold water is allowed.

7. After drying, the AgCl precipitate should be pure white with at most a very faint violet tint. If the precipitate has a violet or grey tint, repeat the analysis.

Chemical analysis (zinc determination)

The following chemicals were used:

- $(NH_4)_2HPO_4$ (p. a., 25 g to 250 ml water, as well as 1% solution)
- NH_4OH (p. a., as 5% aqueous solution)
- Ethanol (p. a., as 50 Vol% aqueous solution)
- Methyl red (acid-base indicator, as 0.1 % solution in 60% ethanol)
- Phenolphthalein (acid-base indicator, as 0. 1% solution in 60% ethanol)

Implementation

1. Five samples of the stock solution are placed in five weighed weighing vials. The zinc content of each solution should be about 100 mg.

2. The jars are sealed and weighed. Weight and mass are calculated.

3. The samples are quantitatively transferred into beakers. Distilled water (about 150 ml) is added together with 2- 3 drops of methyl red solution. Aqueous ammonia solution is added drop by drop (a white precipitate falls) until the pink colour of the solution changes to yellow (pH 6.2- 6.8, see notes). The same procedure is also carried out on a beaker with water, indicator but without sample (blank test).

4. Each solution is heated almost to boiling point and 30 ml of fresh $(NH_4)_2HPO_4$ solution is slowly added. After heating at 90- 95 °C for about half an hour and stirring several times, the precipitate turns into a crystalline form and collects at the bottom of the beaker. The solution should remain yellow, not turn pink again.

5. Leave the beakers at room temperature for 3-4 hours.

6. The precipitate is washed with 1% aqueous $(NH_4)_2HPO_4$ solution and decanted. The precipitate is then aspirated through weighed glass frits and washed again with %1 aqueous $(NH_4)_2HPO_4$ solution until there is no more reaction on chloride (with HNO_3+ $AgNO_3$). The precipitate is finally washed several times with aqueous ethanol to remove excess $(NH_4)_2HPO_4$.

7. The frits are first dried at 95-98 °C and then at 150 °C for 3-5 hours.

8. The frits are dried in a desiccator at weighing temperature. The weight and masses of $ZnNH_4PO_4$ are determined. The density of $ZnNH_4PO_4$ is 3.75 g-cm^{-3}.

The concentration of the stock solution c_{ZnCl2}, is obtained via the following formula:

$$C_{ZnCl2} = 100 \cdot (136.296 / 178.3986) \cdot (M_{ZnNH4PO4} - M_{blank}) / M_{smp} \qquad (2.2)$$

where $M_{ZnNH4PO4}$ is the mass of the $ZnNHPO_{44}$ precipitate, M_{blank} is the mass of the precipitate in the blank test, M_{smp} is the mass of the sample of the stock solution; 136.296 and 178.3986 are the molecular masses of $ZnCl_2$ and $ZnNH_4PO_4$.

Special remarks

1. The weighing vials should have a tight cap and should be closed as soon as possible after sampling. Failure to observe this rule can cause significant errors.

2. To convert the weights into masses (procedure point 2), the solution densities are needed. For this, either the sample volumes or tabulated density values are needed (e.g., from the work NOVOTNÝ and SÖHNEL, 1988).

3. The pH of the solutions (procedure point 3) should be controlled during precipitation. The solubility of the precipitate $ZnNH_4PO_4$ is negligible only at this starting pH.

4. Only fresh $(NH_4)_2HPO_4$ solutions should be used (procedure - point 4). Their suitability is tested in the following way: Addition of a few drops of phenolphthalein solution to the $(NH_4)_2HPO_4$ solution should give a very faint pink colouration. If the colouration is absent, dilute aqueous NH_4OH solution should be added until the colouration appears. A solution with intense colouration cannot be used.

5. Before washing the precipitate, the porous glass filters should be washed out, dried, and weighed under the same circumstances as later filled with precipitate (procedure points 7 and 8).

6. Instead of weighing the precipitate directly, it can also be calcined at 1000 °C to $Zn_2P_2O_7$ and then weighed.

The procedure is described in KOLTHOFF et al. (1969).

The concentration of the stock solution was 20.175 ± 0.008, mass % chloride and 20.178 ± 0.008, mass % zinc. The average concentration was thus 20.177 ± 0.008 mass %.

2.2.2 NaCl and KCl stock solutions

Preparation

The following chemicals were used:

- NaCl ("special purity", Russian)
- KCl (suprapur, Merck)
- H_2O (bidest.)

About 10 g of NaCl or KCl were added to about 90 ml of H_2O, stirred, and then filtered. About 100 g of the colourless solution was obtained for each salt.

Chemical analysis (gravimetric)

1. Several samples of the solution are placed in previously weighed weighing vials. The NaCl or KCl content in each sample should be about 150 -400 mg with no more than 2 - 3 ml of weighed stock solution.
2. The jars are sealed and weighed immediately. Weight and mass are calculated.
3. After drying at 95 -98 °C, the jars were heated at 150 - 250 °C for no less than 2-3 hours.
4. The weighing vials are cooled in the desiccator and then weighed. The weight and mass of the salt are determined. The densities of NaCl and KCl are 2.165 $g \cdot cm^3$ and 1.985 $g \cdot cm^3$ respectively.

Calculations

The concentration of the salt solution C_{MeCl} is calculated according to:

$$C_{MeCl} = 100 \cdot M_{salt} / M_{smp}, \qquad (2.3)$$

where M_{salt} is the mass of the salt after drying and M_{smp} is the mass of the solution sample.

The following points should be observed:

1. Before sampling (procedure point 1), the empty weighing vials should be warmed up and cooled down in the same way as later with sample (procedure point 3).
2. Each weighing vial should have a tight-fitting lid. The vial must be closed immediately after the sample has been added (procedure, point 1). Neglecting this rule can cause serious errors.
3. No solution quantities of more than 2 - 3 ml should be weighed in and dried (procedure, point 1), otherwise salt may "creep" out of the glass.
4. To convert weights into masses (point 2), the solution density is required. This can either be determined directly (e.g., via the sample volume) or taken from suitable tables (e.g., NOVOTNÝ and SÖHNEL, 1988).
5. One should not try to dry the solutions quickly at an elevated temperature (procedure point 3), otherwise solution splashing may occur.

The solution concentrations obtained were:

NaCl solution 1	9.0663 ± 0.0037 mass-%
NaCl solution 2	9.0512 ± 0.0025 mass-%
KCl solution	10.595 ± 0.004 ± mass %.

2.2.3 $MgCl_2$ and $CaCl_2$ stock solutions

Preparation

The following chemicals were used:

- $MgCl_2 \cdot 6H_2O$ (p. a., Merck)
- $CaCl_2 \cdot 4H_2O$ (suprapur, Merck)
- H_2O (bidest.)

About 18.7 g of $MgCl\text{-}6H_2O_2$ or about16.3 g of $CaCl_2 \cdot 4H_2O$ were added to about 81 ml of H_2O or 84 ml of H_2O, respectively, with constant stirring. The solution was filtered. About 100 ml of clear solution was obtained for each salt.

Chemical analysis

The chemical analysis was carried out via the Cl content according to the method described under $ZnCl_2$.

The concentration of $MgCl_2$ or $CaCl_2$ in the stock solution (c_{CaCl2} or c_{MgCl2}respectively) is calculated as follows:

$$C_{MgCl2} = 100 \cdot (95.211 / (2 \cdot 143.323)) \cdot (M_{AgCl} - M_{blanc}) / M_{smp} \qquad (2.4)$$

$$C_{CaCl2} = 100 \cdot (110.984 / (2 \cdot 143.323)) \cdot (M_{AgCl} - M_{blanc}) / M_{smp} \qquad (2.5)$$

where M_{AgCl} is the mass of the AgCl precipitate, M_{blanc} is the mass of the precipitate in the blank test, M_{smp} is the mass of the stock solution and 95.211, 110.984 and 143.323 are the molecular masses of $MgCl_2$, $CaCl_2$ and AgCl, respectively. 2 is the stoichiometric coefficient of Cl in $MeCl_2$.

The following concentrations were obtained for the stock solutions:

$MgCl_2$ solution:	8.7427 ±0.0033 mass-%
$CaCl_2$ solution:	9.9365 ± 0.0033 mass %

2.2.4 $ZnSO_4$ stock solution

Preparation

The following chemicals were used:

- $ZnSO_4 \cdot 7H_2O$ (p. a., Merck)
- H_2O (bidest.)

The details of the preparation are identical to the instructions for $MgCl_2$ and $CaCl_2$.

Chemical analysis (gravimetric)

The details of the analysis correspond to those of the NaCl and KCl solutions (see above), except for point 3:

3. After drying at 95 -98 °C, the weighing vials were heated at 420 - 440 °C for not less than 3- 4 hours.

The density of dry anhydrous zinc sulphate is 3.74 g cm^{-3}.

The composition of the stock solution is 24.554 ± 0.007 wt.%.

2.2.5 $MgSO_4$ stock solution

Preparation

The following chemicals were used:

- $MgSO_4 \cdot 7H_2O$ (GR for analysis, Merck)
- H_2O (twice distilled)

The details of the preparation correspond to those of the $ZnSO_4$ stock solution (see above).

Chemical analysis (gravimetric)

The details of the analysis correspond to those of the $ZnSO_4$ solution. The density of the solid anhydrous $MgSO_4$ is 2.66 g·cm^{-3}. The concentration of the stock solution is 18.864 ± 0.003 wt.-%.

2.3 Preparation of the batches for isopiestic measurements

2.3.1 Preparing the samples for the first measurement

1. The solution quantities required to prepare a series of sample solutions are calculated on the basis of available data on water activity and the concentrations of the stock solutions. It is assumed that the isoactivity lines in ternary systems are linear.

2. The necessary number of crucibles is washed and dried and closed with a lid. These are stored either in air or in a desiccator over water.

3. Each crucible is weighed.

4. The calculated amount of reference solution (NaCl or KCl) is placed in two or three cups and the cups are weighed immediately (reference solutions).

5. The calculated quantities of the stock solutions ($CdCl_2$, metal chloride, metal sulphate) are placed in two or three crucibles and weighed immediately. These cups are not absolutely necessary but are very helpful for comparing the data with other binary measurement data (cups with binary solutions).

6. The calculated quantities of the metal chloride or metal sulphate stock solutions are added to the crucibles and weighed immediately. The calculated quantities of cadmium or zinc solutions are added to the same cups, and these are weighed again (cups with ternary solutions).

7. If necessary, water is added to the cups.

8. The cups are placed in the isopiestic pot without lids. The pot is evacuated to a residual pressure of 22 - 25 mm Hg and the pot is placed in a thermostat.

9. Weights and masses of the stock solutions and their salt content are calculated.

Calculations

The mass of dissolved salts per cup (m_{salt1} and m_{salt2}) is calculated with the following formula:

$$m_{Salz1} = m_{SS\_Salt1} \cdot c_{Salt1} / 100 \text{ and } m_{Salt2} = {}^{m}{}_{SS\_Salt2} \cdot c_{Salt2} / 100 \qquad (2.6)$$

Where m_{SS_Salt1} and m_{SS_Salt2} are the masses of the added stock solutions of the respective salts and c_{Salt1} and c_{Salt2} are the mass concentrations of that salt in their stock solutions.

Special remarks

1. When calculating cup preparations (item 1 above), the total mass or volume of the sample should be within 0.5-2.0 g (or ml).

2. If a mechanical balance is used, the samples should be sorted according to their total mass and then weighed (point 2 above). These speeds up the weighing process and avoids errors due to evaporation.
3. The solutions should be sealed with a lid immediately after weighing. Deviation from this rule is a source of serious problems (points 4-6 above)
4. The required solution quantities should be measured volumetrically (points 4-6 above). It is better to neglect a volume error but to speed up the preparation of the solutions. Weighing should be done as carefully as possible.
5. The preparation of the solutions must not be interrupted until all the crucibles in the pot are in the isopiestic pot.
6. After adding water, weighing is not necessary (point 6 above).
7. Removal of air from the isopiestic should be done slowly to avoid boiling of the solution and splashing (point 7 above). In the case of quite concentrated solutions, the vapour pressure may be 20 - 22 mm Hg.

2.3.2 Preparation of the solutions for the follow-up measurements

Follow-up measurements are measurements with the same cups but with subsequent addition of water. In this way, solutions of lower concentration are obtained for a whole pot. By evacuating and thus removing water, on the other hand, solutions of higher concentration can be achieved.

1. After isopiestic equilibrium is reached, the pot is removed from the thermostat and dried with a cloth. Then air is slowly let into the pot and the pot is opened.
2. All cups are closed with lids as soon as possible.
3. The sealed cups are kept at room temperature near the balance and weighed after the minimum time for thermal equilibration has elapsed (e.g., 10 - 20 minutes). If completely tight lids are used, they should be opened briefly for 2 - 5 seconds before weighing.
4. Weight and mass are determined for each solution and then the mass concentration is calculated.

5. To obtain follow-up points or water activity lines for concentrated solutions, the open cups are placed in a vacuum desiccator with desiccant for a predetermined time.
6. To obtain follow-up points or water activity lines for dilute solutions, a calculated amount of water is added to the cups.
7. The cups are placed in the isopiestic pot without lids. The pot is evacuated to a residual pressure of 22 - 25 mm Hg and the pot is placed in a thermostat.

Calculations

The mass concentrations of the salts in the cups, c_{Salt} are calculated by the following formula:

$$c_{Salt} = 100 \cdot m_{Salt} / m_{solution} \tag{2.7}$$

where $m_{solution}$ is the mass of the solution after isopiestic equilibrium has been reached and m_{Salt} is the mass of salt per crucible (corresponding to the preparation). The activities and the osmotic coefficients of water in the reference solutions are taken from the literature:

- NaCl and KCl solutions: HAMER and WU (1972)
- $CaCl_2$ solutions: STAPLES and NUTTAL (1977)

Comments

1. Care should be taken to remove the thermostat fluid thoroughly, especially in the transition between the lid and the pot (point 1 above).
2. For the conversion of weights into mass (point 4), the solution density is needed. For binary solutions this can be taken from tabulated values, e.g., NOVOTNÝ and SÖHNEL (1988). For ternary solutions, the density is interpolated from the densities of the binary solutions involved.
3. The time needed in the desiccator to remove water from the solutions is determined experimentally in advance. The water loss in our experiments is about 80 mg per hour per crucible with $CaCl_2$ as desiccant and a residual air pressure of 30 mm Hg and room temperature.

2.4 Preparation of the cadmium-containing stock solutions

2.4.1 $CdCl_2$ stock solution

Production

The following compounds were used as starting substances:

- $2CdCl_2 \cdot 5H_2O$, "special purity" (Russian product),
- H_2O (bidest.)

About 96.5 g of $2CdCl_2 \cdot 5H_2O$ was added to about 150 ml of H_2O with constant stirring. The solution was then filtered. About 250 g of a clear, colourless solution was obtained. The chemical analysis was carried out via the chloride content (cf. chap. 2.2.1, S. 6). The concentration of the cadmium chloride solution was calculated with the following formula:

$$c_{CdCl2} = 100 \cdot (183.316 / (2 \cdot 143.323)) \cdot (m_{AgCl} - m_{blanc}) / m_{smp} \qquad (2.8)$$

M_{AgCl}	Mass of AgCl precipitate
M_{blanc}	Mass of precipitation in the blind test
M_{smp}	Sample mass of the stock solution
183.316	Molecular masses of $CdCl_2$
143.323	Molecular masses of AgCl
2	stoichiometric coefficient of Cl in $CdCl_2$.

The stock solution used had a concentration of 31.130 ± 0.008 mass %

2.4.2 $CdSO_4$ stock solution

Production

The starting substances used for the preparation of the cadmium sulphate stock solutions were:

- $3CdSO_4 \cdot 8H_2O$ (for analysis, Merck)
- H_2O (bidest.)

About 27.6 g of $3CdSO_4 \cdot 8H_2O$ was added to about 72.5 ml of H_2O (bidest.) with constant stirring. Filtration was then carried out. About 100 g of a colourless, clear solution was obtained. The chemical analysis was largely identical to the evaporation method for NaCl and KCl (chap. 2.2.2, S. 11). For point 3 of the procedure, the following deviation was made:

3. After drying at 95 -98 °C, the weighing vials were heated at 420 - 440 °C for no less than 3 - 4 hours.

The density for anhydrous $CdSO_4$ was assumed to be 4.69 $g \cdot cm^{-3}$. The stock solution had a concentration of 22.389 ± 0.006 mass %.

2.4.3 Other stock solutions ($MgCl_2$, $CaCl_2$, NaCl, KCl, $MgSO_4$)

The preparation and analysis of the $MgCl_2$ and $CaCl_2$ stock solutions was carried out according to 2.2.3, (P. 12). The stock solutions used had a concentration of 8.7479 ± 0.0029 ($MgCl_2$) and 9.9141 ± 0.0014 mass % ($CaCl_2$).

The sodium and potassium chloride solutions were prepared according to the procedure in chapter 2.2.2, (p. 11). The quantities used were 4.6 g NaCl to 45.5 g H_2O and 2.6 g KCl to 47.5 ml H_2O. This resulted in the following concentrations 9.0061 ± 0.0015 (NaCl) and 5.2741 ± 0.0011 mass % (KCl).

The magnesium sulphate solution was prepared according to chapter 2.2.5 (p. 14). The masses used were 26.1 g $MgSO_4 \cdot 7H_2O$ and 73.9 ml H_2O. The analysis was carried out according to the procedure for cadmium sulphate. The stock solution had a concentration of 12.745 ± 0.003 mass %.

2.4.4 Conversion of concentrations into water activities

The water activity of the equilibrium solutions is derived from the concentration of the reference solutions. For these (NaCl, KCl, $CaCl_2$ and H_2SO_4), extensive and critically evaluated compilations for thermodynamic data already exist. These include regressions to be able to calculate the water activity for a given composition. Depending on which solution was used as a reference for the measurements, the regression equations from the following publications were used:

- NaCl: CLARKE and GLEW (1985)

- KCl: ARCHER (1999)
- $CaCl_2$: RARD and CLEGG (1997)

2.5 Water activity of zinc-containing systems

2.5.1 The system $ZnCl_2$ - H_2O

Numerous measurements were already available for this system. In the course of investigating of some ternary and quaternary systems, we were able to add some more measuring points (Tab. 2.1, Tab. 2.2, Fig. 2.2). The agreement of the literature values with each other and with our new measurements is very good. A more detailed discussion is given in chapter 8.1 (p. 185). For the calculation of the osmotic coefficients, complete dissociation of all electrolytes was assumed.

Tab. 2.1 Experimentally determined water activities of $ZnCl_2$ solutions at 25.0 °C (RUMYANTSEV) I

Concentration $ZnCl_2$ [mol/kg]	Concentration of the stock solution KCl [mol/kg]	Concentration of the stock solution NaCl [mol/kg]	Concentration of the stock solution $CaCl_2$ [mol/kg]	Water activity a_W [ ]	Osmotic coefficient [ ]
0.5417	0.7469			0.9761	0.8255
1.0305		1.3006		0.9564	0.7995
1.0709	1.4231			0.9547	0.8013
1.1751	1.5488	1.4644		0.9507	0.7961
1.2883		1.5828		0.9465	0.7896
1.3707			1.0249	0.9431	0.7902
1.7074	2.2007			0.9297	0.7905
1.7203		2.0541		0.9294	0.7878
1.8205	2.3439	2.1718		0.9250	0.7924
1.9388		2.2940		0.9204	0.7918
2.1882		2.5791		0.9095	0.8025
2.4630	3.1977			0.8968	0.8181
2.5125		2.9519		0.8948	0.8187
2.7066	3.5567	3.1981		0.8848	0.8367
2.9267		3.4612		0.8740	0.8513
2.9862		3.5341		0.8710	0.8559

Tab. 2.2 Experimentally determined water activities of $ZnCl_2$ solutions at 25.0 °C (Rumyantsev) II

Concentration $ZnCl_2$ [mol/kg]	Concentration of the stock solution KCl [mol/kg]	Concentration of the stock solution NaCl [mol/kg]	Concentration of the stock solution $CaCl_2$ [mol/kg]	Water activity a_W [ ]	Osmotic coefficient [ ]
3.1578	4.2482	3.7544		0.8617	0.8722
3.4647	4.7434	4.1527		0.8446	0.9019
3.7075		4.4657		0.8309	0.9248
3.7197			2.3090	0.8298	0.9281
3.8692		4.6880		0.8209	0.9436
4.0102		4.8797		0.8123	0.9592
4.3042		5.2932		0.7933	0.9954
4.6995		5.8596		0.7668	1.0455
4.8106		6.0119		0.7595	1.0578
4.8765		6.1232		0.7542	1.0704
5.8235			3.5141	0.6861	1.1970
7.9718			4.7782	0.5257	1.4926
9.8878			5.9609	0.3952	1.7373
10.6829			6.4769	0.3502	1.8173
12.0756			7.5251	0.2799	1.9508
13.2062			8.4730	0.2343	2.0331

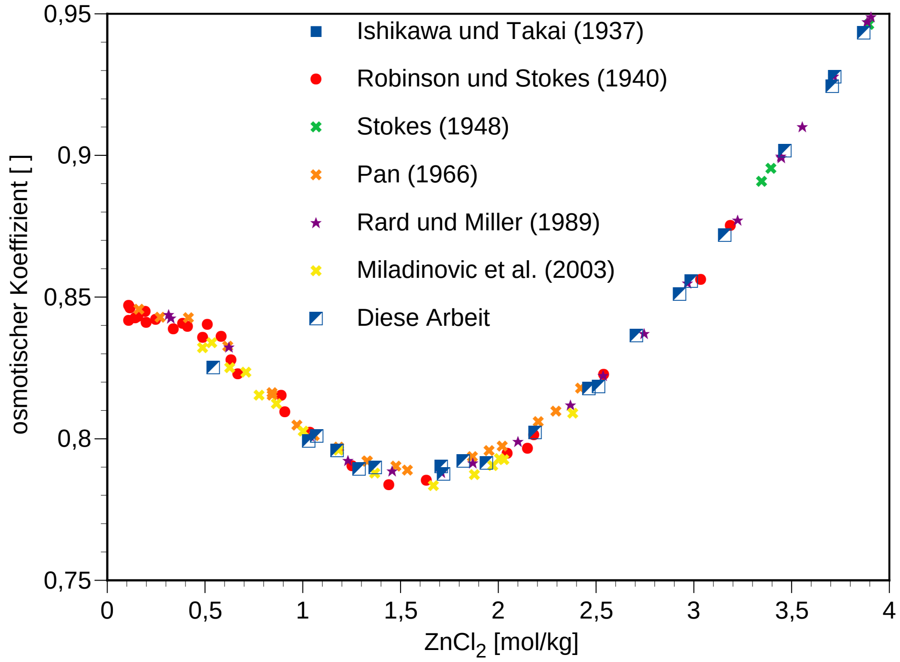

Fig. 2.2 Literature data and own isopiestic measurements in the system $ZnCl_2$ - H_2O

2.5.2 The system $ZnSO_4$ - H_2O

Numerous measurements were already available for this system. In the course of investigating some ternary and quaternary systems, we were able to add some more data points (Tab. 2.3, Fig. 2.3). The agreement of the literature values with each other and with our new measurements is very good. The strongly scattering data of TARTAR et al. (1941), however, are out of the ordinary. A more detailed discussion is given in chapter 8.2 (p. 190).

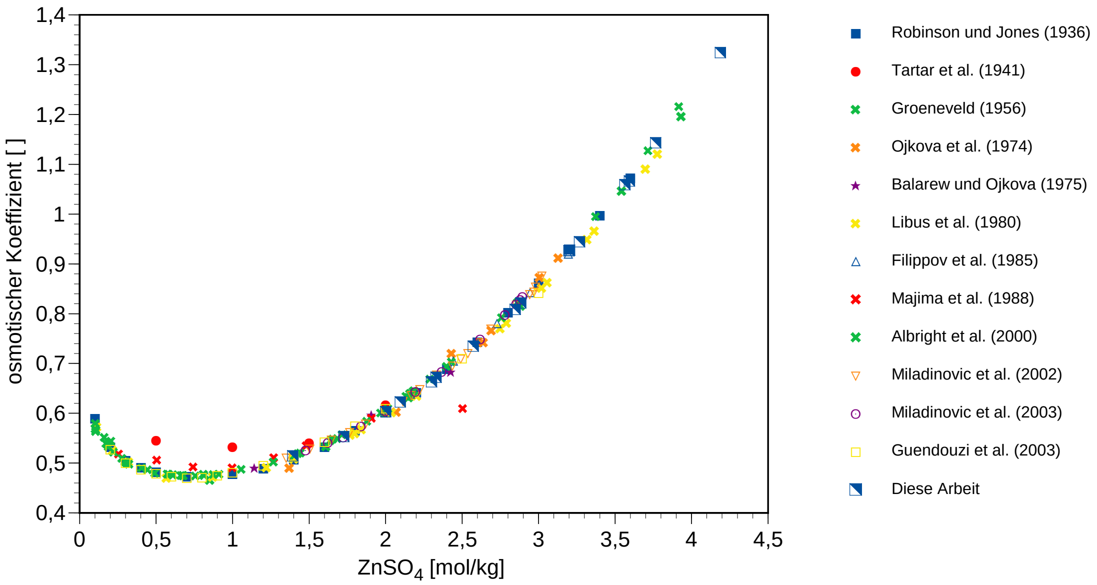

Fig. 2.3 Literature data and own isopiestic measurements in the system $ZnSO_4$ - H_2O

Tab. 2.3 Experimentally determined water activities of $ZnSO_4$ solutions at 25.0 °C (Rumyantsev)

Concentration $ZnSO_4$ [mol/kg]	Concentration of the stock solution NaCl [mol/kg]	Water activity a_W [ ]	Osmotic coefficient [ ]
1.3932	0.7714	0.9745	0.5144
1.7271	1.0191	0.9661	0.5535
2.0004	1.2717	0.9575	0.6032
2.0959	1.3691	0.9541	0.6228
2.3002	1.5828	0.9465	0.6634
2.3297	1.6212	0.9451	0.6722
2.5733	1.9253	0.9341	0.7350
2.8478	2.2940	0.9204	0.8086
2.8837	2.3524	0.9182	0.8218
3.1991	2.8527	0.8987	0.9263
3.2027	2.8596	0.8985	0.9279
3.2675	2.9519	0.8948	0.9444
3.5648	3.4910	0.8728	1.0594
3.5944	3.5341	0.8710	1.0665
3.7654	3.8808	0.8563	1.1432
4.1886	4.7349	0.8188	1.3245

2.5.3 The system $ZnCl_2$- $ZnSO_4$ - H_2O

Up to now, only solubility data were available for this system. Our six isoactivity curves with a total of 48 measuring points homogeneously cover the undersaturated zone up to 5 mol/kg $ZnCl_2$. In some experiments, the formation of solid phases occurred due to supersaturation. Corresponding points were not considered. The curves show a clear concave deviation from linearity (Fig. 2.4, Tab. 2.4, Tab. 2.5), which can be interpreted as an indication of a change in the binding state of the zinc (chloro complex formation).

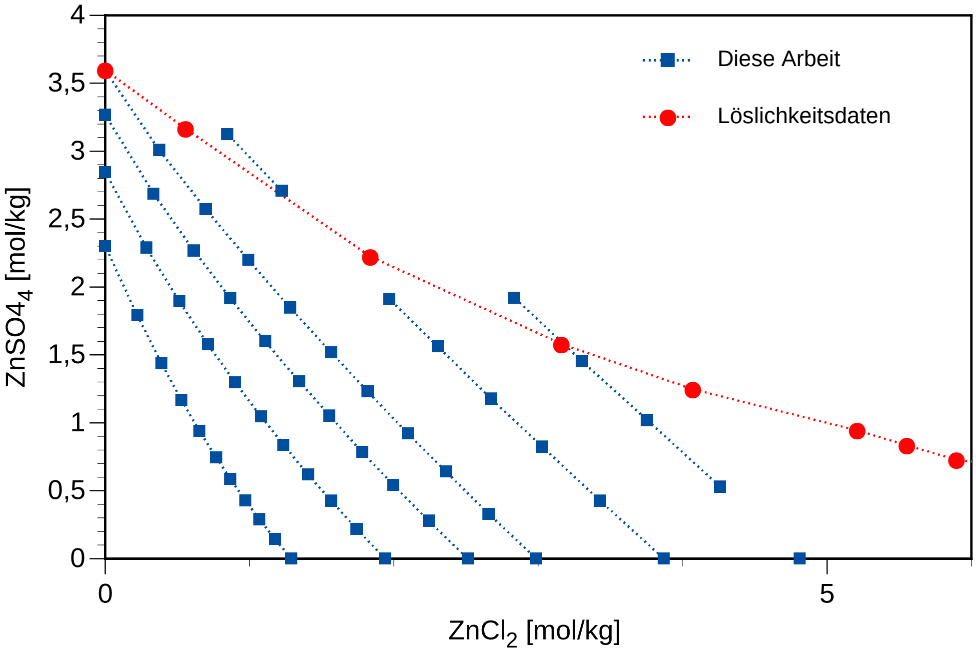

Fig. 2.4 Measured isoactivity curves in the system $ZnCl_2$ - $ZnSO_4$ - H_2O at 25 °C

Tab. 2.4 Measured water activities of solutions of the system $ZnCl_2$ - $ZnSO_4$ - H_2O at 25 °C (I)

$ZnCl_2$ [mol/kg]	**$ZnSO_4$ [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**$ZnSO_4$ [mol/kg]**
1.2878	0.0000	1.9382	0.0000	2.9857	0.0000
1.2887	0.0000	1.9394	0.0000	2.9866	0.0000
1.1750	0.1464	1.7425	0.2171	2.6559	0.3309
1.0697	0.2910	1.5658	0.4259	2.3596	0.6418
0.9719	0.4281	1.4057	0.6192	2.0954	0.9231
0.8673	0.5882	1.2362	0.8384	1.8182	1.2331
0.7683	0.7459	1.0788	1.0474	1.5647	1.5192
0.6528	0.9418	0.9000	1.2985	1.2813	1.8486
0.5280	1.1698	0.7124	1.5784	0.9927	2.1994
0.3902	1.4396	0.5136	1.8950	0.6972	2.5723
0.2233	1.7910	0.2855	2.2901	0.3750	3.0083
0.0000	2.2994	0.0000	2.8472	0.0000	3.5944
0.0000	2.3010	0.0000	2.8484		
Reference solutions [mol/kg]					
NaCl	1.5828	NaCl	2.2940	NaCl	3.5341
a_W	0.9465	a_W	0.9204	a_W	0.8710

Tab. 2.5 Measured water activities of solutions of the system $ZnCl_2$ - $ZnSO_4$ - H_2O at 25 °C (II)

$ZnCl_2$ [mol/kg]	**$ZnSO_4$ [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**$ZnSO_4$ [mol/kg]**
3.8691	0.0000	4.8098	0.0000	2.5122	0.0000
3.8694	0.0000	4.8114	0.0000	2.5127	0.0000
3.4266	0.4269	Crystallisation		2.2413	0.2793
3.0277	0.8235	4.2588	0.5306	1.9975	0.5433
2.6731	1.1776	3.7536	1.0210	1.7807	0.7844
2.3036	1.5623	3.3020	1.4546	1.5530	1.0532
1.9681	1.9109	2.8331	1.9215	1.3443	1.3052
Crystallisation				1.1087	1.5995
1.223	2.710			0.8665	1.9199
0.847	3.126			0.6147	2.2680
				0.3351	2.6884
				0.0000	3.2671
				0.0000	3.2679
Reference solutions [mol/kg]					
NaCl	4.6880	NaCl	6.0119	NaCl	2.9519
a_W	0.8209	a_W	0.7595	a_W	0.8948

2.5.4 The system $ZnCl_2$ - NaCl - H_2O

For this system, only solubility data were available in the literature so far. Isopiestic experiments were carried out by POPOV (1989), but never published due to quality doubts (cf. footnote 10 f., p. 165). The nine newly measured isoactivity lines cover the homogeneous solution range up to about 5 mol/kg $ZnCl_2$ in each case up to the saturation limit of NaCl (Tab. 2.6 ff.). The isoactivity lines show a strongly curved convex course, which becomes almost linear in areas of high $ZnCl_2$/$NaCl_2$ or NaCl/$ZnCl_2$ ratios (Fig. 2.5).

Tab. 2.6 Measured water activities of solutions of the system $ZnCl_2$ - NaCl - H_2O at 25 °C (I)

$ZnCl_2$ [mol/kg]	**NaCl [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**NaCl [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**NaCl [mol/kg]**
0.0000	1.4641	0.0000	2.1714	0.0000	3.1972
0.0000	1.4646	0.0000	2.1723	0.0000	3.1990
0.1272	1.3232	0.1960	2.0390	0.3003	3.1231
0.2413	1.1931	0.3813	1.8848	0.6045	2.9883
0.3558	1.0576	0.5714	1.6986	0.9274	2.7566
0.4660	0.9239	0.7546	1.4962	1.2328	2.4442
0.5723	0.7920	0.9285	1.2850	1.5081	2.0872
0.6715	0.6670	1.0864	1.0792	1.7442	1.7325
0.7660	0.5455	1.2326	0.8777	1.9518	1.3899
0.8515	0.4334	1.3614	0.6929	2.1274	1.0829
0.9282	0.3319	1.4745	0.5272	2.2761	0.8138
1.0197	0.2085	1.6060	0.3285	2.4434	0.4997
1.0962	0.1060	1.7127	0.1657	2.5758	0.2491
1.1746	0.0000	1.8200	0.0000	2.7061	0.0000
1.1751	0.0000	1.8201	0.0000	2.7065	0.0000
1.1757	0.0000	1.8215	0.0000	2.7073	0.0000
Reference solutions [mol/kg]					
NaCl	1.4644	NaCl	2.1718	NaCl	3.1981
a_W	0.9507	a_W	0.9250	a_W	0.8848

Tab. 2.7 Measured water activities of solutions of the system $ZnCl_2$ - NaCl - H_2O at 25 °C (II)

$ZnCl_2$ [mol/kg]	NaCl [mol/kg]	$ZnCl_2$ [mol/kg]	NaCl [mol/kg]	$ZnCl_2$ [mol/kg]	NaCl [mol/kg]
0.0000	4.1512	0.0000	5.2921	0.0000	6.1210
0.0000	4.1541	0.0000	5.2943	0.0000	6.1253
0.3961	4.1202	0.5086	5.2905	0.5891	6.1272
0.8151	4.0295	1.0593	5.2368	1.2318	6.0896
1.2784	3.8001	1.6985	5.0489	1.9928	5.9236
1.7112	3.3927	2.2974	4.5550	2.7252	5.4031
2.0767	2.8741	2.7602	3.8200	3.2545	4.5042
2.3701	2.3543	3.1059	3.0852	3.6238	3.5996
2.6184	1.8647	3.3875	2.4123	3.9272	2.7967
2.8217	1.4363	3.6126	1.8388	4.1583	2.1166
2.9901	1.0691	3.7949	1.3569	4.3506	1.5556
3.1770	0.6498	3.9977	0.8176	4.5608	0.9327
3.3245	0.3215	4.1533	0.4017	4.7187	0.4564
3.4638	0.0000	4.3044	0.0000	4.8783	0.0000
3.4643	0.0000	4.3047	0.0000	4.8732	0.0000
3.4661	0.0000	4.3034	0.0000	4.8782	0.0000
Reference solutions [mol/kg]					
NaCl	4.1527	NaCl	5.2932	NaCl	6.1232
a_W	0.8446	a_W	0.7933	a_W	0.7542

Tab. 2.8 Measured water activities of solutions of the system $ZnCl_2$ - NaCl - H_2O at 25 °C (III)

$ZnCl_2$ [mol/kg]	NaCl [mol/kg]	$ZnCl_2$ [mol/kg]	NaCl [mol/kg]	$ZnCl_2$ [mol/kg]	NaCl [mol/kg]
3.5678	7.0737	0.0000	3.7557	0.0000	4.8794
4.2128	5.8304	0.0000	3.7532	0.0000	4.8801
4.6149	4.5841	0.3560	3.7031	0.4678	4.8663
4.9297	3.5106	0.7270	3.5939	0.9720	4.8052
5.1868	2.6401	1.1300	3.3589	1.5467	4.5977
5.3907	1.9275	1.5080	2.9898	2.0841	4.1321
5.6127	1.1479	1.8368	2.5421	2.5146	3.4801
5.7736	0.5584	2.1079	2.0938	2.8426	2.8236
5.9396	0.0000	2.3414	1.6674	3.1119	2.2161
5.9325	0.0000	2.5327	1.2892	3.3302	1.6951
5.9360	0.0000	2.6939	0.9632	3.5110	1.2553
		2.8750	0.5880	3.7071	0.7582
		3.0158	0.2917	3.8607	0.3734
		3.1570	0.0000	4.0089	0.0000
		3.1573	0.0000	4.0098	0.0000
		3.1589	0.0000	4.0119	0.0000
Reference solutions [mol/kg]					
$ZnCl_2$	5.9360	NaCl	3.7544	NaCl	4.8797
a_W	0.6773*	a_W	0.8617	a_W	0.8123

* calculated from the linear trend of the measured values for $ZnCl_2$ from Rard and Miller (1989) between the concentrations 5.0 and 7.1

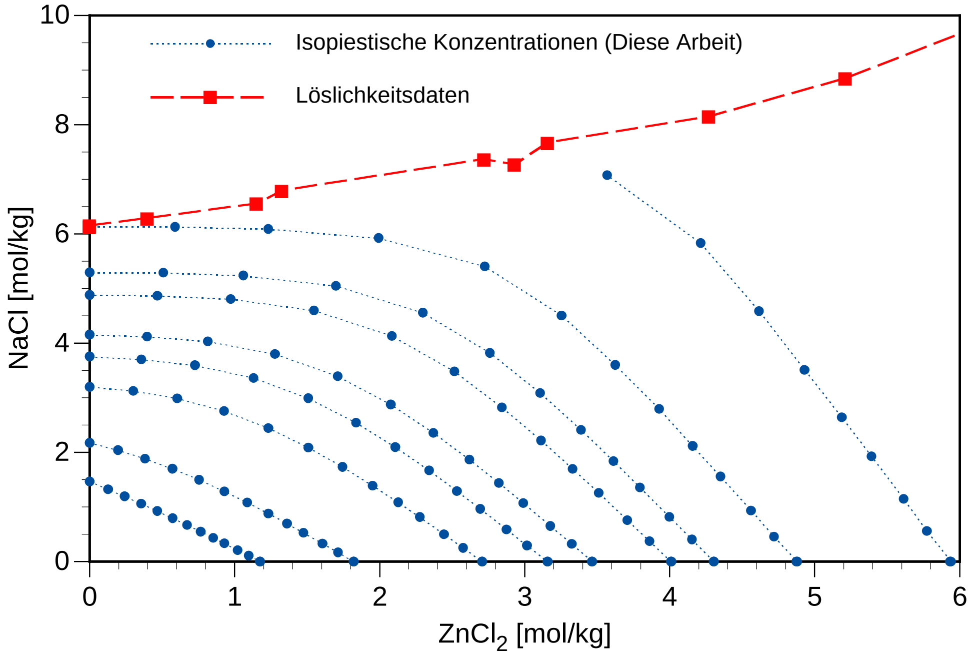

Fig. 2.5 Isopiestic concentrations in the system $ZnCl_2$ - NaCl - H_2O at 25 °C

2.5.5 The system $ZnCl_2$ - KCl - H_2O

So far, only a few direct vapour pressure measurements (SARNOWSKI and ŚCIEŃSKA 1960) and a few unfortunately poorly documented isopiestic investigations (STOKES 1948a; MAZGAJ et al. 1965) were available for this system. A more detailed discussion of the available data is given in chap. 8.7 (p. 201). The system was investigated with nine new isoactivity lines. Compared to the previously discussed $ZnCl_2$-NaCl-H_2O system, the isoactivity lines (Tab. 2.9f., Fig. 2.6) showed a considerably more convex curvature. This is particularly clear from the outermost line, which begins at 5 mol/kg $ZnCl_2$. While the curve in the system $ZnCl_2$-NaCl-H_2O inclines towards the NaCl axis (towards the "inside" as isopiestic lines normally do), the curve in the system $ZnCl_2$- KCl - H_2O bulges from the KCl axis towards the "outside". The addition of KCl to a 5 mol/kg $ZnCl_2$ solution obviously leads to a strong increase of the water activity. This can only be explained by the fact that the number of free species decreases with the addition of KCl (and thus the mole fraction of the water in the solution increases).

Such behaviour can only be justified with a strong complex formation, e.g., according to the following formula:

$$2\,K^+ + 2\,Cl^- + Zn^{2+} \rightleftharpoons 2\,K^+ + [ZnCl_4]^{2-} \qquad (2.9)$$

Tab. 2.9 Measured water activities of solutions of the system $ZnCl_2$ - KCl - H_2O at 25 °C (I)

$ZnCl_2$ [mol/kg]	KCl [mol/kg]	$ZnCl_2$ [mol/kg]	KCl [mol/kg]	$ZnCl_2$ [mol/kg]	KCl [mol/kg]
1.1746	0.0000	1.8200	0.0000	2.7061	0.0000
1.1751	0.0000	1.8201	0.0000	2.7065	0.0000
1.1757	0.0000	1.8215	0.0000	2.7073	0.0000
1.1202	0.1030	1.7644	0.1623	2.6654	0.2452
1.0524	0.2221	1.6893	0.3565	2.6087	0.5505
0.9880	0.3311	1.6158	0.5414	2.5513	0.8549
0.9087	0.4606	1.5176	0.7692	2.4675	1.2507
0.8247	0.5908	1.4066	1.0076	2.3658	1.6947
0.7318	0.7277	1.2715	1.2644	2.2236	2.2112
0.6269	0.8731	1.1040	1.5374	2.0113	2.8011
0.5086	1.0251	0.8973	1.8084	1.6734	3.3725
0.3835	1.1726	0.6661	2.0366	1.2077	3.6925
0.2680	1.2988	0.4510	2.1860	0.7711	3.7374
0.1315	1.4341	0.2102	2.2931	0.3358	3.6621
0.0000	1.5492	0.0000	2.3438	0.0000	3.5558
0.0000	1.5483	0.0000	2.3440	0.0000	3.5576
Reference solutions [mol/kg]					
NaCl	1.4644	NaCl	2.1718	NaCl	3.1981
a_W	0.9507	aW	0.9250	aW	0.8848

Tab. 2.10 Measured water activities of solutions of the system $ZnCl_2$ - KCl - H_2O at 25 °C (II)

$ZnCl_2$ [mol/kg]	**KCl [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**KCl [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**KCl [mol/kg]**
3.4638	0.0000	4.3044	0.0000	4.8783	0.0000
3.4643	0.0000	4.3047	0.0000	4.8732	0.0000
3.4661	0.0000	4.3034	0.0000	4.8782	0.0000
3.4441	0.3168	4.3122	0.3967	4.9040	0.4511
3.4139	0.7204	4.3215	0.9119	4.9413	1.0427
3.3849	1.1342	4.3337	1.4521	4.9905	1.6721
3.3392	1.6925	4.3506	2.2051	5.0489	2.5591
3.2838	2.3523	4.3676	3.1288	5.1379	3.6805
3.1900	3.1722	4.3762	4.3517	5.2391	5.2098
3.0128	4.1958	4.3354	6.0378	5.3403	7.4372
2.5819	5.2037	3.8680	7.7956	4.8829	9.8410
1.7893	5.4710				
1.0871	5.2691				
0.4568	4.9827				
0.0000	4.7420				
0.0000	4.7448				
Reference solutions [mol/kg]					
NaCl	4.1527	NaCl	5.2932	NaCl	6.1232
aW	0.8446	a_W	0.7933	a_W	0.7542

Tab. 2.11 Measured water activities of solutions of the system $ZnCl_2$ - KCl - H_2O at 25 °C (III)

$ZnCl_2$ [mol/kg]	**KCl [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**KCl [mol/kg]**	**$ZnCl_2$ [mol/kg]**	**KCl [mol/kg]**
5.9396	0.0000	3.1570	0.0000	4.0089	0.0000
5.9325	0.0000	3.1573	0.0000	4.0098	0.0000
5.9360	0.0000	3.1589	0.0000	4.0119	0.0000
6.0026	0.5522	3.1303	0.2879	4.0080	0.3687
6.1042	1.2881	3.0895	0.6519	4.0030	0.8447
6.2179	2.0834	3.0458	1.0206	4.0012	1.3407
6.3906	3.2392	2.9833	1.5121	3.9917	2.0233
6.6245	4.7455	2.9021	2.0789	3.9813	2.8520
6.9384	6.8996	2.7834	2.7678	3.9518	3.9298
7.3831	10.2822	2.5819	3.5957	3.8522	5.3648
7.1056	14.3206	2.1866	4.4070	3.3839	6.8200
		1.5422	4.7155	2.2596	6.9088
		0.9562	4.6346	4.0080	0.3687
		0.4063	4.4319	4.0030	0.8447
		0.0000	4.2476		
		0.0000	4.2488		
Reference solutions [mol/kg]					
$ZnCl_2$	5.9360	NaCl	3.7544	NaCl	4.8797
a_W	0.6773*	a_W	0.8617	a_W	0.8123

* These low water activities could no longer be measured with the reference solutions used (NaCl or KCl). Instead, the $ZnCl_2$ solution itself was used. This was done on the basis of the measurement data of Rard and Miller (1989), which show a linear trend between the concentrations 5.0 and 7.1mol/kg.

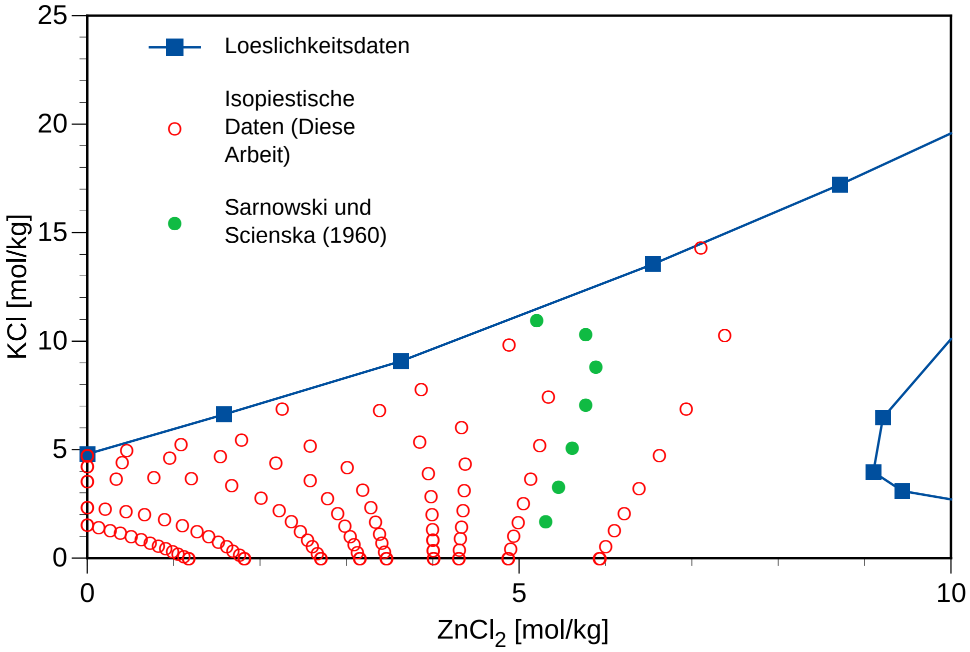

Fig. 2.6 Isopiestic concentrations in the system $ZnCl_2$ - KCl - H_2O at 25 °C

2.5.6 The system $ZnCl_2$- $MgCl_2$ - H_2O

Apart from a few isopiestic measuring points by STOKES (1948a), no information on undersaturated solutions was available so far. We investigated the system with eight additional isoactivity lines (Tab. 2.12 f.). Like the system before, they show a strong deviation from linearity. However, a special feature is noticeable here: While the isoactivity lines in the systems with sodium and potassium show a more or less uniform curvature over the entire course, here they consist of two almost linear sections connected with short arcs (Fig. 2.7). This behaviour indicates the presence of two Zdanovksy-like subsystems, each of which are dominated by two main species. A mixture of $Zn^{2+}(Cl^{-})_2$ + $Mg^{2+}[ZnCl_4]^{2-}$ (+$[ZnCl_2]^0$) on the zinc-rich side and $Mg^{2+}[ZnCl_4]^{4-}$ + $Mg^{2+}(Cl^{-})_2$ (+$[ZnCl_2]^0$) on the magnesium-rich side would be conceivable. The two branches of the isoactivity line intersect at Mg:Zn=1. A similar but weaker behaviour can also be observed in the systems NaCl-$ZnCl_2$-H_2O and KCl-$ZnCl_2$-H_2O. Possibly, double-charged ions species such as $[ZnCl_4]^{2-}$ and Zn^{2+} are stabilized in $MgCl_2$ solutions, e.g., by formation of ion pairs and ternary complexes.

Tab. 2.12 Measured water activities of solutions of the system $ZnCl_2$ - $MgCl_2$ - H_2O at 25 °C (I)

$ZnCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]
0.0000	0.9781	0.0000	2.1504	0.0000	3.2390	0.0000	4.3532
0.0000	0.9775	0.0000	2.1502	0.0000	3.2383	0.0000	4.3543
0.1145	0.9181	0.2645	2.1198	0.3986	3.1950	0.5345	4.2837
0.2212	0.8577	0.5368	2.0811	0.8119	3.1478	1.0861	4.2110
0.3460	0.7815	0.8903	2.0112	1.3615	3.0755	1.8239	4.1199
0.4757	0.6952	1.2900	1.8849	2.0245	2.9583	2.7302	3.9894
0.6038	0.6052	1.6876	1.6916	2.7179	2.7244	3.7334	3.7422
0.7497	0.4981	2.1161	1.4059	3.4074	2.2638	4.6936	3.1183
0.9020	0.3810	2.5368	1.0716	4.0474	1.7097	5.5565	2.3471
1.0548	0.2596	2.9369	0.7227	4.6485	1.1439	6.3722	1.5681
1.2057	0.1366	3.3170	0.3758	5.2206	0.5914	7.1495	0.8099
1.3703	0.0000	3.7200	0.0000	5.8228	0.0000	7.9700	0.0000
1.3710	0.0000	3.7193	0.0000	5.8242	0.0000	7.9736	0.0000
Reference solutions [mol/kg]							
$CaCl_2$	1.0249	$CaCl_2$	2.3090	$CaCl_2$	3.5141	$CaCl_2$	4.7782
a_W	0.9431	a_W	0.8298	a_W	0.6861	a_W	0.5257

Tab. 2.13 Measured water activities of solutions of the system $ZnCl_2$ - $MgCl_2$ - H_2O at 25 °C (II)

$ZnCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]
0.0000	5.2861	0.0000	6.1884	7.4615	4.9572	0.6894	5.5256
0.0000	5.2878	0.0000	6.1854	8.9442	3.7781	1.3993	5.4251
0.6480	5.1934	0.7578	6.0735	10.3725	2.5525	2.3494	5.3071
1.3161	5.1025	2.5870	5.8439	11.7464	1.3307	3.5279	5.1551
2.2093	4.9905	3.8929	5.6884	13.2049	0.0000	4.8780	4.8896
3.3090	4.8352	5.4089	5.4218	13.2075	0.0000	6.1925	4.1141
4.5694	4.5803	6.9032	4.5863			7.3700	3.1131
5.7797	3.8399	8.2564	3.4875			8.4826	2.0875
6.8584	2.8970	9.5401	2.3477			9.5362	1.0803
7.8800	1.9392	10.7685	1.2199			10.6814	0.0000
8.8441	1.0019	12.0739	0.0000			10.6845	0.0000
9.8920	0.0000	12.0773	0.0000				
9.8835	0.0000						
Reference solutions [mol/kg]							
$CaCl_2$	5.9609	$CaCl_2$	7.5251	$CaCl_2$	8.4730	$CaCl_2$	6.4769
a_W	0.3952	a_W	0.2799	a_W	0.2343	a_W	0.3502

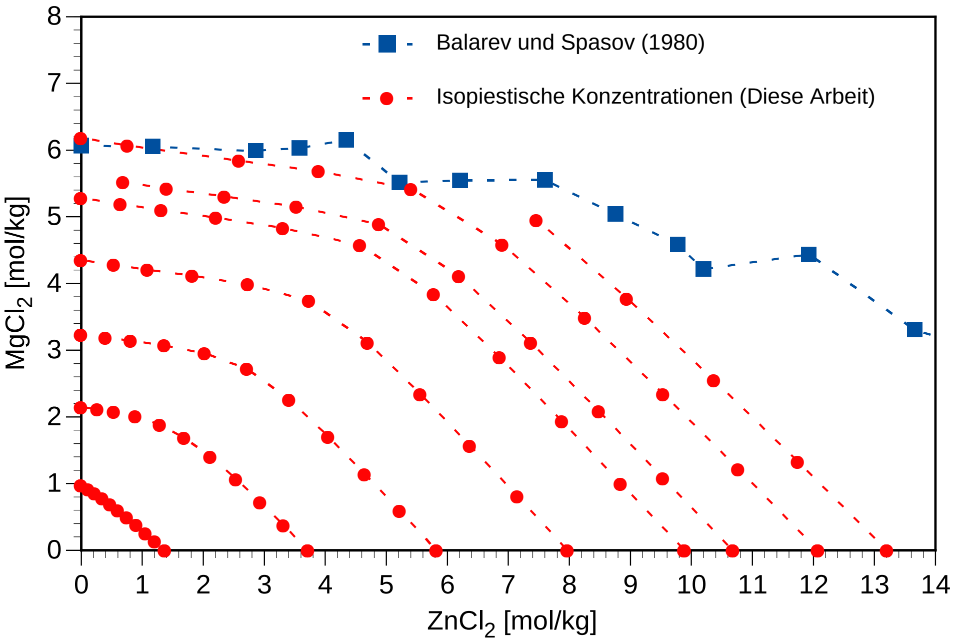

Fig. 2.7 Isopiestic concentrations in the system $ZnCl_2$ - $MgCl_2$ - H_2O at 25 °C

2.5.7 The system $ZnCl_2$ - $CaCl_2$ - H_2O

So far, no isopiestic studies have been available for this system. The isoactivity lines in this system deviate strongly from linearity (Tab. 2.14 f., Fig. 2.8). The same behaviour is observed as in the system with $MgCl_2$. Another peculiarity is the S-shaped expression of the second most concentrated mixture series. While inward and outward curved isopiestic lines are well known in the literature, this system is the first proof that both curvatures can occur in one line[2].

Tab. 2.14 Measured water activities of solutions of the system $ZnCl_2$ - $CaCl_2$ - H_2O at 25 °C (I)

$ZnCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]
1.3703	0.0000	3.7200	0.0000	5.8228	0.0000	7.9700	0.0000
1.3710	0.0000	3.7193	0.0000	5.8242	0.0000	7.9736	0.0000
1.2107	0.1450	3.3421	0.4003	5.2595	0.6300	7.1962	0.8620
1.0718	0.2681	3.0012	0.7506	4.7531	1.1888	6.5014	1.6261
0.9192	0.3954	2.6170	1.1257	4.1787	1.7974	5.7229	2.4617
0.7787	0.5094	2.2385	1.4643	3.6082	2.3603	4.9541	3.2407
0.6346	0.6210	1.8176	1.7789	2.9361	2.8735	4.0212	3.9355
0.4891	0.7275	1.3593	2.0216	2.1358	3.1764	2.8763	4.2778
0.3514	0.8212	0.9251	2.1623	1.4208	3.3209	1.8884	4.4138
0.2232	0.9018	0.5535	2.2363	0.8430	3.4058	1.1350	4.5857
0.1140	0.9648	0.2691	2.2779	0.4092	3.4641	0.5531	4.6820
0.0000	1.0248	0.0000	2.3091	0.0000	3.5136	0.0000	4.7783
0.0000	1.0251	0.0000	2.3090	0.0000	3.5146	0.0000	4.7781
Reference solutions [mol/kg]							
$CaCl_2$	1.0249	$CaCl_2$	2.3090	$CaCl_2$	3.5141	$CaCl_2$	4.7782
a_W	0.9431	a_W	0.8298	a_W	0.6861	a_W	0.5257

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[2] Based on theoretical considerations by Čarykov and Rumjancev, so far only suspected but never proven (Rumyantsev, personal communication).

Tab. 2.15 Measured water activities of solutions of the system $ZnCl_2$ - $CaCl_2$ - H_2O at 25 °C (II)

$ZnCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$ZnCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]
9.8920	0.0000	12.0739	0.0000	13.2049	0.0000	10.6814	0.0000
9.8835	0.0000	12.0773	0.0000	13.2075	0.0000	10.6845	0.0000
8.9074	1.0669	10.8135	1.2952	11.7918	1.4124	9.6003	1.1499
8.0266	2.0076	9.6955	2.4250	10.5417	2.6366	8.6329	2.1592
7.0441	3.0300	8.4539	3.6364	9.1503	3.9359	7.5598	3.2518
6.0687	3.9698	7.2420	4.7373	7.7978	5.1009	6.5090	4.2578
4.9017	4.7972	5.7804	5.6572	6.2048	6.0725	5.2252	5.1138
3.4899	5.1902	4.1240	6.1332	0.0000	8.4722	3.7193	5.5314
2.3214	5.4259	2.7881	6.5167	0.0000	8.4738	2.4885	5.8165
1.3929	5.6276	1.6967	6.8551			1.4974	6.0499
0.6842	5.7924	0.8465	7.1657			0.7389	6.2548
0.0000	5.9606	0.0000	7.5228			0.0000	6.4770
0.0000	5.9612	0.0000	7.5274			0.0000	6.4767
Reference solutions [mol/kg]							
$CaCl_2$	5.9609	$CaCl_2$	7.5251	$CaCl_2$	8.4730	$CaCl_2$	6.4769
a_W	0.3952	a_W	0.2799	a_W	0.2343	a_W	0.3502

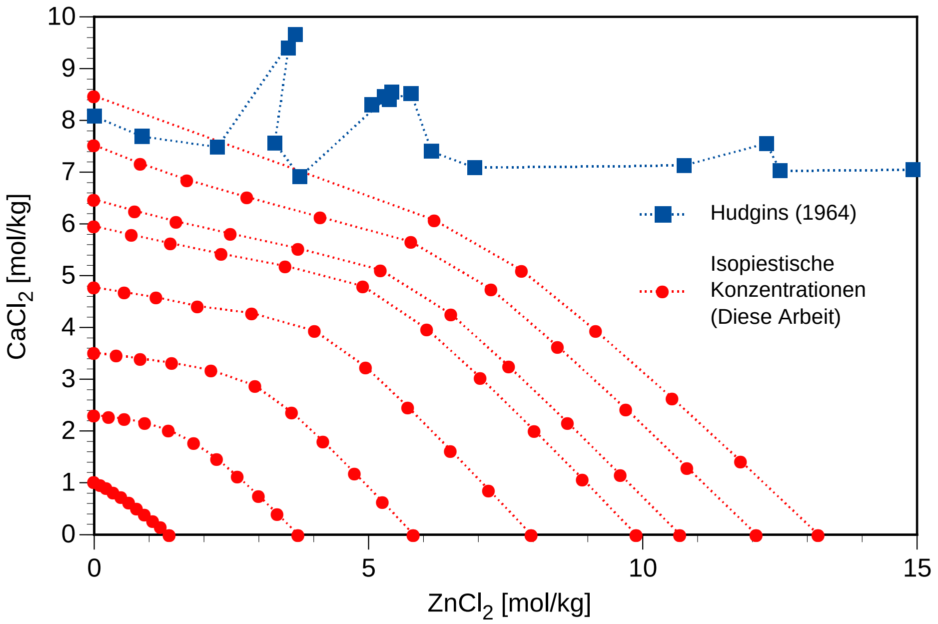

Fig. 2.8 Isopiestic concentrations in the system $ZnCl_2$ - $CaCl_2$ - H_2O at 25 °C

2.5.8 The quaternary system Zn, Na | Cl, SO_4 - H_2O

The investigation of some quaternary zinc-containing systems should serve as a safeguard for the parameter sets to be determined. The first system of this kind is Zn, Na | Cl, SO_4-H_2O. It can be divided into two quasi-ternary[3] systems, which were also investigated separately: $ZnCl_2$ – Na_2SO_4 - H_2O (Tab. 2.18 f.) and $ZnSO_4$ - NaCl - H_2O (Tab. 2.16 f.). In the system $ZnSO_4$ - NaCl -H_2O, an almost linear course of the isoactivity lines is observed in the three preparations with the highest water activity (> 0.96). With increasing chloride concentration, a curvature becomes more and more noticeable (Fig. 2.9). In contrast, the isoactivity lines in the system $ZnCl_2$ – Na_2SO_4 - H_2O show almost no curvature, but they are frequently interrupted by fields in which (i.e., in the corresponding solution mixtures in the crucibles) the formation of a solid was observed (crystallisation, Fig. 2.10). In this system, no change in chloride supply occurs, so that complex formation cannot shift towards higher complexes.

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[3] Here, ´quasi-ternary´ means that in the four-ion system Na, Zn, Cl, SO_4 actually only two concentrations are varied, namely those of NaCl and $ZnSO_4$.

Tab. 2.16 Measured water activities of solutions of the system $ZnSO_4$ - NaCl - H_2O at 25 °C (I)

$ZnSO_4$ [mol/kg]	**NaCl [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**NaCl [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**NaCl [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**NaCl [mol/kg]**
0	1.3685	0	1.6202	0	2.8601	0	0.7714
0	1.3693	0	1.6216	0	2.8593	0	0.7716
0	1.3696	0	1.6217	0	2.8592	0	0.7711
0.1330	1.3194	0.1594	1.5821	0.2986	2.9629	0.0737	0.7313
0.2525	1.2536	0.3036	1.5069	0.5785	2.8720	0.1399	0.6943
0.3828	1.1742	0.4594	1.4092	0.8662	2.6569	0.2128	0.6527
0.5671	1.0552	0.6766	1.2590	1.2311	2.2908	0.3180	0.5917
0.7158	0.9556	0.8485	1.1327	1.4952	1.9961	0.4057	0.5416
0.9274	0.8132	1.0885	0.9545	1.8310	1.6056	0.5360	0.4700
1.1150	0.6859	1.2975	0.7982	2.0963	1.2896	0.6552	0.4031
1.3127	0.5509	1.5116	0.6343	2.3493	0.9858	0.7886	0.3309
1.6134	0.3428	1.8310	0.3890	2.6988	0.5734	1.0052	0.2136
1.8384	0.1846	2.0653	0.2074	2.9352	0.2947	1.1789	0.1184
2.0962	0	2.3306	0	3.2036	0	1.3937	0
2.0956	0	2.3288	0	3.2018	0	1.3926	0
Reference solutions [mol/kg]							
NaCl	1.3691	NaCl	1.6212	NaCl	2.8596	NaCl	0.7714
a_W	0.9541	a_W	0.9451	a_W	0.8985	a_W	0.9745
KCl	1.4345	KCl	1.7154	KCl	3.1368	KCl	0.7915
a_W	0.9543	a_W	0.9453	a_W	0.8989	a_W	0.9747

Tab. 2.17 Measured water activities of solutions of the system $ZnSO_4$ - NaCl - H_2O at 25 °C (II)

$ZnSO_4$ [mol/kg]	NaCl [mol/kg]	$ZnSO_4$ [mol/kg]	NaCl [mol/kg]	$ZnSO_4$ [mol/kg]	NaCl [mol/kg]
0	1.0192	0	2.3524	0	3.4902
0	1.0193	0	2.3525	0	3.4919
0	1.0187	0.2396	2.3773	0.3739	3.7102
0.0978	0.9709	0.4599	2.2830	0.7353	3.6500
0.1856	0.9216	0.6924	2.1238	1.0965	3.3633
0.2822	0.8655	1.0090	1.8775	1.5457	2.8762
0.4241	0.7891	1.2301	1.6422	1.8292	2.4419
0.5355	0.7149	1.5388	1.3494	2.1993	1.9285
0.7045	0.6178	1.7836	1.0973	2.4707	1.5199
0.8562	0.5267	2.0262	0.8503	2.7276	1.1446
1.0222	0.4289	2.3681	0.5031	3.0688	0.6520
1.2838	0.2727	2.6125	0.2623	3.3055	0.3319
1.4866	0.1493	2.8842	0	3.5638	0
1.7273	0	2.8831	0	3.5657	0
1.7269	0				
Reference solutions [mol/kg]					
NaCl	1.0191	NaCl	2.3524	NaCl	3.4910
a_W	0.9661	a_W	0.9182	a_W	0.8728
KCl	1.0576	KCl		KCl	
a_W	0.9663	a_W		a_W	

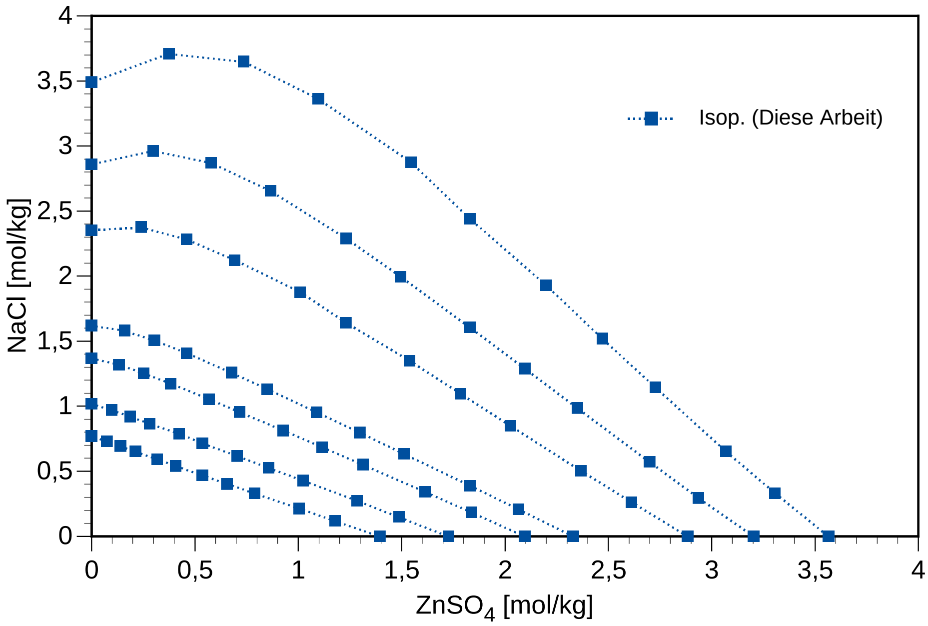

Fig. 2.9 Isoactivity lines in the quasi-ternary system $ZnSO_4$ - NaCl - H_2O at 25 °C

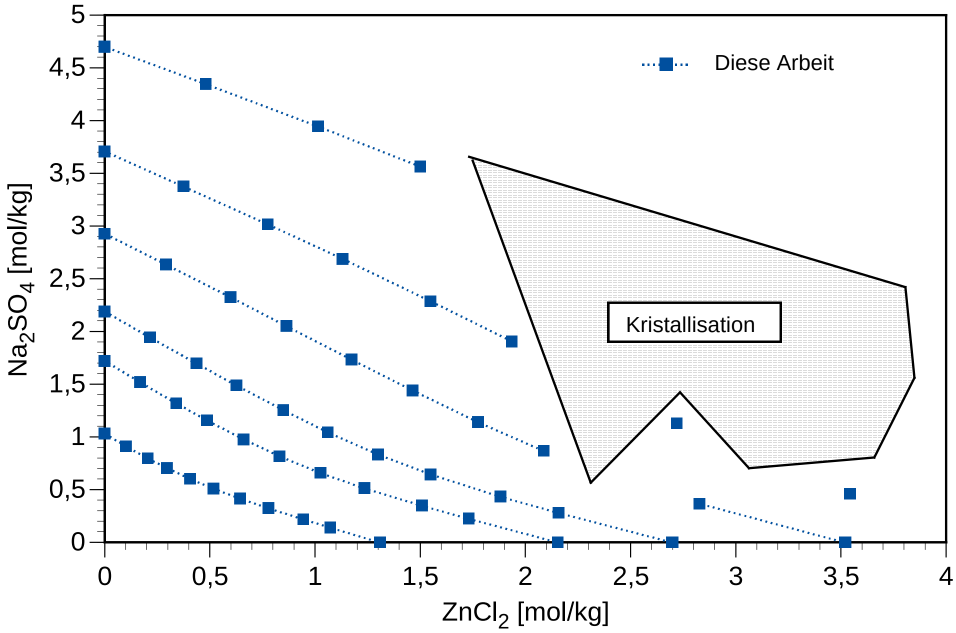

Fig. 2.10 Isoactivity lines in the quasi-ternary system $ZnCl_2$ – Na_2SO_4 - H_2O at 25 °C

Tab. 2.18 Measured water activities of solutions of the system $ZnCl_2$ - Na_2SO_4 - H_2O at 25 °C (I)

Na_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]	Na_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]	Na_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]	Na_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]
0.0000	1.0304	0.0000	1.7202	0.0000	2.1880	0.0000	2.9267
0.0000	1.0305	0.0000	1.7203	0.0000	2.1884	0.0000	2.9267
0.1010	0.9112	0.1684	1.5195	0.2155	1.9452	0.2920	2.6350
0.2050	0.7967	0.3397	1.3203	0.4367	1.6976	0.5981	2.3251
0.2963	0.7041	0.4868	1.1570	0.6265	1.4890	0.8637	2.0526
0.4070	0.6010	0.6609	0.9760	0.8491	1.2539	1.1741	1.7339
0.5172	0.5090	0.8306	0.8175	1.0608	1.0441	1.4634	1.4403
0.6447	0.4140	1.0254	0.6585	1.2988	0.8340	1.7752	1.1400
0.7784	0.3237	1.2344	0.5133	1.5497	0.6444	2.0871	0.8679
0.9447	0.2182	1.5076	0.3482	1.8809	0.4344	Crystallisation	
1.0733	0.1394	1.7302	0.2247	2.1581	0.2802	2.8273	0.3671
1.3081	0.0000	2.1538	0.0000	2.6975	0.0000	3.5174	0.0000
1.3091	0.0000	2.1537	0.0000	2.6996	0.0000	3.5208	0.0000
Reference solutions [mol/kg]							
NaCl	1.3006	NaCl	2.0541	NaCl	2.5791	NaCl	3.4612
a_W	0.9565	a_W	0.9294	a_W	0.9095	a_W	0.8740

2.5.9 The quaternary system Zn, K | Cl, SO_4 - H_2O

In this system, only solubility data from D'Ans and Kaufmann (1957) were previously available. They provided little information on the solubility ratios in the quasi-ternary subsystems $ZnSO_4$ – KCl – H_2O (Tab. 2.20 f.) and $ZnCl_2$ – K_2SO_4 – H_2O (Tab. 2.22 f.). It is therefore hardly surprising that in several isopiestical experiments solids were formed because previously unknown solubility limits were exceeded. In most cases, the solid phases formed are probably the double salt $K_2SO \cdot ZnSO_4 \cdot 6H_2O$, which according to D'Ans and Kaufmann (1957) has a very large stability area in the quaternary system $ZnSO_4$ – KCl – H_2O. The crystallisation field in the system $ZnCl_2$ – K_2SO_4 – H_2O possibly hints at the formation of $K_2SO_4 \cdot 2ZnCl_2 \cdot 5H_2O$ that what described by D'Ans and Kaufmann (1957). The occurrence of single measuring points beyond this crystallisation area may indicate strongly supersaturated solutions that were also observed in this system by the above-mentioned authors. However, the solid phases were not investigated further.

Tab. 2.19 Measured water activities of solutions of the system $ZnCl_2$ - Na_2SO_4 - H_2O at 25 °C (II)

Na_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]	Na_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]
0.0000	3.7081	0.0000	4.6991
0.0000	3.7069	0.0000	4.7000
0.3741	3.3760	0.4816	4.3464
0.7759	3.0160	1.0146	3.9442
1.1311	2.6883	1.4997	3.5642
1.5484	2.2866	Crystallisation	
1.9358	1.9053		
Crystallisation			
2.7195	1.1308		
Crystallisation			
3.5436	0.4601		
Reference solutions [mol/kg]			
NaCl	4.4657	NaCl	5.8596
a_W	0.8309	a_W	0.7668

Compared to the analogous sodium system, the observable homogeneous solution areas are significantly smaller due to the lower solubilities of the potassium salts. The curves of the isoactivity lines are very similar. In the system $ZnCl_2$ – K_2SO_4 – H_2O they are almost straight, in the system $ZnSO_4$ – KCl – H_2O slightly convex (Fig. 2.11 f.).

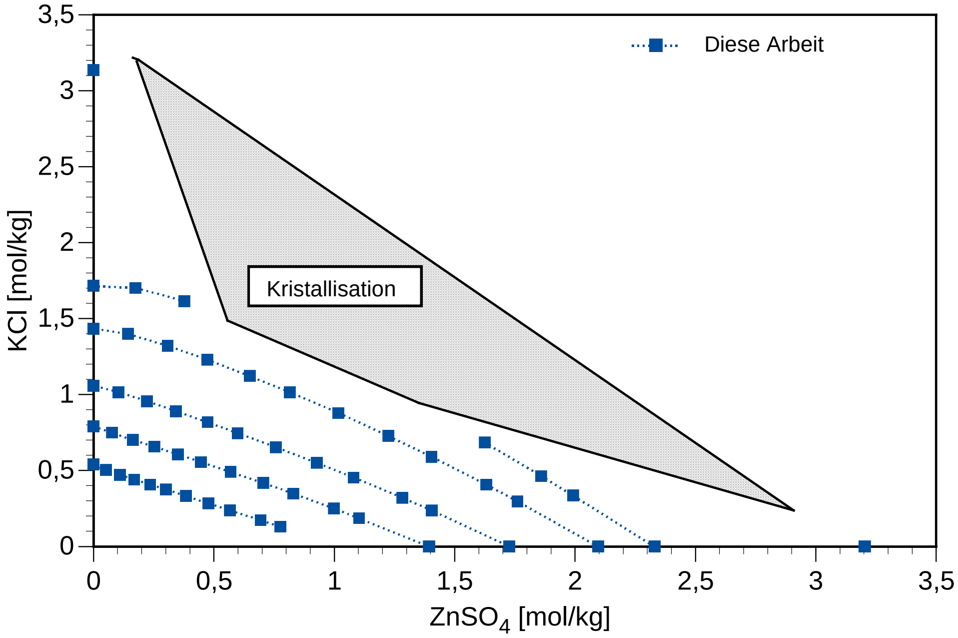

Fig. 2.11 Isoactivity lines in the quasi-ternary system $ZnSO_4$ – KCl – H_2O at 25°C

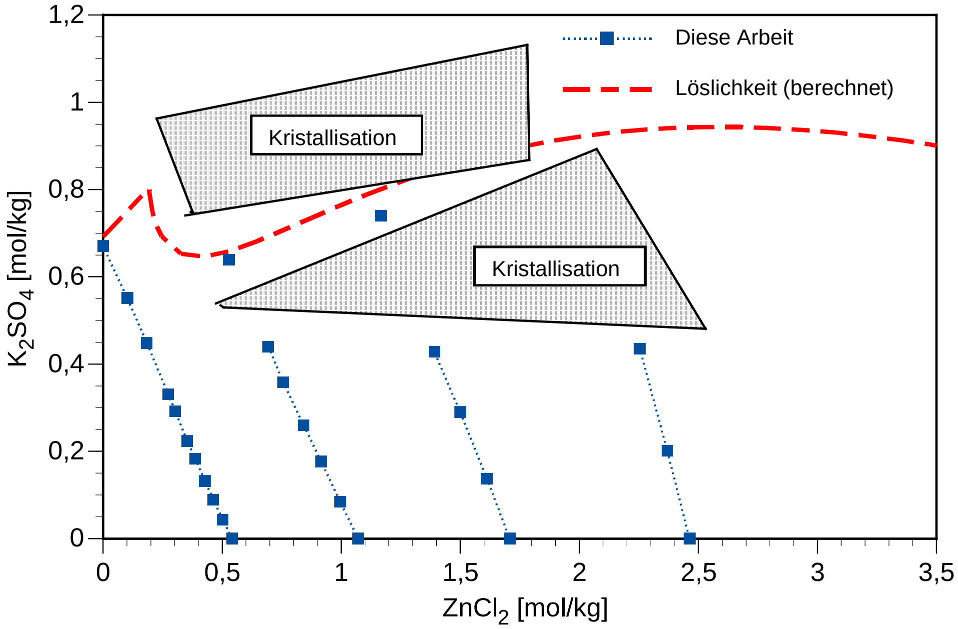

Fig. 2.12 Isoactivity lines in the quasi-ternary system $ZnCl_2$ – K_2SO_4 – H_2O at 25°C

Tab. 2.20 Measured water activities of solutions of the system $ZnSO_4$ – KCl – H_2O at 25 °C (I)

$ZnSO_4$ [mol/kg]	**KCl [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**KCl [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**KCl [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**KCl [mol/kg]**
2.0962	0	2.3306	0	3.2036	0	1.3937	0
2.0956	0	2.3288	0	3.2018	0	1.3926	0
1.7607	0.2966	1.9916	0.3355	Crystallisation		1.1022	0.1857
1.6315	0.4075	1.8589	0.4643	0	3.1364	0.9992	0.2495
1.4036	0.5905	1.6257	0.6840	0	3.1373	0.8291	0.3488
1.2246	0.7280	Crystallisation		0	3.1366	0.7048	0.4190
1.0170	0.8792	0.3765	1.6161			0.5693	0.4922
0.8144	1.0161	0.1743	1.7021			0.4460	0.5564
0.6490	1.1222	0	1.7152			0.3506	0.6063
0.4726	1.2297	0	1.7163			0.2526	0.6572
0.3079	1.3217	0	1.7146			0.1635	0.7018
0.1433	1.3991					0.0767	0.7491
0	1.4346					0	0.7918
0	1.4350					0	0.7911
0	1.4340					0	0.7915
Reference solutions [mol/kg]							
NaCl	1.3691	NaCl	1.6212	NaCl	2.8596	NaCl	0.7714
a_W	0.9541	a_W	0.9451	a_W	0.8985	a_W	0.9745
KCl	1.4345	KCl	1.7154	KCl	3.1368	KCl	0.7915
a_W	0.9543	a_W	0.9453	a_W	0.8989	a_W	0.9747

Tab. 2.21 Measured water activities of solutions of the system $ZnSO_4$ - KCl - H_2O at 25 °C (II)

$ZnSO_4$ [mol/kg]	KCl [mol/kg]	$ZnSO_4$ [mol/kg]	KCl [mol/kg]
1.7273	0	0.7757	0.1307
1.7269	0	0.6934	0.1732
1.4049	0.2367	0.5666	0.2384
1.2832	0.3205	0.4774	0.2838
1.0799	0.4543	0.3845	0.3324
0.9270	0.5511	0.3007	0.3752
0.7567	0.6542	0.2361	0.4082
0.5986	0.7467	0.1695	0.4410
0.4733	0.8185	0.1098	0.4714
0.3425	0.8911	0.0516	0.5034
0.2227	0.9560	0	0.5394
0.1040	1.0160	0	0.5401
0	1.0578	0	0.5401
0	1.0575		
0	1.0576		
Reference solutions [mol/kg]			
NaCl	1.0191		
a_W	0.9661		
KCl	1.0576	KCl	0.5399
a_W	0.9663	a_W	0.9827

Tab. 2.22 Measured water activities of solutions of the system $ZnCl_2$ – K_2SO_4 - H_2O at 25 °C

K_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]	K_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]	K_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]	K_2SO_4 [mol/kg]	$ZnCl_2$ [mol/kg]
0	0.5416	0	1.0707	0	1.7071	0	2.4635
0	0.5419	0	1.0711	0	1.7077	0	2.4624
0.04267	0.5024	0.0846	0.9957	0.1369	1.6116	0.2012	2.3692
0.0893	0.4624	0.1769	0.9156	0.2898	1.4999	0.4354	2.2539
0.1318	0.4278	0.2596	0.8426	0.4285	1.3909	Crystallisation	
0.1827	0.3864	0.3579	0.7567	Crystallisation			
0.2235	0.3526	0.4399	0.6939	0.7394	1.1662		
0.2918	0.3028	Crystallisation		Crystallisation			
0.3310	0.2729	0.6391	0.5270				
0.4480	0.1833	Crystallisation					
0.5515	0.1018						
0.6702	0						
0.6698	0						
Reference solutions [mol/kg]							
KCl	0.74687	KCl	1.4231	KCl	2.2007	KCl	3.1977
a_W	0.97612	a_W	0.9547	a_W	0.9297	a_W	0.8968

2.5.10 The quaternary system Zn, Mg | Cl, SO_4 - H_2O

The two quasi-ternary systems $ZnCl_2$-$MgSO_4$-H_2O and $ZnSO_4$-$MgCl_2$-H_2O were studied with six isoactivity lines each (Tab. 2.25f., Tab. 2.23f.). It is striking that the isoactivity lines in the $ZnSO_4$ - $MgCl_2$ - H_2O system are much more outwardly curved than in the corresponding Na and K analogues (Fig. 2.13). The picture of the $ZnCl_2$ - $MgSO_4$ -H_2O system, on the other hand, differs only slightly from the alkali metal systems investigated previously (Fig. 2.14). The nature of the precipitates observed in some cases can only be speculated on, as systematic solubility studies in these systems are lacking so far.

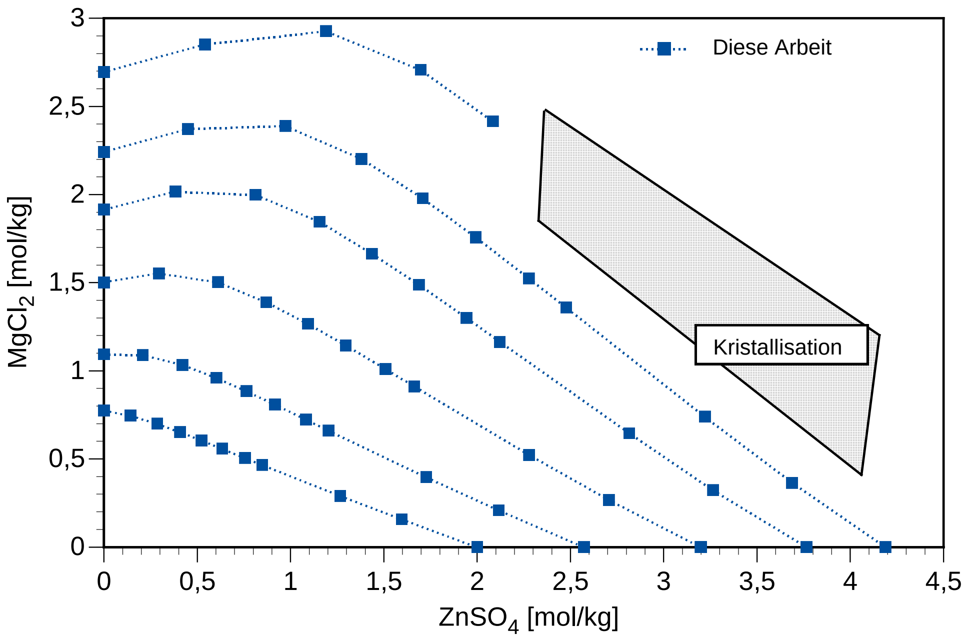

Fig. 2.13 Isoactivity lines in the quasi-ternary system $ZnSO_4$ - $MgCl_2$ - H_2O at 25 °C

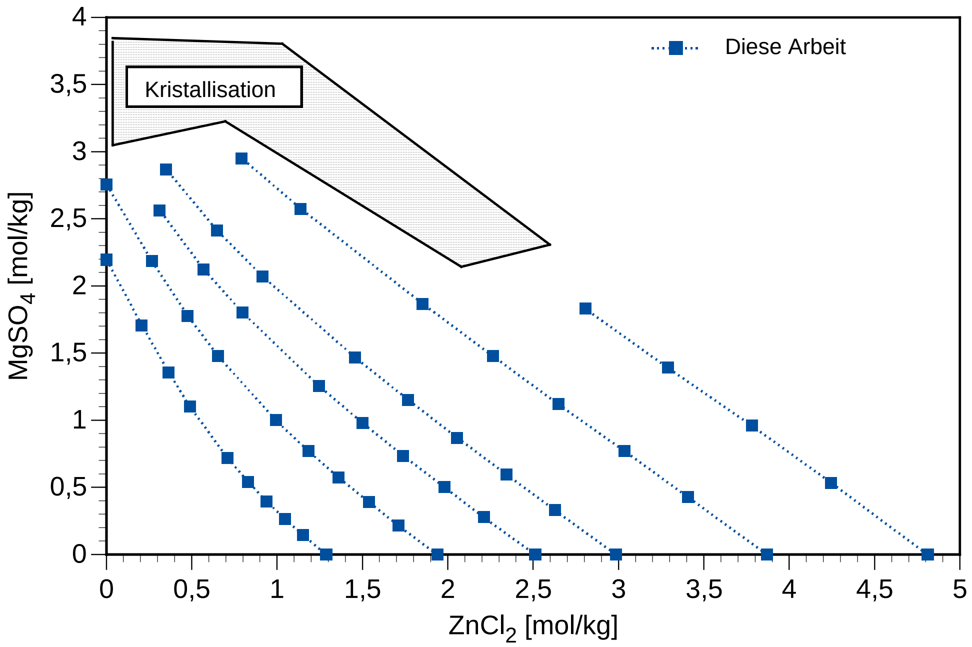

Fig. 2.14 Isoactivity lines in the quasi-ternary system $ZnCl_2$ - $MgSO_4$ - H_2O at 25 °C

Tab. 2.23 Measured water activities of solutions of the system $ZnSO_4$ - $MgCl_2$ - H_2O at 25 °C (I)

$ZnSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]
0	0.7754	0	1.5017	0.0000	2.2418	0.0000	1.0940
0	0.7754	0	1.5018	0.0000	2.2424	0.0000	1.0938
0.1416	0.7466	0.2944	1.5528	0.4497	2.3719	0.2066	1.0898
0.2847	0.7000	0.6112	1.5026	0.9717	2.3892	0.4205	1.0339
0.4085	0.6521	0.8703	1.3892	1.3800	2.2028	0.6017	0.9605
0.5222	0.6052	1.0932	1.2670	1.7075	1.9789	0.7636	0.8850
0.6327	0.5583	1.2964	1.1439	1.9922	1.7578	0.9165	0.8087
0.7556	0.5056	1.5091	1.0099	2.2774	1.5241	1.0821	0.7241
0.8486	0.4657	1.6621	0.9121	2.4773	1.3595	1.2044	0.6609
1.2661	0.2907	2.2779	0.5231	3.2208	0.7396	1.7262	0.3964
1.5962	0.1577	2.7058	0.2673	3.6876	0.3643	2.1156	0.2090
2.0002	0	3.1982	0	4.1886	0	2.5733	0
2.0006	0	3.2001	0				
Reference solutions [mol/kg]							
NaCl	1.2717	NaCl	2.8527	NaCl	4.7349	NaCl	1.9253
a_W	0.9575	a_W	0.8987	a_W	0.8188	a_W	0.9341

Tab. 2.24 Measured water activities of solutions of the system $ZnSO_4$ - $MgCl_2$ - H_2O at 25 °C (II)

$ZnSO_4$ [mol/kg]	**$MgCl_2$ [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**$MgCl_2$ [mol/kg]**
0	1.9162	0	2.6957
0	1.9152	0	2.6953
0.3826	2.0179	0.5408	2.8521
0.8129	1.9987	1.1903	2.9264
1.1562	1.8456	1.6963	2.7078
1.4361	1.6644	2.0842	2.4156
1.6872	1.4887	Crystallisation	
1.9432	1.3004		
2.1219	1.1644		
2.8146	0.6463		
3.2645	0.3225		
3.7654	0		
Reference solutions [mol/kg]			
NaCl	3.8808	$MgCl_2$	2.6955
a_W	0.8563	a_W	0.7611

Tab. 2.25 Measured water activities of solutions of the system $ZnCl_2$ - $MgSO_4$ - H_2O at 25 °C (I)

$ZnSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$ZnSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]
0	2.1948	0	2.7539	Crystallisation		Crystallisation	
0	2.1952	0	2.7548	0.3498	2.8692	0.7933	2.9501
0.2078	1.7046	0.2663	2.1841	0.6490	2.4133	1.1393	2.5749
0.3645	1.3553	0.4773	1.7748	0.9161	2.0706	1.8530	1.8664
0.4882	1.1033	0.6540	1.4781	1.4569	1.4674	2.2647	1.4776
0.7109	0.7160	0.9930	1.0002	1.7672	1.1529	2.6470	1.1192
0.8297	0.5413	1.1828	0.7717	2.0545	0.8687	3.0361	0.7694
0.9379	0.3966	1.3594	0.5748	2.3454	0.5944	3.4061	0.4273
1.0460	0.2651	1.5376	0.3896	2.6277	0.3296	3.8691	0
1.1509	0.1444	1.7119	0.2147	2.9857	0	3.8694	0
1.2878	0	1.9382	0	2.9866	0		
1.2887	0	1.9394	0				
Reference solutions [mol/kg]							
NaCl	1.5828	NaCl	2.2940	NaCl	3.5341	NaCl	4.6880
a_W	0.9465	a_W	0.9204	a_W	0.8710	a_W	0.8209

Tab. 2.26 Measured water activities of solutions of the system $ZnCl_2$ - $MgSO_4$ - H_2O at 25 °C (II)

$ZnSO_4$ [mol/kg]	**$MgCl_2$ [mol/kg]**	**$ZnSO_4$ [mol/kg]**	**$MgCl_2$ [mol/kg]**
Crystallisation		Crystallisation	
2.8061	1.8308	0.3125	2.5637
3.2897	1.3910	0.5710	2.1231
3.7827	0.9586	0.7967	1.8006
4.2463	0.5327	1.2459	1.2549
4.8098	0.0000	1.5002	0.9788
4.8114	0.0000	1.7388	0.7352
		1.9795	0.5016
		2.2114	0.2774
		2.5122	0
		2.5127	0
Reference solutions [mol/kg]			
NaCl	6.0119	NaCl	2.9519
a_W	0.7595	a_W	0.8948

2.6 Systems containing cadmium

2.6.1 The $CdCl_2$ - H_2O system

Numerous isopiestic studies were already available for this system. The additional data we obtained are listed in Tab. 2.27 listed. They agree very well with the literature data (Fig. 2.15). A more detailed discussion of the available data follows in chapter 7.4 (p. 154).

Tab. 2.27 Experimentally determined water activities of $CdCl_2$ solutions at 25.0 °C (RUMYANTSEV)

Concentration $CdCl_2$ [mol/kg]	Concentration of the stock solution KCl [mol/kg]	Concentration of the stock solution NaCl [mol/kg]	Water activity a_W [ ]	Osmotic Coefficient [ ]
1.4691	0.7908		0.97474	0.4834
2.0027	1.2169		0.96124	0.5478
2.1207		1.2717	0.95745	0.5690
2.5085	1.7362		0.94467	0.6298
2.7641		1.9253	0.93413	0.6842
2.9015	2.2291		0.92873	0.7072
3.3770	2.9199		0.90605	0.8109
3.4998		2.8527	0.89873	0.8467
3.7260	3.4835		0.88727	0.8909
4.2310		3.8808	0.85633	1.0174
4.8294		4.7349	0.81884	1.1486

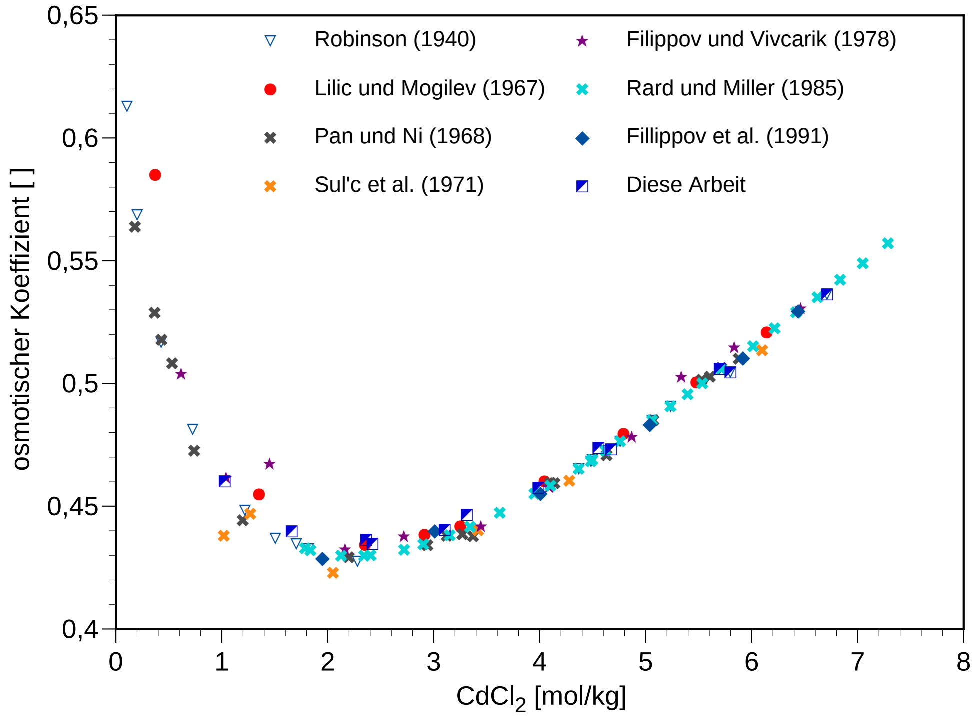

Fig. 2.15 Experimentally determined osmotic coefficients of $CdCl_2$ solutions at 25.0 °C (literature data and this work)

2.6.2 The $CdSO_4$ - H_2O system

Isopiestic measurements for this system were previously only available from ROBINSON and JONES (1936) and FILIPPOV et al. (1973, 1985). ROBINSON and JONES published only smoothed data. Because data are otherwise lacking, especially in the lower concentration range, we have conducted some additional measurements. They also cover the supersaturated range (above 3.7 mol/kg) for the first time (Tab. 2.28). They agree well with the earlier results (Fig. 2.16).

Tab. 2.28 Isopiestic concentrations and water activities of cadmium sulphate solutions (This work)

Concentration $CdSO_4$ [mol/kg]	Concentration of the stock solution KCl [mol/kg]	Concentration of the stock solution NaCl [mol/kg]	Water activity a_W [ ]	Osmotic coefficient [ ]
1.3874		0.7201	0.9763	0.4798
1.4691	0.7908		0.9747	0.4841
1.7717		0.9833	0.9674	0.5192
2.0027	1.2169		0.9613	0.5470
2.1207		1.2717	0.9575	0.5684
2.1293		1.2796	0.9573	0.5688
2.5085	1.7362		0.9448	0.6282
2.6126		1.7550	0.9405	0.6517
2.7641		1.9253	0.9343	0.6824
2.9011	2.2275		0.9291	0.7035
2.9015	2.2291		0.9290	0.7045
3.1187		2.3527	0.9184	0.7575
3.1500	2.5784		0.9177	0.7567
3.3770	2.9199		0.9064	0.8077
3.4682		2.8079	0.9008	0.8360
3.4998		2.8527	0.8990	0.8444
3.7260	3.4835		0.8877	0.8873
3.9548		3.4953	0.8729	0.9540
4.2310		3.8808	0.8566	1.0153
4.8294		4.7349	0.8189	1.1482

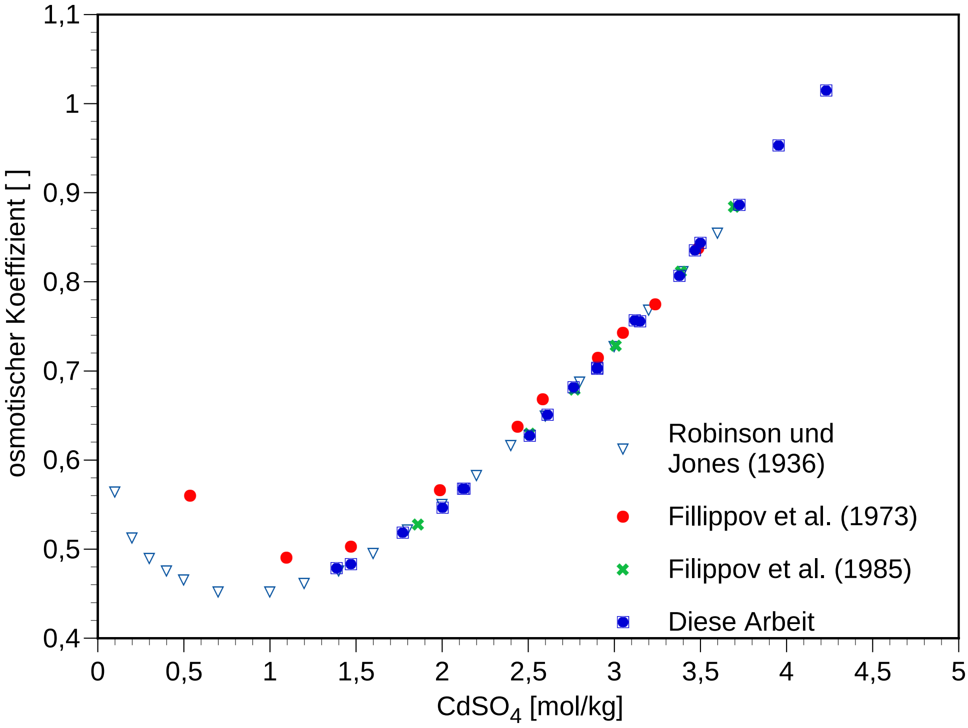

Fig. 2.16 Experimentally determined osmotic coefficients of $CdSO_4$ solutions at 25.0 °C (literature data and this work)

2.6.3 The system $CdSO_4$ - $CdCl_2$ - H_2O

Up to now, no data was available for this system, only one isoactivity was mentioned but not documented by FILIPPOV et al. (1991). According to the authors, it is a straight line, thus the system $CdSO_4$ - $CdCl_2$ - H_2O represents a Zdanovsky system. We were able to confirm this statement to a large extent with our measurements (Tab. 2.29). The deviation from linearity is indeed very small (Fig. 2.17).

Tab. 2.29 Measured water activities of solutions of the system $CdCl_2$-$CdSO_4$-H_2O at 25°°C (I)

$CdCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]	$CdCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]	$CdCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]	$CdCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]
1.0285	0	1.6612	0	2.4213	0	3.1035	0
1.0284	0	1.6622	0	2.4223	0	3.1043	0
0.9366	0.1427	1.4802	0.2255	2.1100	0.3215	2.6606	0.4053
0.8419	0.2823	1.3042	0.4373	1.8258	0.6122	2.2781	0.7638
0.7423	0.4216	1.1322	0.6431	1.5596	0.8859	1.9255	1.0937
0.6473	0.5585	0.9701	0.8370	1.3180	1.1371	1.6131	1.3918
0.5379	0.7150	0.7908	1.0512	1.0584	1.4069	1.2838	1.7066
0.4421	0.8493	0.6405	1.2304	0.8476	1.6284	1.0192	1.9580
0.3349	1.0001	0.4778	1.4270	0.6236	1.8625	0.7437	2.2211
0.2256	1.1530	0.3171	1.6205	0.4081	2.0861	0.4822	2.4647
0.1052	1.3218	0.1455	1.8270	0.1845	2.3178	0.2154	2.7061
0	1.4691	0	2.0020	0	2.5082	0	2.9016
0	1.4691	0	2.0033	0	2.5087	0	2.9014
Reference solutions [mol/kg]							
KCl	0.7908	KCl	1.2169	KCl	1.7362	KCl	2.2291
a_W	0.9747	a_W	0.9613	a_W	0.9448	a_W	0.9290

Tab. 2.30 Measured water activities of solutions of the system $CdCl_2$ - $CdSO_4$ - H_2O at 25°°C (II)

$CdCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]	$CdCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]	$CdCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]
3.9878	0	4.6738	0	5.7971	0
3.9884	0	4.6723	0	5.7990	0
3.3737	0.5140	3.9246	0.5979	4.8379	0.7370
2.8608	0.9592	3.3051	1.1082	4.0503	1.3581
2.3975	1.3618	2.7591	1.5673	3.3705	1.9145
1.9948	1.7211	2.2823	1.9691	2.7730	2.3925
1.5709	2.0882	1.7901	2.3795	2.1567	2.8669
1.2363	2.3750	1.4026	2.6946	1.6805	3.2284
0.8936	2.6688	1.0062	3.0052	1.1955	3.5706
0.5738	2.9331	0.6416	3.2795		
0.2536	3.1848	0.2817	3.5383		
0	3.3760	0	3.7249		
0	3.3779	0	3.7272		
Reference solutions [mol/kg]					
KCl	2.9199	KCl	3.4835	KCl	4.4775
a_W	0.9064	a_W	0.8877	a_W	0.8538

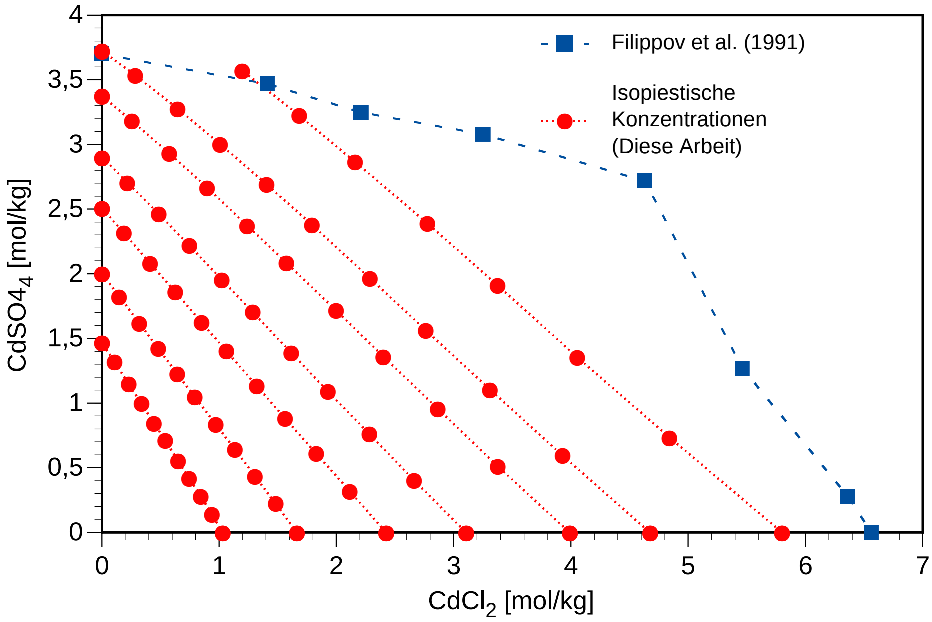

Fig. 2.17 Isopiestic concentrations in the system $CdCl$-$CdSO_4$-H_2O at 25 °C

2.6.4 The system $CdCl_2$ - $MgCl_2$ - H_2O

The system $CdCl_2$- $MgCl_2$ - H_2O was investigated by us for the first time (Tab. 2.31 f.). Despite the high chloride concentrations occurring, the curvature of the isoactivity lines is weak, but increases with higher chloride concentrations (Fig. 2.18).

Tab. 2.31 Measured water activities of solutions of the system $CdCl_2$ - $MgCl_2$ - H_2O at 25°°C (I)

$CdCl_2$ [mol/kg]	**$MgCl_2$ [mol/kg]**	**$CdCl_2$ [mol/kg]**	**$MgCl_2$ [mol/kg]**	**$CdCl_2$ [mol/kg]**	**$MgCl_2$ [mol/kg]**	**$CdCl_2$ [mol/kg]**	**$MgCl_2$ [mol/kg]**
0	0.9420	0	1.2301	0	1.5955	0	1.9255
0	0.9421	0	1.2299	0	1.5962	0	1.9260
0.1837	0.8953	0.2431	1.1845	0.3191	1.5549	0.3875	1.8882
0.4009	0.8336	0.5381	1.1191	0.7155	1.4878	0.8767	1.8231
0.5871	0.7751	0.7968	1.0520	1.0706	1.4135	1.3219	1.7453
0.8549	0.6831	1.1760	0.9397	1.6009	1.2792	1.9961	1.5950
1.1050	0.5892	1.5350	0.8185	2.1078	1.1239	2.6427	1.4091
1.3686	0.4823	1.9136	0.6743	2.6409	0.9306	3.3248	1.1715
1.6115	0.3755	2.2618	0.5270	3.1267	0.7285	3.9370	0.9173
1.8690	0.2545	2.6276	0.3578	3.6294	0.4942	4.5635	0.6214
2.1012	0.1389	2.9512	0.1950	4.0674	0.2688	5.1040	0.3373
2.3620	0	3.3130	0	4.5524	0	5.6965	0
2.3609	0	3.3125	0	4.5529	0	5.6983	0
Reference solutions [mol/kg]							
NaCl	1.6018	NaCl	2.2199	NaCl	3.0732	NaCl	3.8967
a_W	0.9460	a_W	0.9234	a_W	0.8902	a_W	0.8559

Tab. 2.32 Measured water activities of solutions of the system $CdCl_2$ - $MgCl_2$ - H_2O at 25°°C (II)

$CdCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$MgCl_2$ [mol/kg]
0	2.2075	0	2.4880	0	3.1794	0	4.1460
0	2.2084	0	2.4887	0	3.1802	0	4.1448
0.4461	2.1739	0.5041	2.4565	0.6463	3.1495	0.8463	4.1240
1.0160	2.1127	1.1539	2.3995	1.4913	3.1011	1.9627	4.0816
1.5410	2.0345	1.7586	2.3219	2.2923	3.0265	3.0365	4.0090
2.3447	1.8736	2.6915	2.1508	3.5633	2.8474		
3.1201	1.6636	3.6042	1.9218	4.8232	2.5718		
3.9337	1.3861	4.5616	1.6073	6.1675	2.1732		
4.6578	1.0852	5.4007	1.2583				
5.3929	0.7344	6.2507	0.8512				
6.0218	0.3979	6.9704	0.4606				
6.7096	0						
6.7110	0						
Reference solutions [mol/kg]							
NaCl	4.6382	NaCl	5.3951	$CaCl_2$	3.4449	$CaCl_2$	4.5313
a_W	0.8233	a_W	0.7885	a_W	0.6949	a_W	0.5549

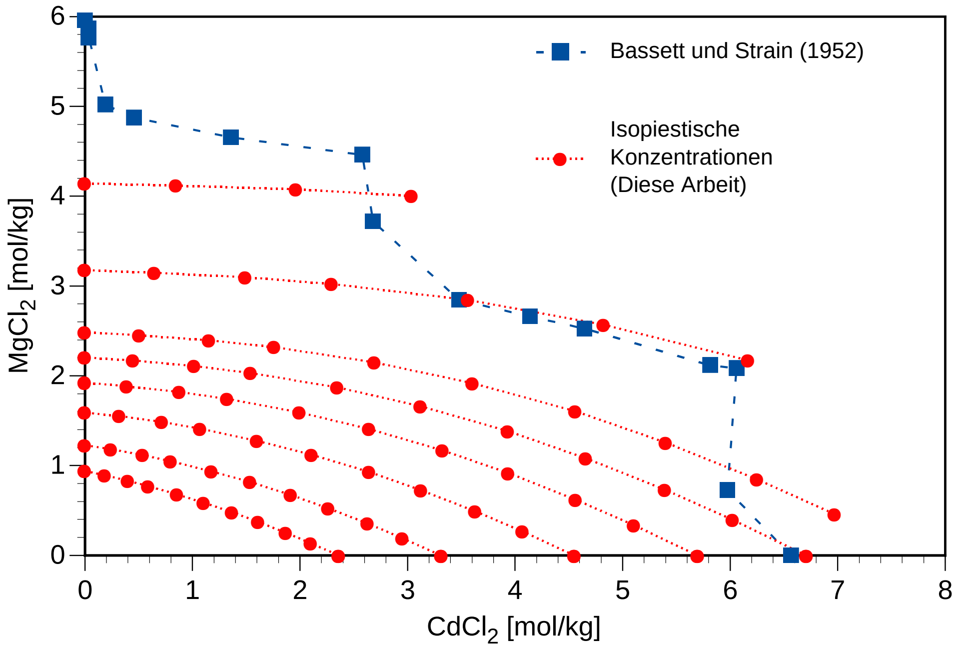

Fig. 2.18 Experimentally determined isoactivity lines in the system $CdCl_2$- $MgCl_2$ - H_2O at 25 °C

2.6.5 The system $CdCl_2$- $CaCl_2$ - H_2O

We also examined this system isopiestically for the first time (Tab. 2.33). The shape of the isoactivity lines strongly resembles the analogous system with magnesium (see above, Fig. 2.19).

Tab. 2.33 Measured water activities of solutions of the system $CdCl_2$ - $CaCl_2$ - H_2O at 25°°C (I)

$CdCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]
2.3620	0	3.3130	0	4.5524	0	5.6965	0
2.3609	0	3.3125	0	4.5529	0	5.6983	0
2.1328	0.1370	3.0043	0.1930	4.1420	0.2662	5.1970	0.3339
1.9212	0.2561	2.7119	0.3616	3.7550	0.5006	4.7197	0.6292
1.6666	0.3880	2.3534	0.5479	3.2676	0.7607	4.1222	0.9596
1.4267	0.5022	2.0124	0.7084	2.7945	0.9837	3.5293	1.2423
1.1498	0.6210	1.6119	0.8706	2.2316	1.2053	2.8126	1.5191
0.9108	0.7141	1.2668	0.9932	1.7409	1.3649	2.1812	1.7102
0.6626	0.8013	0.9104	1.1008	1.2368	1.4955	1.5387	1.8605
0.4132	0.8795	0.5595	1.1910	0.7496	1.5955	0.9233	1.9653
0.2052	0.9373	0.2740	1.2516	0.3624	1.6554	0.4428	2.0226
0	0.9868	0	1.2982	0	1.6971	0	2.0588
0	0.9865	0	1.2981	0	1.6967	0	2.0589
Reference solutions [mol/kg]							
NaCl	1.6018	NaCl	2.2199	NaCl	3.0732	NaCl	3.8967
a_W	0.9460	a_W	0.9234	a_W	0.8902	a_W	0.8559

Tab. 2.34 Measured water activities of solutions of the system $CdCl_2$ - $CaCl_2$ - H_2O at 25°°C (II)

$CdCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]	$CdCl_2$ [mol/kg]	$CaCl_2$ [mol/kg]
6.7096	0	7.1011	0.4563	6.5052	2.2899	5.2010	4.0778
6.7110	0	6.4628	0.8616	5.1002	2.7547	3.5624	4.3076
6.1292	0.3938	5.6373	1.3123	3.8966	3.0550	2.0877	4.4437
5.5725	0.7429	4.8382	1.7031	2.6944	3.2580	0.9841	4.4956
4.8708	1.1339	3.8320	2.0697	1.5836	3.3707	0	4.5312
4.1766	1.4702	2.9535	2.3156	0.7477	3.4156	0	4.5314
3.3230	1.7948	2.0600	2.4909	0	3.4453		
2.5691	2.0142	1.2212	2.5993	0	3.4449		
1.8006	2.1772	0.5801	2.6499				
1.0732	2.2842	0	2.6792				
0.5119	2.3385	0	2.6793				
0	2.3712						
0	2.3699						
Reference solutions [mol/kg]							
NaCl	4.6382	NaCl	5.3951	$CaCl_2$	3.4449	$CaCl_2$	4.5313
a_w	0.8233	a_w	0.7885	a_w	0.6949	a_w	0.5549

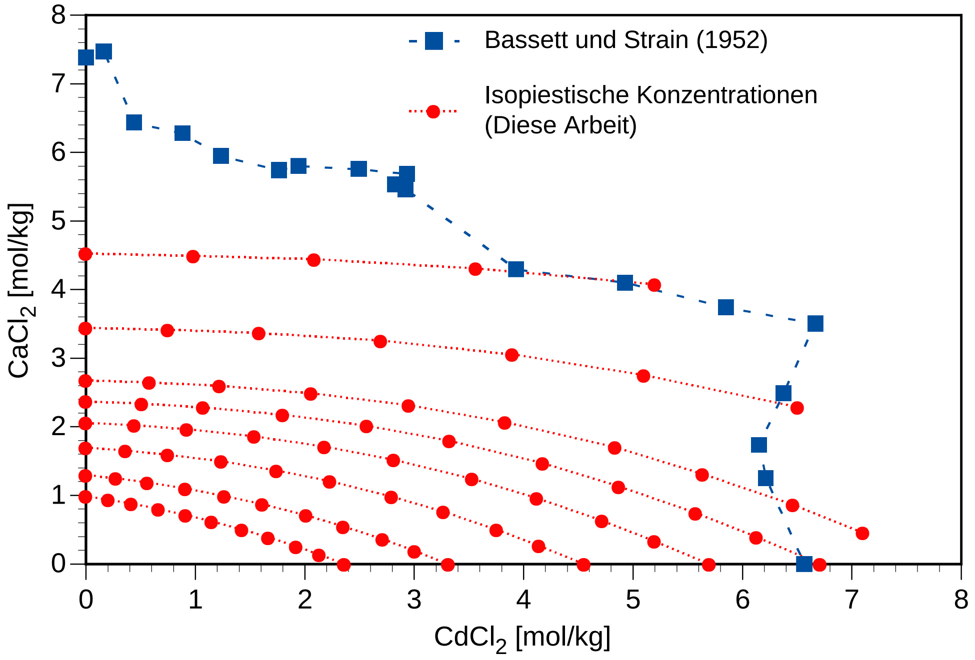

Fig. 2.19 Experimentally determined isoactivity lines in the system $CdCl_2$- $CaCl_2$ - H_2O at 25 °C

2.6.6 The quaternary system Cd, Na | Cl, SO_4 - H_2O

Apart from some solubility measurements by FILIPPOV et al. (1991), no data were available so far. Our measurements were devoted to the cross systems $CdCl_2$ - Na_2SO_4 - H_2O and $CdSO_4$ - NaCl - H_2O (Tab. 2.35 f.). The isoactivity lines in the system $CdSO_4$- NaCl-H_2O show a strong curvature towards higher sodium chloride concentrations (Fig. 2.20), an indication of the increasing binding of chloride and cadmium in chloro complexes. The curvature is just the opposite in the system $CdCl_2$ - Na_2SO_4 - H_2O: with increasing sodium sulphate concentration, chloro complex formation is obviously suppressed and thus the concentration of free cadmium ions is increased (Fig. 2.21).

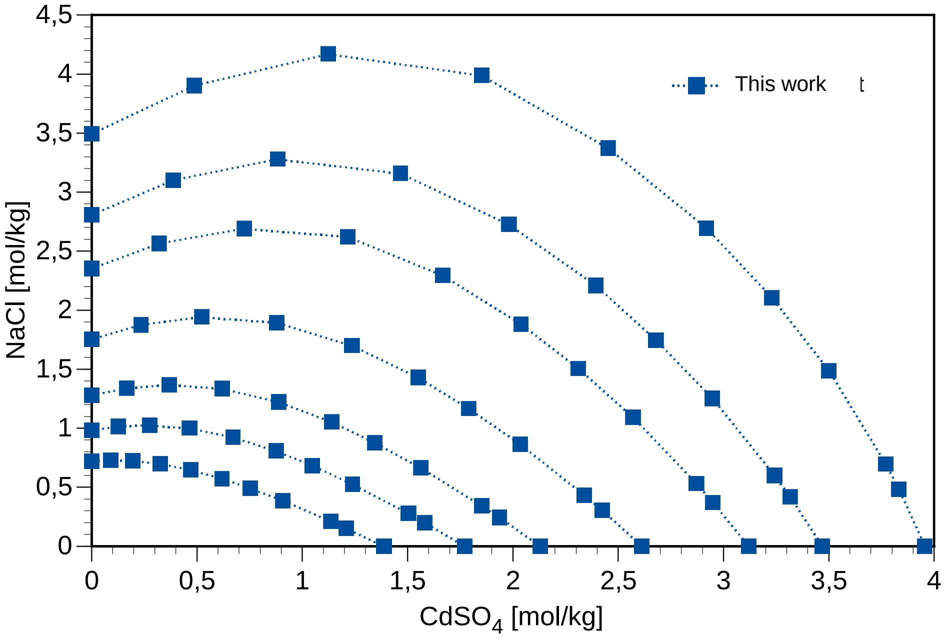

Fig. 2.20 Isopiestic concentrations in the system $CdSO_4$ - NaCl - H_2O at 25 °C

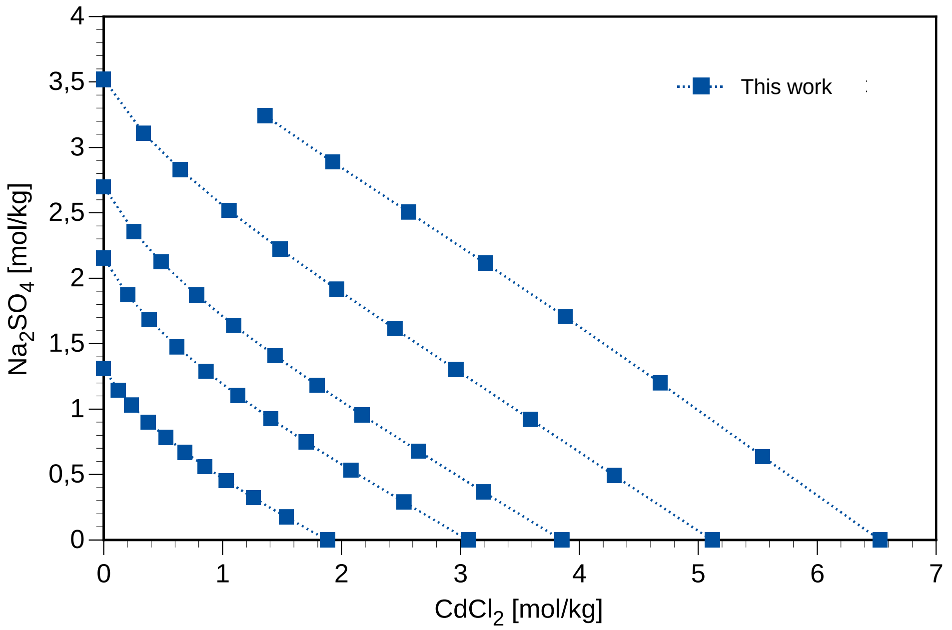

Fig. 2.21 Isopiestic concentrations in the system $CdCl_2$ - Na_2SO_4 - H_2O at 25 °C

Tab. 2.35 Measured water activities of solutions of the system $CdSO_4$ - NaCl - H_2O at 25 °C (I)

$CdSO_4$ [mol/kg]	NaCl [mol/kg]	$CdSO_4$ [mol/kg]	NaCl [mol/kg]	$CdSO_4$ [mol/kg]	NaCl [mol/kg]	$CdSO_4$ [mol/kg]	NaCl [mol/kg]
0	1.2796	0	1.7549	0	2.8080	0	0.7201
0	1.2798	0	1.7556	0	2.8086	0	0.7202
0	1.2794	0	1.7544	0	2.8071	0	0.7198
0.1675	1.3396	0.2344	1.8752	0.3876	3.1006	0.0911	0.7291
0.3685	1.3676	0.5235	1.9430	0.8838	3.2805	0.1950	0.7239
0.6200	1.3359	0.8792	1.8943	1.4662	3.1591	0.3250	0.7004
0.8883	1.2224	1.2359	1.7008	1.9811	2.7264	0.4706	0.6476
1.1407	1.0526	1.5502	1.4305	2.3935	2.2086	0.6191	0.5713
1.3450	0.8766	1.7901	1.1667	2.6793	1.7463	0.7528	0.4907
1.5628	0.6638	2.0353	0.8644	2.9471	1.2517	0.9081	0.3857
1.8515	0.3422	2.3380	0.4322	3.2420	0.5993	1.1361	0.2100
1.9365	0.2437	2.4235	0.3050	3.3159	0.4174	1.2089	0.1522
2.1295	0	2.6126	0	3.4683	0	1.3869	0
2.1294	0	2.6126	0	3.4679	0	1.3875	0
2.1290	0	2.6125	0	3.4685	0	1.3879	0
Reference solutions [mol/kg]							
NaCl	1.2796	NaCl	1.7550	NaCl	2.8079	NaCl	0.72005
a_W	0.9573	a_W	0.9405	a_W	0.9008	a_W	0.9763

Tab. 2.36 Measured water activities of solutions of the system $CdSO_4$ - NaCl - H_2O at 25 °C (II)

$CdSO_4$ [mol/kg]	NaCl [mol/kg]	$CdSO_4$ [mol/kg]	NaCl [mol/kg]	$CdSO_4$ [mol/kg]	NaCl [mol/kg]
0	0.9836	0	2.3533	0	3.4952
0	0.9830	0	2.3531	0	3.4954
0	0.9832	0	2.3517	0	3.4952
0.1269	1.0150	0.3207	2.5655	0.4879	3.9029
0.2760	1.0243	0.7250	2.6911	1.1235	4.1701
0.4646	1.0011	1.2164	2.6209	1.8512	3.9888
0.6715	0.9241	1.6667	2.2937	2.4516	3.3739
0.8758	0.8082	2.0389	1.8814	2.9191	2.6936
1.0478	0.6830	2.3103	1.5058	3.2290	2.1046
1.2378	0.5257	2.5702	1.0916	3.4999	1.4864
1.5044	0.2781	2.8716	0.5308	3.7700	0.6969
1.5816	0.1991	2.9491	0.3712	3.8318	0.4823
1.7714	0	3.1187	0	3.9548	0
1.7716	0				
1.7720	0				
Reference solutions [mol/kg]					
NaCl	0.9833	NaCl	2.3527	NaCl	3.4953
a_W	0.9674	a_W	0.9184	a_W	0.8729

Tab. 2.37 Measured water activities of solutions of the system $CdCl_2$ - Na_2SO_4 - H_2O at 25 °C (I)

Na_2SO_4 [mol/kg]	**$CdCl_2$ [mol/kg]**	**Na_2SO_4 [mol/kg]**	**$CdCl_2$ [mol/kg]**	**Na_2SO_4 [mol/kg]**	**$CdCl_2$ [mol/kg]**	**Na_2SO_4 [mol/kg]**	**$CdCl_2$ [mol/kg]**
1.3081	0	2.1538	0	2.6975	0	3.5174	0
1.3091	0	2.1537	0	2.6996	0	3.5208	0
1.1449	0.1240	1.8725	0.2028	2.3556	0.2551	3.1067	0.3364
1.0298	0.2344	1.6830	0.3830	2.1251	0.4836	2.8299	0.6440
0.8997	0.3761	1.4756	0.6169	1.8719	0.7826	2.5188	1.0531
0.7837	0.5230	1.2885	0.8600	1.6400	1.0945	2.2232	1.4838
0.6693	0.6851	1.1030	1.1290	1.4072	1.4404	1.9161	1.9612
0.5613	0.8516	0.9267	1.4060	1.1833	1.7953	1.6141	2.4489
0.4530	1.0306	0.7486	1.7029	0.9553	2.1732	1.3022	2.9622
0.3235	1.2590	0.5342	2.0795	0.6799	2.6463	0.9219	3.5884
0.1761	1.5357	0.2897	2.5260	0.3665	3.1952	0.4926	4.2945
0	1.8833	0	3.0669	0	3.8529	0	5.1176
0	1.8843	0	3.0668	0	3.8509	0	5.1159
Reference solutions [mol/kg]							
NaCl	1.3006	NaCl	2.0541	NaCl	2.5791	NaCl	3.4612
a_W	0.9565	a_W	0.9294	a_W	0.9095	a_W	0.8740

Tab. 2.38 Measured water activities of solutions of the system $CdCl_2$ – $NaSO_4$-H_2O at 25 °C (II)

Na_2SO_4 [mol/kg]	**$CdCl_2$ [mol/kg]**
Crystallisation	
3.2433	1.3560
2.8884	1.9278
2.5057	2.5648
2.1157	3.2099
1.7058	3.8804
1.2018	4.6782
0.6357	5.5424
0	6.5281
0	6.5269
Reference solutions	
NaCl	4.4657
a_W	0.8309

2.6.7 The quaternary system Cd, K | Cl, SO_4 - H_2O

There have been no published studies on this system so far. Our results for the subsystems $CdSO_4$ - KCl - H_2O (Tab. 2.39 f.) and $CdCl_2$ - K_2SO_4 -$_2$ HO (Tab. 2.41 f.) show that the isoactivity lines are interrupted by crystallisation regions even at relatively low potassium concentrations. At this stage, we can only speculate about the nature of the solid phases formed. Possible phases are arcanite (K_2SO_4) as well as the numerous K,Cd double salts known from the systems $CdSO_4$- K_2SO_4 - H_2O and $CdCl_2$ - KCl - H_2O. The recorded lines show an even stronger curvature than in the analogous sodium system (Fig. 2.22). It can be assumed that the potassium ion stabilises the cadmium chloro complexes better than sodium. Otherwise, we refer to the discussion of the analogous zinc systems. Because of the low solubility of potassium chloride, the concentration ratios that can be investigated are limited to narrow sections along the $CdCl_2$ axis. Fig. 2.23 gives a qualitative indication of the type of curve curvature occurring there. It is rather weakly pronounced.

Tab. 2.39 Measured water activities of solutions of the system $CdSO_4$ - KCl - H_2O at 25 °C (I)

$CdSO_4$ [mol/kg]	KCl [mol/kg]	$CdSO_4$ [mol/kg]	KCl [mol/kg]	$CdSO_4$ [mol/kg]	KCl [mol/kg]	$CdSO_4$ [mol/kg]	KCl [mol/kg]
2.1295	0	2.6126	0	3.4683	0	1.3869	0
2.1294	0	2.6126	0	3.4679	0	1.3875	0
2.1290	0	2.6125	0	3.4685	0	1.3879	0
2.0328	0.2148	2.5409	0.2685	3.5111	0.3710	1.2726	0.1345
1.9295	0.4257	2.4598	0.5427	3.4579	0.7629	1.1589	0.2557
1.7737	0.6935	2.3315	0.9115	3.4245	1.3389	1.0108	0.3952
1.5609	0.9945	2.1314	1.3580	3.3170	2.1135	0.8371	0.5334
1.3784	1.1966	1.9373	1.6817	3.1576	2.7410	0.7090	0.6155
1.0292	1.4508	1.5109	2.1298	Crystallisation		0.5067	0.7143
0.7534	1.5402	1.1422	2.3350	0	3.0750	0.3697	0.7558
0.4366	1.5312	0.6477	2.2717	0	3.0749	0.2203	0.7725
0.1743	1.4403	0.2502	2.0673	0	3.0745	0.0924	0.7637
0	1.3359	0	1.8589			0	0.7396
0	1.3360	0	1.8578			0	0.7392
0	1.3358	0	1.8573			0	0.7392
Reference solutions [mol/kg]							
NaCl	1.2796	NaCl	1.7550	NaCl	2.8079	NaCl	0.72005
a_W	0.9573	a_W	0.9405	a_W	0.9008	a_W	0.9763

Tab. 2.40 Measured water activities of solutions of the system $CdSO_4$ - KCl - H_2O at 25 °C (II)

$CdSO_4$ [mol/kg]	KCl [mol/kg]	$CdSO_4$ [mol/kg]	KCl [mol/kg]	$CdSO_4$ [mol/kg]	KCl [mol/kg]
1.7714	0	3.1499	0	2.9008	0
1.7716	0	3.1501	0	2.9014	0
1.7720	0	3.1212	0.3298	2.8510	0.3012
1.6619	0.1756	3.0779	0.6790	2.7894	0.6154
1.5477	0.3414	3.0015	1.1735	2.6836	1.0492
1.3906	0.5437	2.8525	1.8175	2.5014	1.5938
1.1885	0.7573	Crystallisation		2.3116	2.0066
1.0288	0.8931	0	2.5788	Crystallisation	
0.7488	1.0555	0	2.5786	0	2.2276
0.5442	1.1125	0	2.5780	0	2.2277
0.3184	1.1166			0	2.2271
0.1302	1.0757				
0	1.0195				
0	1.0192				
0	1.0193				
Reference solutions [mol/kg]					
NaCl	0.9833	KCl	2.5784	KCl	2.2275
a_W	0.9674	a_W	0.9177	a_W	0.9291

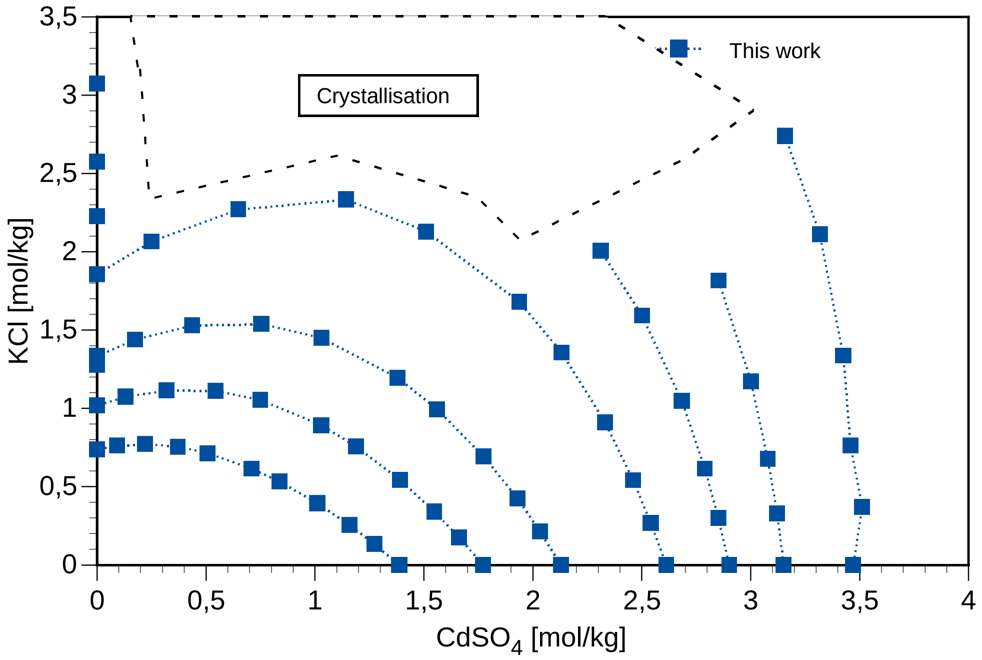

Fig. 2.22 Isopiestic concentrations in the system $CdSO_4$ - KCl - H_2O at 25 °C

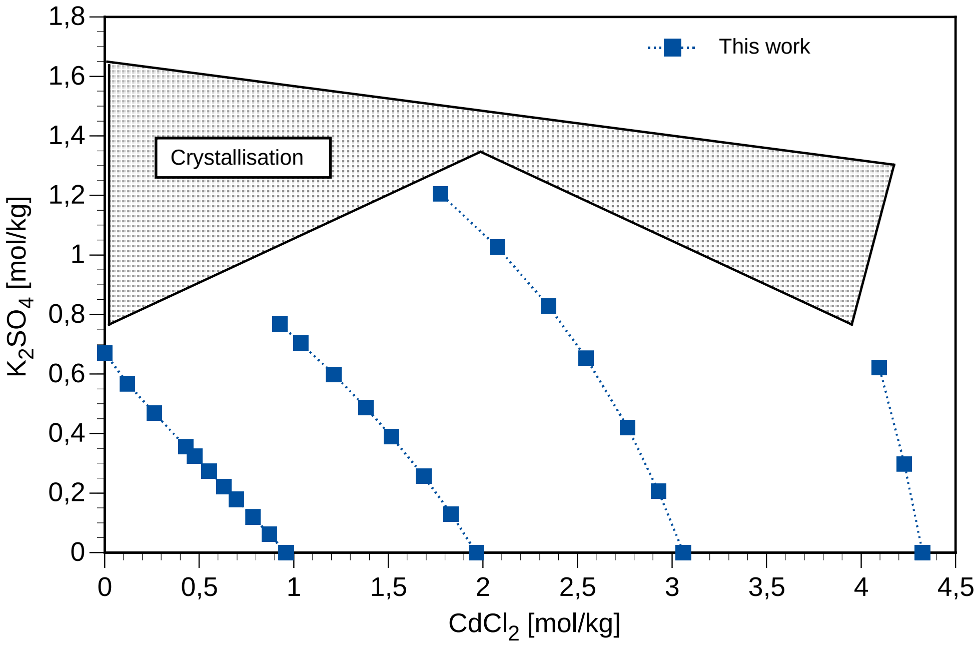

Fig. 2.23 Isopiestic concentrations in the system $CdCl_2$ - K_2SO_4 - H_2O at 25 °C

Tab. 2.41 Measured water activities of solutions of the system $CdCl_2$ - K_2SO_4 - H_2O at 25 °C

K_2SO_4 [mol/kg]	**$CdCl_2$ [mol/kg]**	**K_2SO_4 [mol/kg]**	**$CdCl_2$ [mol/kg]**	**K_2SO_4 [mol/kg]**	**$CdCl_2$ [mol/kg]**	**K_2SO_4 [mol/kg]**	**$CdCl_2$ [mol/kg]**
0.6702	0	Crystallisation		Crystallisation		Crystallisation	
0.6698	0	0.7683	0.9274	1.2059	1.7758	0.6217	4.0952
0.5674	0.1214	0.7041	1.0369	1.0262	2.0773	0.2981	4.2283
0.4686	0.2634	0.5987	1.2119	0.8275	2.3477	0	4.3242
0.3555	0.4291	0.4871	1.3820	0.6531	2.5461	0	4.3255
0.3236	0.4765	0.3892	1.5172	0.4199	2.7659		
0.2731	0.5528	0.2563	1.6879	0.2064	2.9281		
0.2218	0.6294	0.1292	1.8322	0	3.0590		
0.1788	0.6970	0	1.9654	0	3.0600		
0.1193	0.7855	0	1.9658				
0.0614	0.8712						
0	0.9604						
0	0.9608						
Reference solutions [mol/kg]							
KCl	0.74687	KCl	1.4231	KCl	2.2007	KCl	3.1977
a_W	0.97612	a_W	0.9547	a_W	0.9297	a_W	0.8968

2.6.8 The quaternary system Cd,Mg | Cl,SO_4 - H_2O

The measured data for the two subsystems $CdCl_2$- $MgSO_4$ - H_2O and $CdSO_4$ - $MgCl_2$ - H_2O (Tab. 2.42.) are very similar to the results in the analogous sodium systems: strong curvature in the system $CdSO_4$ - $MgCl_2$ - H_2O, weak, opposite curvature in the system $CdCl_2$ - $MgSO_4$ - H_2O (Fig. 2.24 and Fig. 2.25).

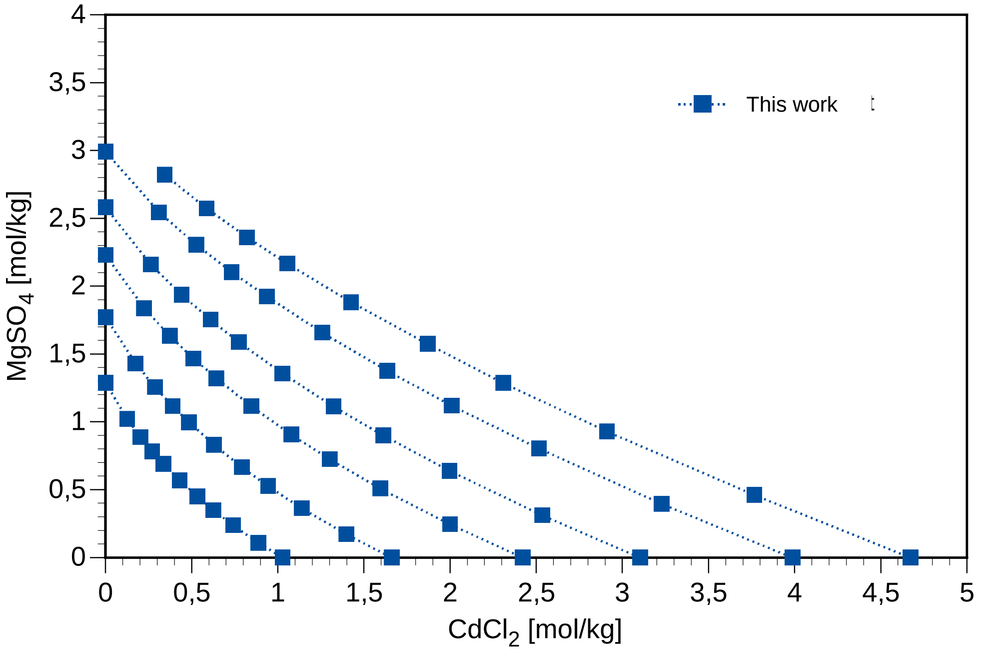

Fig. 2.24 Isopiestic concentrations in the system $CdCl_2$ - $MgSO_4$ - H_2O at 25 °C

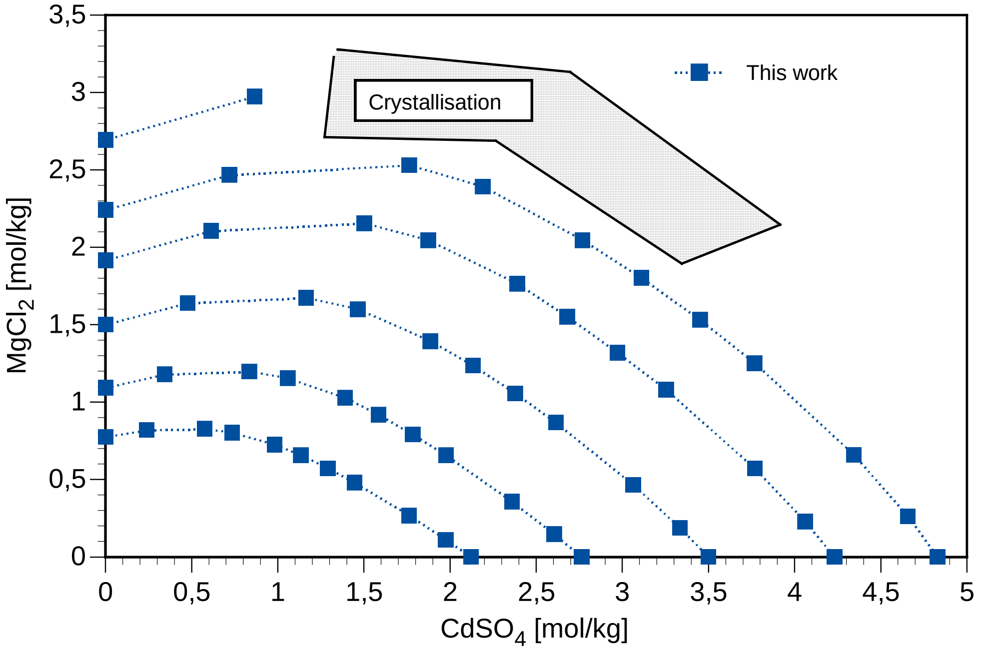

Fig. 2.25 Isopiestic concentrations in the system $CdSO_4$ - $MgCl_2$ - H_2O at 25 °C at 25°C

Tab. 2.42 Measured water activities of solutions of the system $CdCl_2$ - $MgSO_4$ - H_2O at 25 °C (I)

$CdCl_2$ [mol/kg]	**$MgSO_4$ [mol/kg]**	**$CdCl_2$ [mol/kg]**	**$MgSO_4$ [mol/kg]**	**$CdCl_2$ [mol/kg]**	**$MgSO_4$ [mol/kg]**	**$CdCl_2$ [mol/kg]**	**$MgSO_4$ [mol/kg]**
0	1.2882	0	1.7708	0	2.2310	0	2.5811
0	1.2890	0	1.7719	0	2.2302	0	2.5801
0.1244	1.0224	0.1741	1.4310	0.2236	1.8373	0.2628	2.1597
0.2028	0.8883	0.2869	1.2570	0.3729	1.6335	0.4422	1.9373
0.2720	0.7816	0.3887	1.1169	0.5104	1.4667	0.6102	1.7535
0.3365	0.6908	0.4853	0.9963	0.6435	1.3210	0.7739	1.5888
0.4306	0.5681	0.6296	0.8308	0.8461	1.1164	1.0278	1.3561
0.5334	0.4490	0.7915	0.6662	1.0783	0.9075	1.3237	1.1141
0.6261	0.3492	0.9435	0.5263	1.3006	0.7254	1.6130	0.8997
0.7414	0.2368	1.1386	0.3637	1.5952	0.5096	1.9982	0.6384
0.8878	0.1091	1.3981	0.1717	1.9999	0.2457	2.5361	0.3115
1.0285	0	1.6612	0	2.4213	0	3.1035	0
1.0284	0	1.6622	0	2.4223	0	3.1043	0
Reference solutions [mol/kg]							
KCl	0.7908	KCl	1.2169	KCl	1.7362	KCl	2.2291
a_W	0.9747	a_W	0.9613	a_W	0.9448	a_W	0.9290

Tab. 2.43 Measured water activities of solutions of the system $CdCl_2$ - $MgSO_4$ - H_2O at 25 °C (II)

$CdCl_2$ [mol/kg]	**$MgSO_4$ [mol/kg]**	**$CdCl_2$ [mol/kg]**	**$MgSO_4$ [mol/kg]**
0	2.9925	0.3433	2.8210
0	2.9911	0.5874	2.5735
0.3098	2.5455	0.8213	2.3603
0.5263	2.3057	1.0553	2.1663
0.7323	2.1043	1.4260	1.8816
0.9371	1.9237	1.8712	1.5749
1.2575	1.6592	2.3086	1.2877
1.6357	1.3767	2.9099	0.9296
2.0092	1.1207	3.7652	0.4625
2.5164	0.8039	4.6738	0
3.2270	0.3964	4.6723	0
3.9878	0		
3.9884	0		
Reference solutions [mol/kg]			
KCl	2.9199	KCl	3.4835
a_W	0.9064	a_W	0.8877

Tab. 2.44 Measured water activities of solutions of the system $CdSO_4$ - $MgCl_2$ - H_2O at 25 °C (I)

$CdSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]	$CdSO_4$ [mol/kg]	$MgCl_2$ [mol/kg]
2.1207	0	3.4999	0	4.8286	0	2.7639	0
2.1208	0	3.4997	0	4.8302	0	2.7643	0
1.9746	0.1118	3.3332	0.1887	4.6569	0.2637	2.6039	0.1474
1.7616	0.2677	3.0630	0.4654	4.3430	0.6599	2.3589	0.3584
1.4454	0.4804	2.6146	0.8691	3.7676	1.2523	1.9769	0.6571
1.2905	0.5731	2.3785	1.0562	3.4502	1.5322	1.7833	0.7919
1.1341	0.6572	2.1330	1.2362	3.1105	1.8027	1.5851	0.9187
0.9817	0.7257	1.8867	1.3948	2.7688	2.0469	1.3914	1.0286
0.7347	0.8026	1.4648	1.6003	2.1899	2.3924	1.0577	1.1555
0.5759	0.8274	1.1648	1.6736	1.7620	2.5316	0.8342	1.1985
0.2390	0.8206	0.4778	1.6408	0.7189	2.4688	0.3435	1.1796
0	0.7754	0	1.5017	0	2.2418	0	1.0940
0	0.7754	0	1.5018	0	2.2424	0	1.0938
Reference solutions [mol/kg]							
NaCl	1.2717	NaCl	2.8527	NaCl	4.7349	NaCl	1.9253
a_W	0.9575	a_W	0.8990	a_W	0.8189	a_W	0.9343

Tab. 2.45 Measured water activities of solutions of the system $CdSO_4$ - $MgCl_2$ - H_2O at 25 °C (II)

$CdSO_4$ [mol/kg]	**$MgCl_2$ [mol/kg]**	**$CdSO_4$ [mol/kg]**	**$MgCl_2$ [mol/kg]**
4.2299	0	0.8663	2.9749
4.2320	0	0	2.6957
4.0619	0.2300	0	2.6953
3.7685	0.5726		
3.2534	1.0814		
2.9721	1.3198		
2.6798	1.5531		
2.3893	1.7664		
1.8729	2.0461		
1.5011	2.1568		
0.6135	2.1066		
0	1.9162		
0	1.9152		
Reference solutions [mol/kg]			
NaCl	3.8808	MgCl2	2.6955
a_W	0.8566	aW	0.7627

3 Raman spectroscopic investigation of solutions containing zinc and cadmium chloride

3.1 Overview

The investigation of zinc and cadmium complex formation in chloride-containing solutions was carried out in two steps. In a first step, it was tested whether the chloro complexes of zinc and cadmium can be observed with the existing measuring equipment and under the selected chemical-physical boundary conditions. For this purpose, $Zn(ClO_4)_2$ and $Cd(ClO_4)_2$ solutions with increasing LiCl content were prepared. Lithium chloride was chosen because of its high solubility. Subsequently, in the second step, series measurements were carried out in solutions of KCl, NaCl, $MgCl_2$ and $CaCl_2$. The measurements were carried out by Wolfram Rudolph (TU Dresden) in cooperation with Gert Irmer (TU Bergakademie Freiberg).

3.2 Basics of Raman spectroscopy

The investigation of dissolved ions using Raman spectroscopy is particularly recommended for solutions that show no or only weak UV absorption. It is also important that the species to be investigated have Raman-active vibrational bands. This is the case for both the aquo and chloro complexes of cadmium and zinc. The measurement range of Raman spectroscopy is usually limited to a window between about 50 to 1000 cm^{-1}. The bandwidth of the Raman peaks is around 50 to 100 cm^{-1} at half height, some side bands can be even considerably wider, so that in principle strong overlaps are to be expected both between the bands of one species and between the bands of different species. In the past, this has made the evaluation of Raman spectra considerably more difficult.

The exploitation of polarisation effects has proven to be very helpful. The lasers used in modern Raman spectrometers deliver monochromatic and ideally polarised light. Depending on the type of excited oscillation, the Raman scattered radiation is polarised or depolarised (Fig. 3.1). Thus, symmetrical oscillations lead to scattered radiation whose polarisation corresponds to that of the excitation radiation. Non-symmetrical oscillations, on the other hand, lead to a strongly depolarised, i.e., isotropic, scattered radiation. Polarised and depolarised scattered radiation can be observed separately by applying a polarisation filter. If the filter is set parallel to the plane of polarisation of the excitation radiation, the Raman intensity $I_{||}$ is measured at each wavenumber; a perpendicular setting leads to the Raman intensity $I_\perp$. The Raman intensity I is measured at the same time as the polarisation of the excitation radiation. The isotropic Raman intensity I_{iso} can be derived from both quantities:

$$I_{iso} = I_{\parallel} - 4/3\, I_\perp \qquad (3.1)$$

For the evaluation of the measurement results, the isotropic Raman bands are of particular importance: especially the aquo and chloro complexes of zinc and cadmium with their coordination numbers between 4 and 6 always show asymmetric vibration modes, but not necessarily symmetric ones.

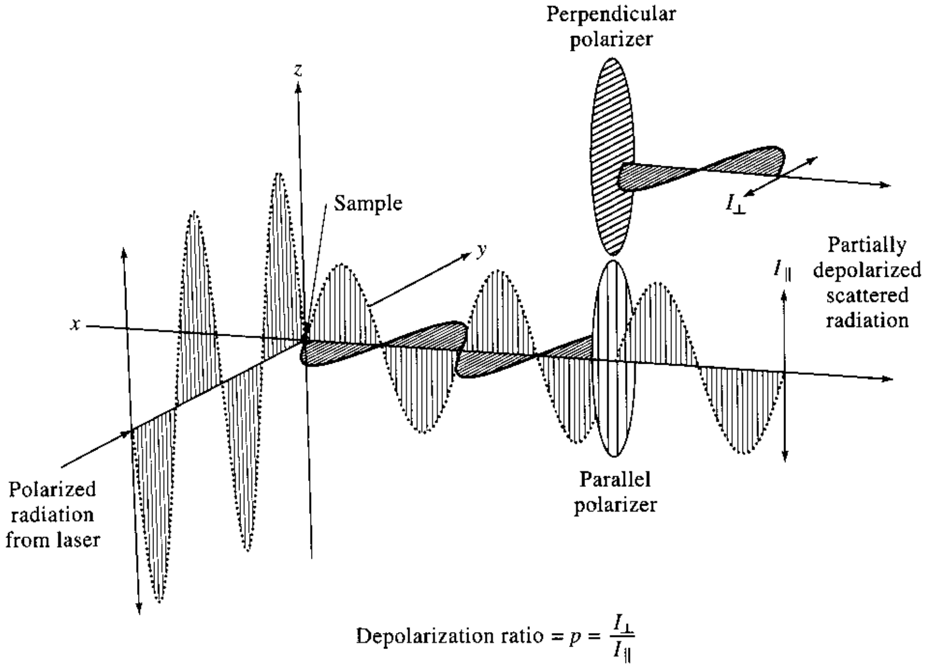

Fig. 3.1 Polarised and depolarised scattered radiation (SKOOG et al. 1998)

3.3 Description of the measurement technology used and the preparation of the measured values

3.3.1 Measurement technology used and measurement conditions

The following devices were employed for the recording of Raman spectra:

1. T64000 (Jobin-Yvon):
   Triple monochromator (focal length 640 mm)
   Holographic grating, 1800 dashes/mm
   Multi-channel detection: CCD, N-cooled$_2$

2. GDM1000L (Zeiss Jena):
   Double monochromator (focal length 1000 mm)
   grating 1350 lines/mm
   single channel detection: photomultiplier EMI 9635 QA, Peltier cooling

3. LabRamHR (Horiba/ Jobin-Yvon):
   Single monochromator (focal length 800 mm)
   Super notch filter
   Holographic grating, 1800 lines/mm
   Multi-channel detection: CCD, Peltier cooling

Most of the measurements were carried out on the spectrometer T64000. Due to a failure of the CCD on this device for several weeks, whereby a repair at the manufacturer was necessary, the measurements for the system Cd-$MgCl_2$ (22 samples) were carried out on the spectrometer GDM1000L. To check the reproducibility of the measurements and to ensure the comparability of the measurements carried out on different spectrometers, a sample (sample CCC5, Cd-$CaCl_2$) already measured on the spectrometer T64000 was re-measured on the spectrometers GDM1000L and LabRamHR (Fig. 3.2).

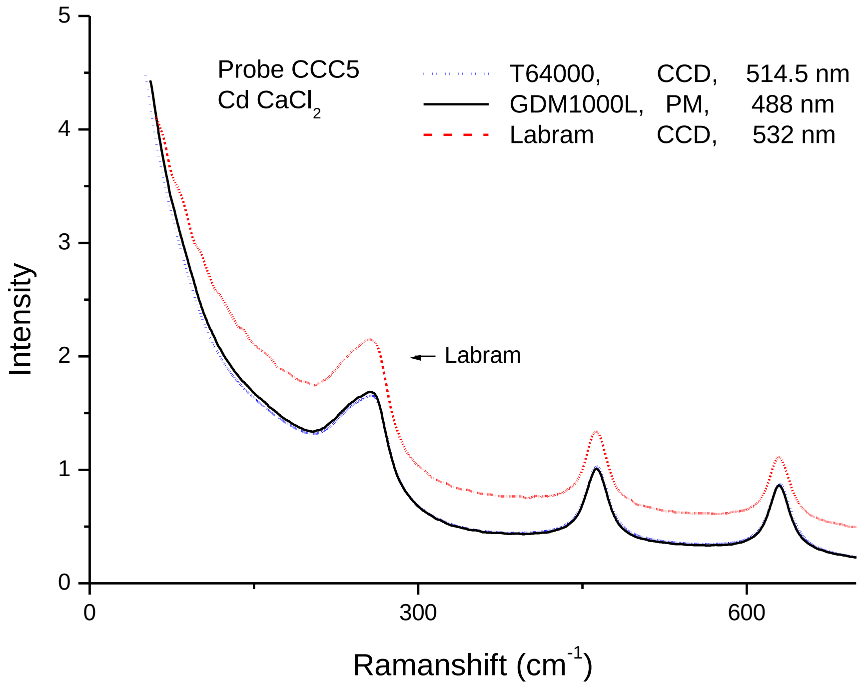

Fig. 3.2 Comparative measurements for a sample with different measuring arrangements

The Raman spectra recorded by the spectrometers T64000 and GDM1000L showed very good agreement. However, there were deviations in the low-frequency range from the Raman spectra measured on the LabRamHR device, so that this device was not used for the further measurements.

The deviations are caused by the use of the notch filters, which in principle only allow an undistorted Raman spectrum above a certain minimum distance of the frequency from the laser frequency. Therefore, the use of this very light-intensive spectrometer (because only a single monochromator is used) is unfortunately not recommended for measurements down to 50 cm^{-1}. A low-frequency option obtained from the manufacturer with two notch filters connected in series has already been used.

3.3.2 Measurements on the spectrometer T64000

The measurements of the solutions were carried out with the macro arrangement of the spectrometer T64000 from Jobin-Yvon, using a 90° scattering geometry. The excitation of the Raman spectra was carried out with the argon ion laser ILA 120 from Zeiss Jena at a wavelength of 514.5 nm and a laser light power of 400 mW. In order to ensure the required precision of the polarisation-dependent measurements, the entire beam path, including the two polarisation rotators and the analyser, was adjusted before each series of measurements. The adjustment was made using the total symmetrical band at 459 cm^{-1} of CCl_4, whose degree of depolarisation could be set to <0.005.

To minimise shifts in the wavelength scale of the spectrometer due to temperature influence during the measurements, the temperature in the room was stabilised to ± 1 °C with an air conditioner. The air conditioning was switched on at least 24 h before the start of the measurements.

Showing the reproducibility of the wavelength position at different measurement times Fig. 3.3 and Fig. 3.4 with measurements of neon lines from a calibration lamp. The frequency position of the measured neon band at 286.7 cm^{-1} was determined by fitting the Gaussian function.

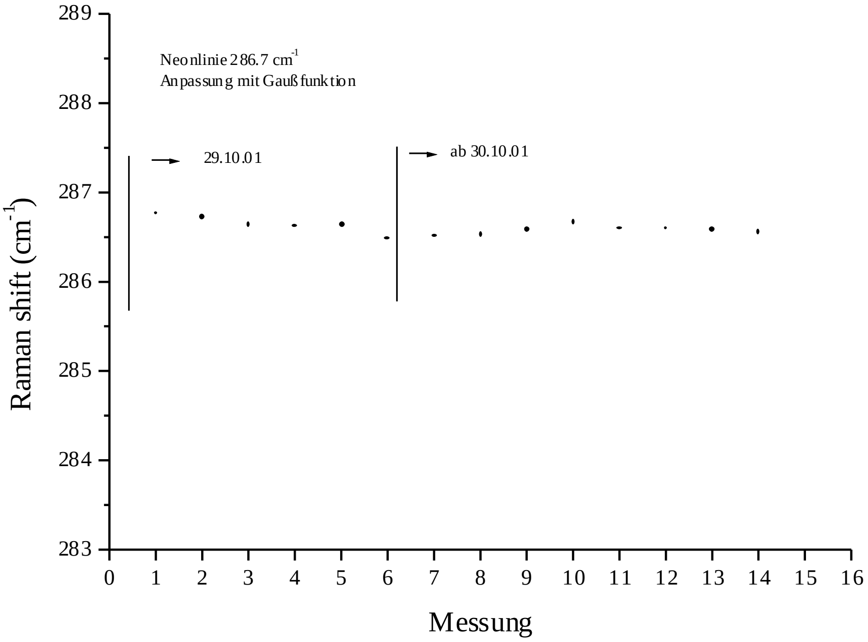

Fig. 3.3 Wavenumber drift of the spectrometer T640000

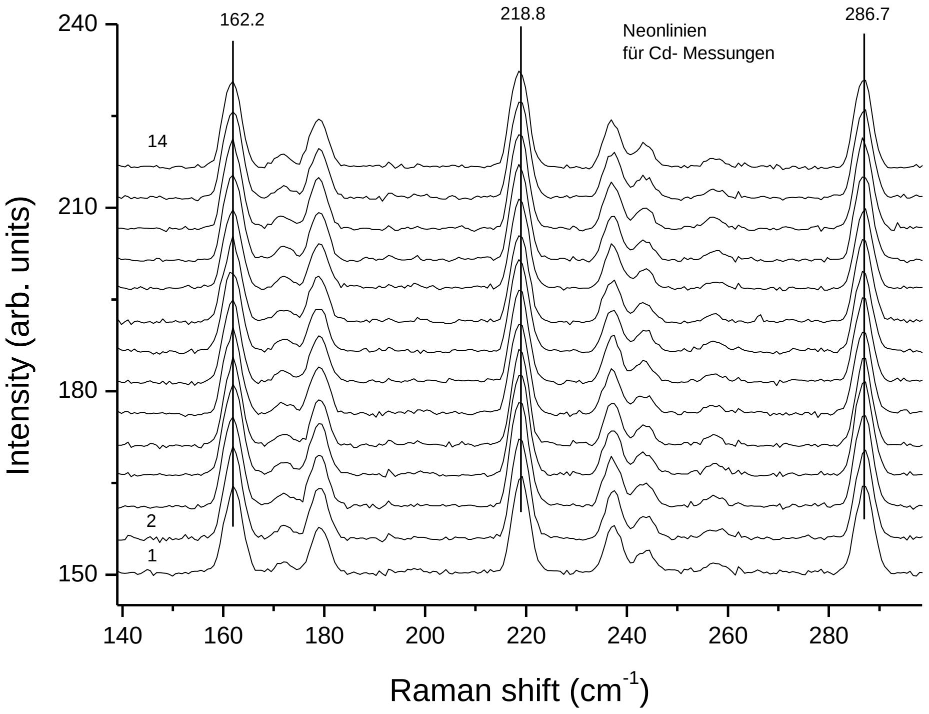

Fig. 3.4 Neon lines of the calibration lamp

In order to eliminate any remaining wavelength drifts and non-linearities of the wavelength scale, calibration measurements using the HeNe calibration lamp were carried out before a new sample was placed in the instrument.

For the creation of the linear compensation curves for the wavelength correction, the neon lines listed in Tab. 3.1 were measured.

Tab. 3.1 Shift to laser line 514.532 nm

Wavelength [nm]	Wavenumber [cm^{-1}]	Shift relative to laser line 514.532 nm [cm^{-1}]
518.861	19272.98	162.15
519.322	19255.88	179.26
520.39	19216.36	218.78
522.235	19148.47	286.67
523.403	19105.74	329.40
529.819	18874.37	560.77
530.476	18850.99	584.14
532.64	18774.41	660.73
533.078	18758.98	676.16
534.109	18722.77	712.37

In the following Fig. 3.5 an example of a neon line measurement is shown. The Raman shift values for the Zn10 measurement were converted with the compensation curve fitted to the measured values.

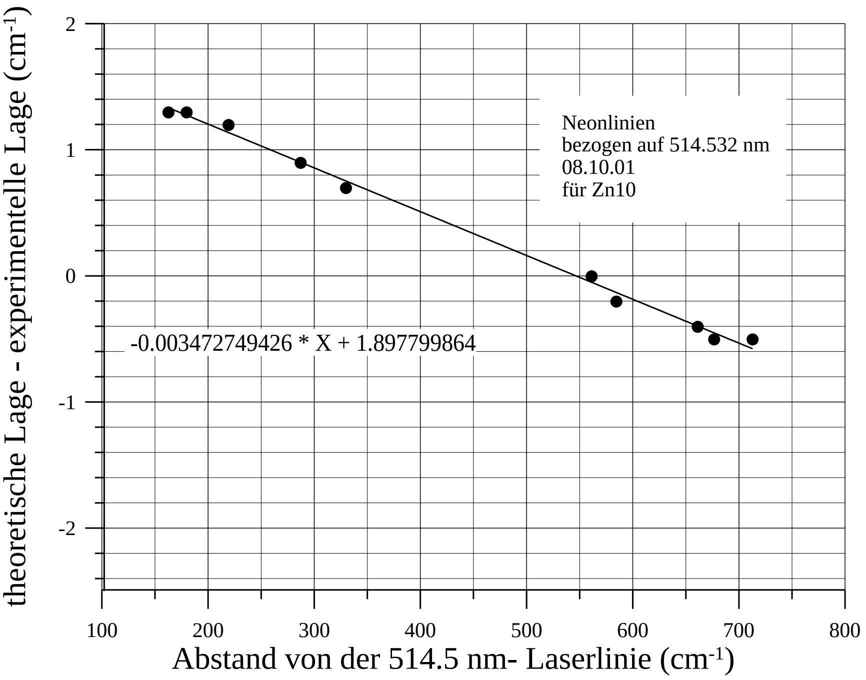

Fig. 3.5 Wavenumber correction

The Raman spectra were measured in the subtractive mode of the spectrometer. To suppress the influence of parasitic laser light, a metal diaphragm was made and placed in the beam path between the cuvette and the imaging optics. The metal diaphragm blocks the laser reflections that occur at the glass-liquid transitions in the cuvette. The measured spectrum contains practically no extraneous light components, even at low wavenumbers. This is illustrated by the test spectra shown in the following figure, which were recorded at different positions of the laser line to the CCD detector and are essentially congruent even at low wavenumbers.

The Raman spectra were measured in eight cycles of eight accumulations each to better eliminate any spikes that might occur in the CCD detector (see Fig. 3.7).

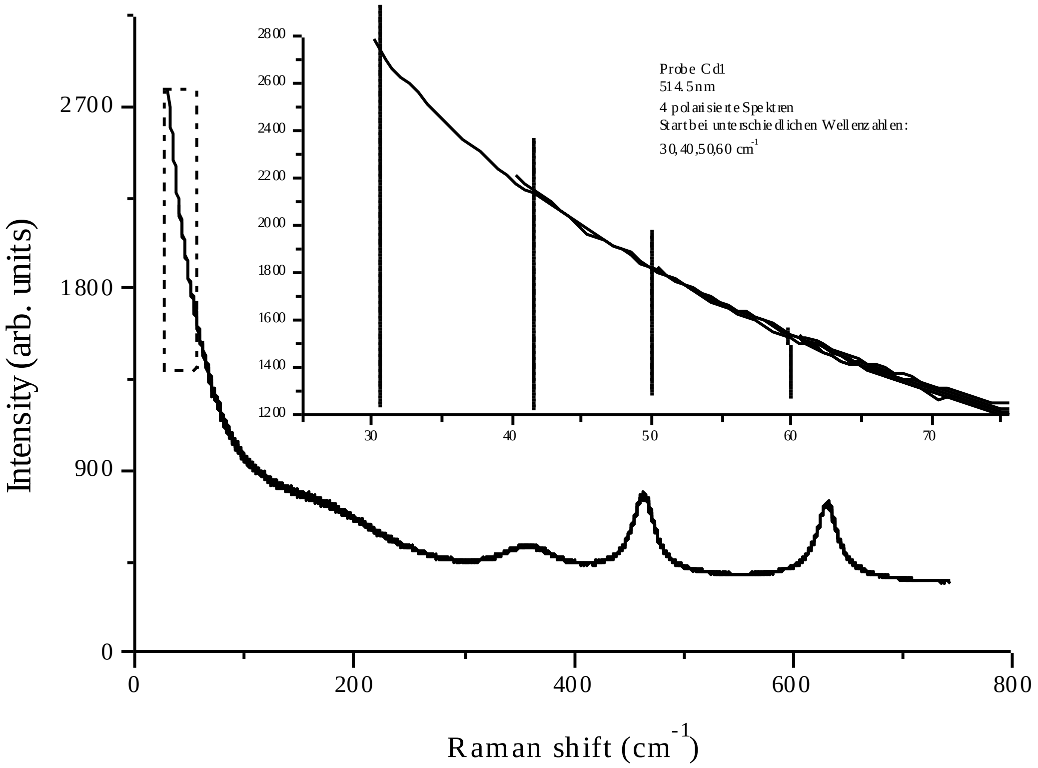

Fig. 3.6 Freedom from stray light of the spectrometer T64000 in ´subtractive mode´.

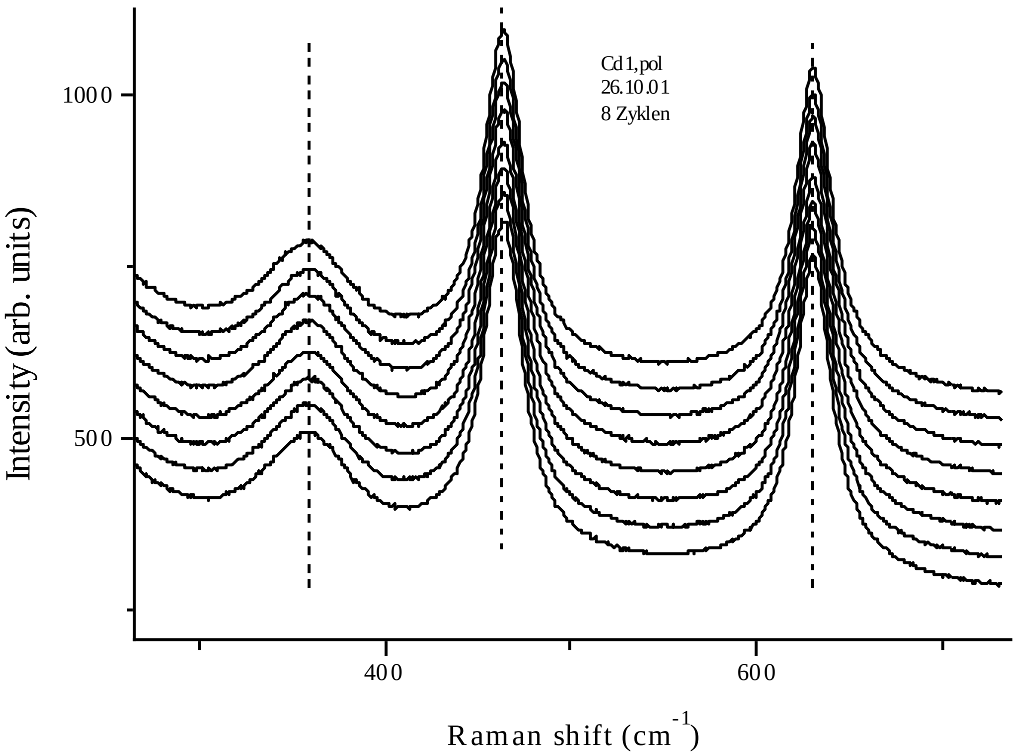

Fig. 3.7 Spectra accumulation

3.3.3 Influence of instrument-related wavenumber shifts of the depolarised versus the polarised spectrum on the determination of the isotropic spectrum

The isotropic spectrum I_{iso} results from the polarised spectrum I_p and the depolarised spectrum I_d according to the relationship

$$I_{iso} = I_p - \tfrac{4}{3} I_d \qquad (3.2)$$

For the 90° scattering geometry we use, there is the following correlation of the measured intensities to the invariants a ("mean polarizability") and γ ("anisotropy") of the Raman scattering sensor:

$$I_p : \frac{45a^2 + 4\gamma^2}{45}, I_d : \frac{\gamma^2}{15} \qquad (3.3)$$

For a depolarised band, which has no elements of the Raman tensor on the main diagonal, the following expression is obtained

$$I_{iso} = I_p - \tfrac{4}{3} I_d = 0 \qquad (3.4)$$

To investigate the influence of shifts in the wavenumber scale during the measurements, the isotropic spectrum $I_{iso} = f_1 - f_2$ was calculated for depolarised model bands, where $f_1 = I_p$ and $f_2 = \tfrac{4}{3} I_d$ were set. The model bands used were Lorentz bands

$$f_{1L} = \frac{1}{1 + \left[\frac{2(\omega + d/2)}{b}\right]^2}, \qquad f_{2L} = \frac{1}{1 + \left[\frac{2(\omega - d/2)}{b}\right]^2} \qquad (3.5)$$

ω Wavenumber at band maximum
b Half width

or Gaussian bands

$$f_{1G} = \exp\left[-4\ln(2)\left(\frac{\omega + d/2}{b}\right)^2\right], \qquad f_{2G} = \exp\left[-4\ln(2)\left(\frac{\omega - d/2}{b}\right)^2\right] \qquad (3.6)$$

The maxima of the bands (with intensity 1) are at ω_{max} = -d/2 (bands f_{1L} and f_{1G}) or at ω_{max} = d/2 (bands f_{2L} and f_{2G}), the half width is b (FWHH = full width at half height). The bands f_1 and f_2 are therefore shifted against each other by d on the wavenumber scale.

The differential band $f_{diff} = f_1 - f_2$ is shown in Fig. 3.8. The distance d_{diff} between its maximum and its minimum is approximately independent of d and almost constant for small values of d/b (this is realised for the present experimental conditions; b is of the order of 10 cm^{-1}). For d/b << 1, the limit values can be calculated:

$$\frac{d_{diff}}{b} = \frac{\sqrt{3}}{3} \cong 0{,}577 \text{ (Lorentz bands)} \qquad (3.7)$$

$$\frac{d_{diff}}{b} = \frac{1}{\sqrt{2\ln(2)}} \cong 0{,}849 \text{ (Gauss bands)} \qquad (3.8)$$

For d/b >> 1, d_{diff} = d.

The distance d_{diff} that is normalized to the band half-width b can be expressed as a function of the normalized parameter d/b. It is shown in Fig. 3.9. For Lorentz bands, the expression d_{diff} /b can also be given analytically:

$$d_{diff}/b = \tfrac{\sqrt{3}}{3}\sqrt{(d/b)-1+2\sqrt{(d/b)^4+(d/b)^2+1}} \qquad (3.9)$$

Since the relative distance d_{diff}/b in the region of interest depends only slightly on d/b, this parameter is not suitable for assessing wavenumber shifts d/b. However, the relative area A/A_{diff} of the difference band depends sensitively on the relative wavenumber shift d/b, (Fig. 3.10) with numerically determined values. A_{diff} is the area under the difference band f_1- f_2, A is the area under an output band (f_1 or f_2). The parameter d can be determined from the determined area ratio A/A_{diff}.

To estimate the correlation of the area under a residual band in the isotropic spectrum I_{iso} with wavenumber shift, in Fig. 3.11 for an example, the depolarised spectra were shifted with respect to the polarised spectra by the wavenumber d before the spectrum I_{iso} was calculated. The initial bands have half-value widths of about 25 cm^{-1}.

A band analysis shows that the bands have almost pure Lorentz contours. In Fig. 3.11 the measured values (solid curve) for the band at 632 cm^{-1} were fitted with a pure Lorentz curve (dots) with the half-value width b =24.5 cm^{-1}.

Conclusions

Based on the areas A_{diff} of the residual bands f_1 - f_2 observed in the isotropic spectra, a wavenumber shift $d < 0.1$ cm^{-1} can be assumed.

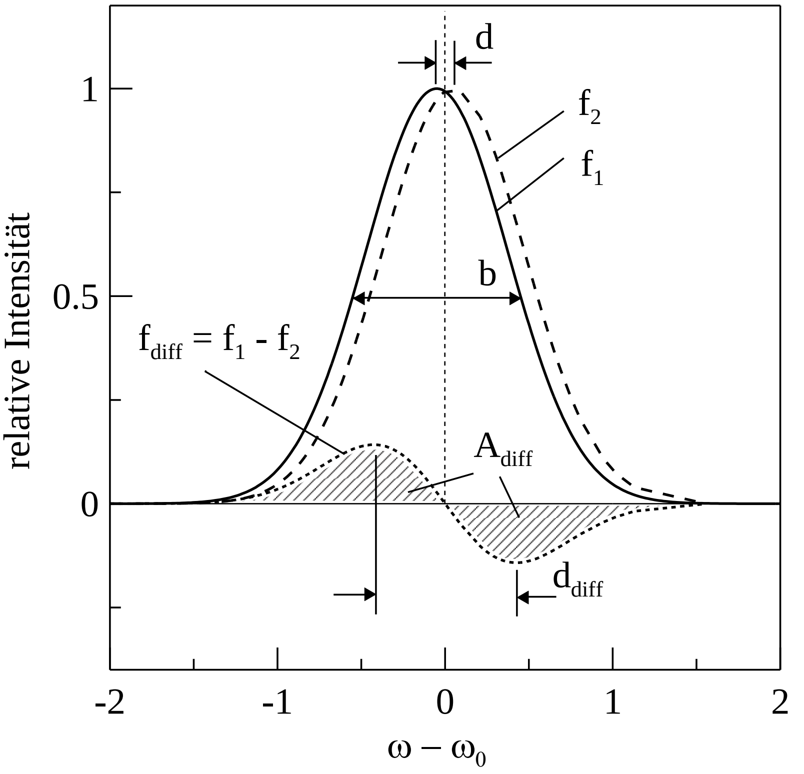

Fig. 3.8 Difference band $f_{diff} = f_1 - f_2$ of two bands shifted by d

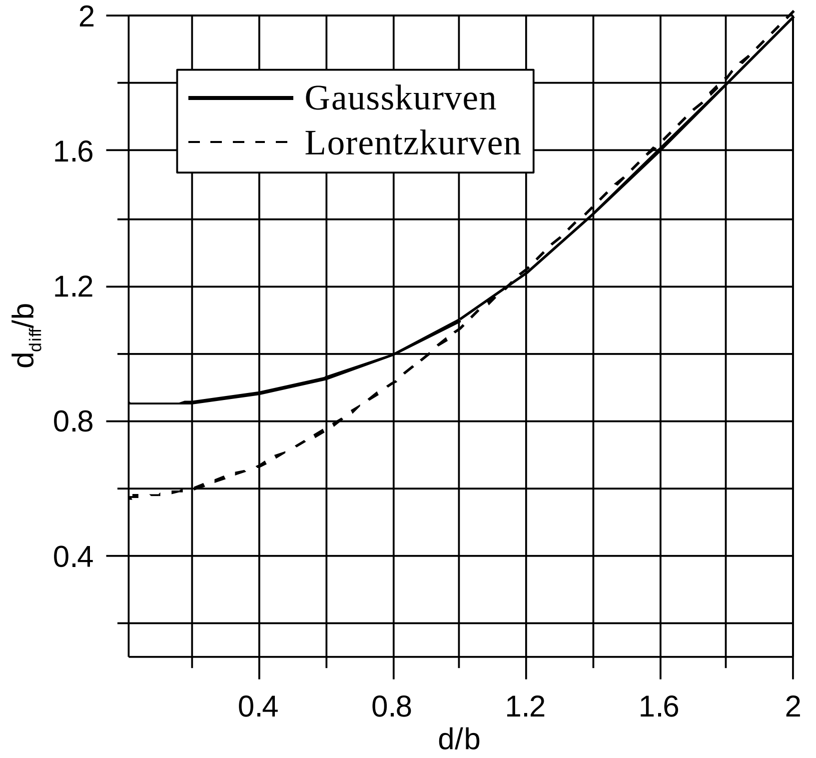

Fig. 3.9 Relative distance d/b_{diff} of the extreme value positions of f_1 - f_2 as a function of the relative wavenumber shift

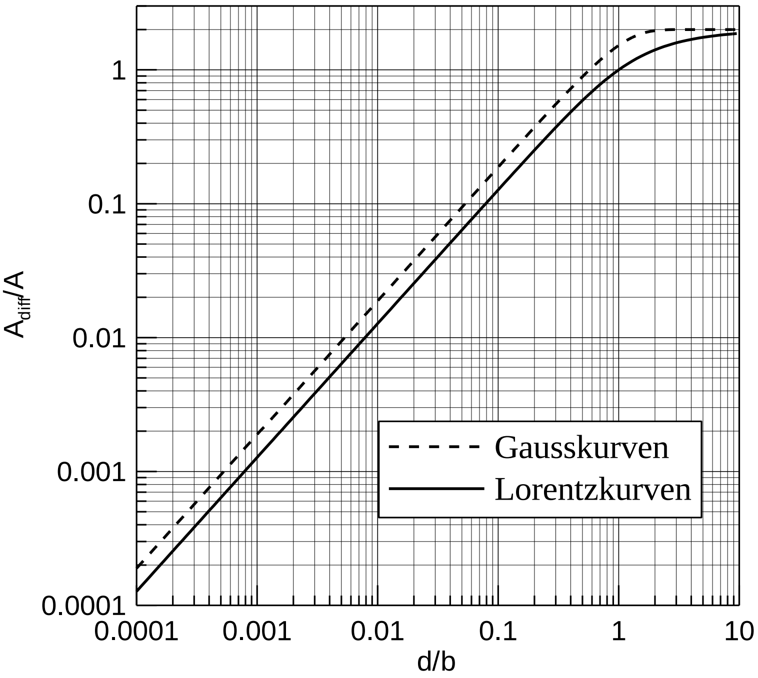

Fig. 3.10 Normalised area A/A_{diff} under the curve f_1-f_2 as a function of the relative wavenumber shift d/b

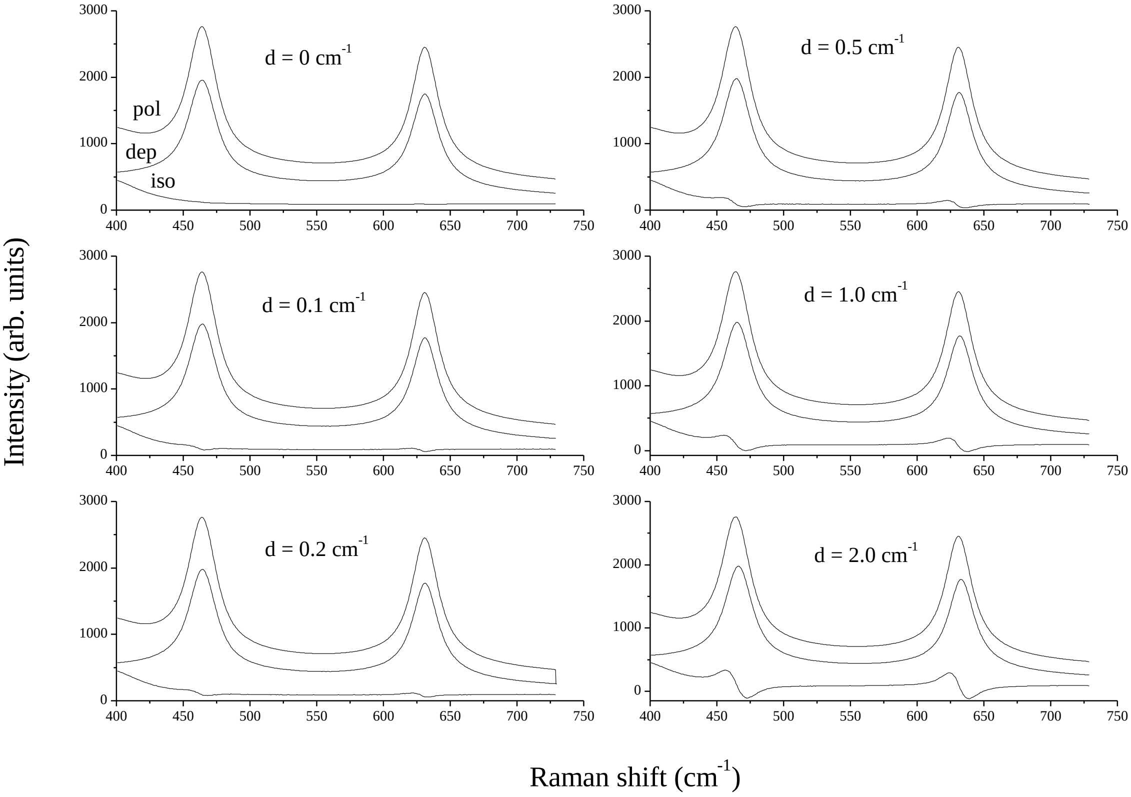

Fig. 3.11 The depolarised spectra were shifted by d compared to the polarised spectra before the isotropic spectrum was formed (example measurement Ca9, 0.3858 mol/l $CaCl_2$).

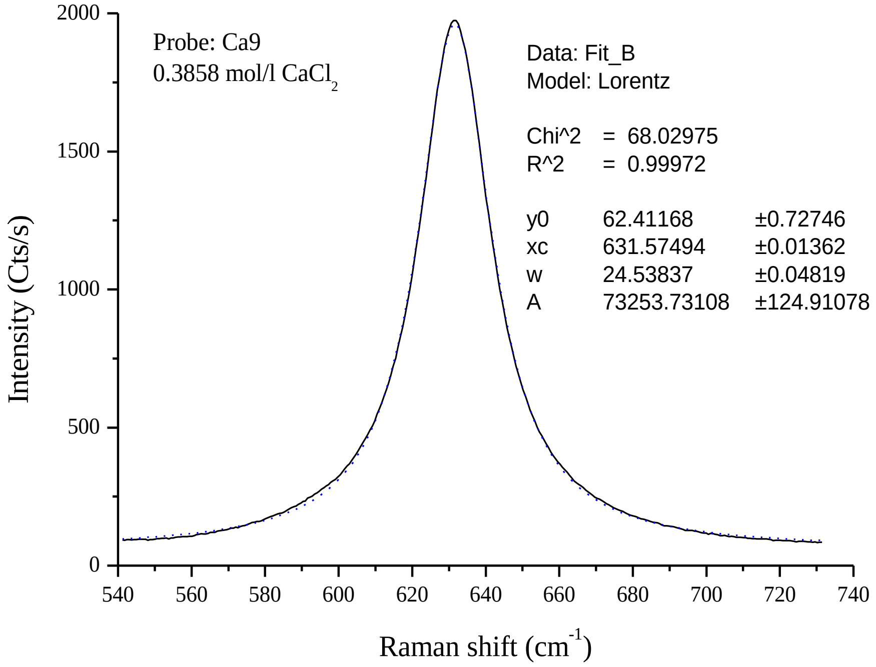

Fig. 3.12 Adjustment of the band at 632 cm^{-1} by a Lorentz band

The spectra measured in this way are called I-spectra. They will be corrected for the Bose-Einstein temperature distribution B and the frequency factor :

$$B = 1 - e^{-\frac{hc\omega}{k_B T}} \tag{3.10}$$

The reduced R spectra are obtained:

$$R(\omega) = I(\omega)\ \omega \cdot B \cdot \tag{3.11}$$

Here, too, the isotropic spectra can be derived from the polarised and depolarised spectra:

$$R(\omega)_{iso} = R(\omega)_{||} - 4/3\ R(\omega)_{\perp} \tag{3.12}$$

Fig. 3.13 and Fig. 3.14 show a comparison of the I and R spectra.

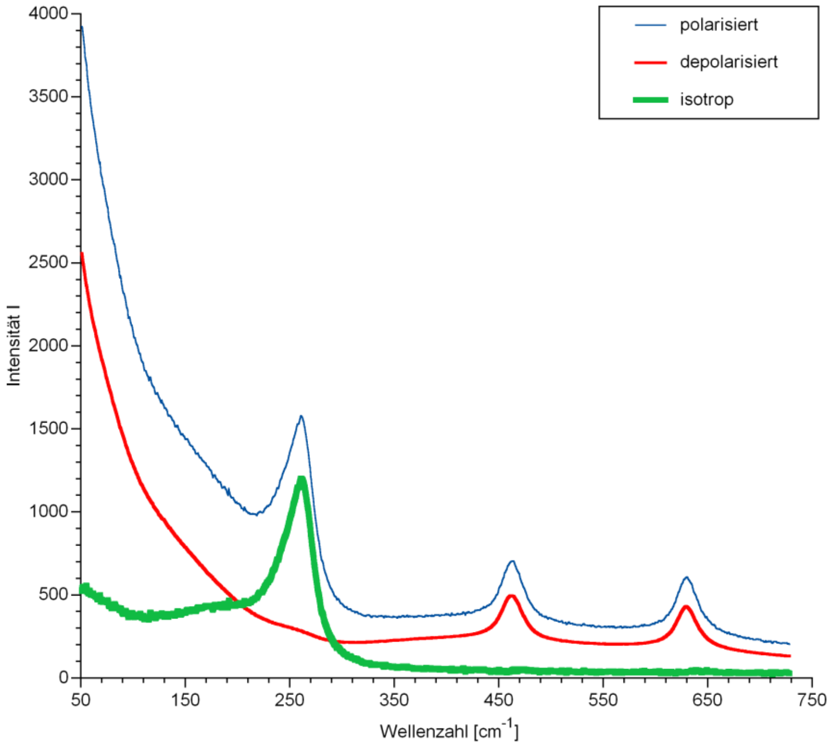

Fig. 3.13 Polarised, depolarised and isotropic I-measurement spectra of the sample Cd-Li-Cl-15

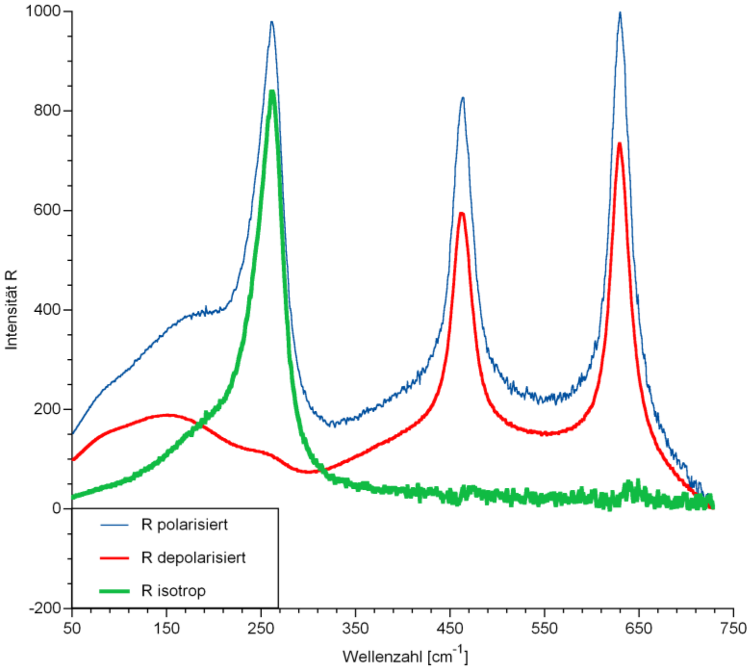

Fig. 3.14 Polarised, depolarised and isotropic R-measurement spectra of the sample Cd-Li-Cl-15

3.4 First measurements to test the spectroscopic separation of chloro complexes

3.4.1 Preparing solutions and carrying out the measurements

Preparation of the solutions: $Zn(ClO_4)_2$ solutions with increasing amounts of LiCl

17 solutions were prepared with a concentration of $Zn(ClO_4)_2$ between 0.6-1.2 mol/l and LiCl concentrations between 0 and 5.6 mol/l (for compositions see Tab. 13.5, S. 475). The solutions were prepared by weighing stock solutions and solids. For this purpose, LiCl (Sigma; SigmaUltra; min. 99% LiCl), water (tridest.) and zinc perchlorate stock solution (2.463 mol/L; density at 23C ° = 1.4735 g/ml) were weighed in 10 ml volumetric flasks. The accuracy of the volume was 0.02 %. It should be mentioned that a white crystal mush precipitates in solutions with high LiCl concentration and high perchlorate content. This was the case, for example, in an earlier - discarded - preparation with 5.1246 mol/l LiCl + 1.2421 mol/l $Zn(ClO_4)_2$, where a white crystalline precipitate was observed after two hours. Presumably, this was $LiClO_4$, whose solubility at 20°C is about 5.3 mol/kg (D'ANS and LAX, 1967). For this reason, smaller zinc perchlorate concentrations were chosen for the more concentrated LiCl solutions.

Preparation of the solutions: $Cd(ClO_4)_2$ solutions with increasing amounts of LiCl

15 solutions were prepared, the composition of which is shown in Tab. 13.8 (p. 477). The solutions were prepared by weighing in stock solutions and solids. LiCl (Sigma; SigmaUltra; min. 99 % Li), water (tridest.) and cadmium perchlorate stock solution (2.500 mol/l; density at 23 °C =1.5772 g/ml) were weighed in. 10 ml volumetric flasks were used for the solutions. The accuracy of the volume was 0.02 %. The same problems concerning the $LiClO_4$ solubility were observed in the Cd solutions. Here, too, lower Cd concentrations were used from solution 9 onwards.

Carrying out the measurements

The measurements of the solutions were carried out with the macro arrangement of the spectrometer T64000 from Jobin-Yvon, using a 90° scattering geometry. The excitation of the Raman spectra was carried out with the argon ion laser ILA 120 from Zeiss Jena at a wavelength of 514.5 nm and a laser light power of 800 mW. The working temperature was 21±1°C. Further details can be found in the method description above.

3.4.2 Results of the measurements in LiCl solutions

In Fig. 3.15 and Fig. 3.16 the isotropic Raman spectra (in R format) of the above-mentioned zinc and cadmium perchlorate solutions with increasing amounts of LiCl are shown. In the pure zinc and cadmium perchlorate solution (Zn-Li-1 and Cd-Li-1, respectively), the v_1 modes of ZnO_6 and CdO_6, respectively, are observed. The v_1 mode of the hexaquazinc(II) cation is observed at 390 cm^{-1} and the v_1 mode of the hexaquacadmium(II) cation at 360 cm^{-1}. With increasing chloride concentration, Zn or Cd chloro complexes are observed whose concentrations increase with increasing LiCl concentrations. The mode(s) of the Zn-Cl vibration(s) shifts to lower wavenumbers, namely from about 286.5 cm^{-1} (Zn-Li-2) to 280.5 cm^{-1} (Zn-Li-17). This is clear evidence that several chloro complexes of zinc exist in the measured solutions. In the solution Zn-Li-17, in the solution with the highest Cl/Zn^{-2+} ratio, only one complex ($ZnCl_4^{2-}$) is present. The v_1 mode of the hexaquazinc(II) cation has completely disappeared.

In the cadmium perchlorate solutions with increasing amounts of LiCl, several complex species are also present. With increasing chloride concentration, the free hexaquacadmium(II) cation also disappears. A mode observed at low Cl concentrations at about 244 cm^{-1} disappears and gives way to a strong mode at 261.5 cm^{-1}.

In conclusion, the Raman spectroscopy method is suitable for investigating complex formation. Different solution species can be observed. So far, three different modes could be identified for both cadmium and zinc.

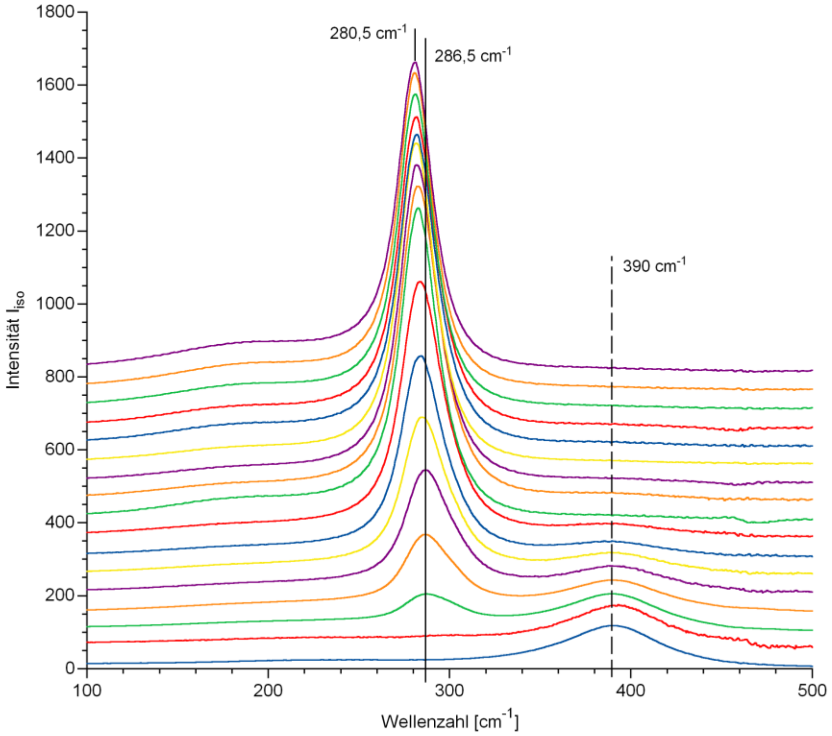

Fig. 3.15 Raman spectra of $Zn(ClO_4)_2$ solutions with increasing LiCl concentration

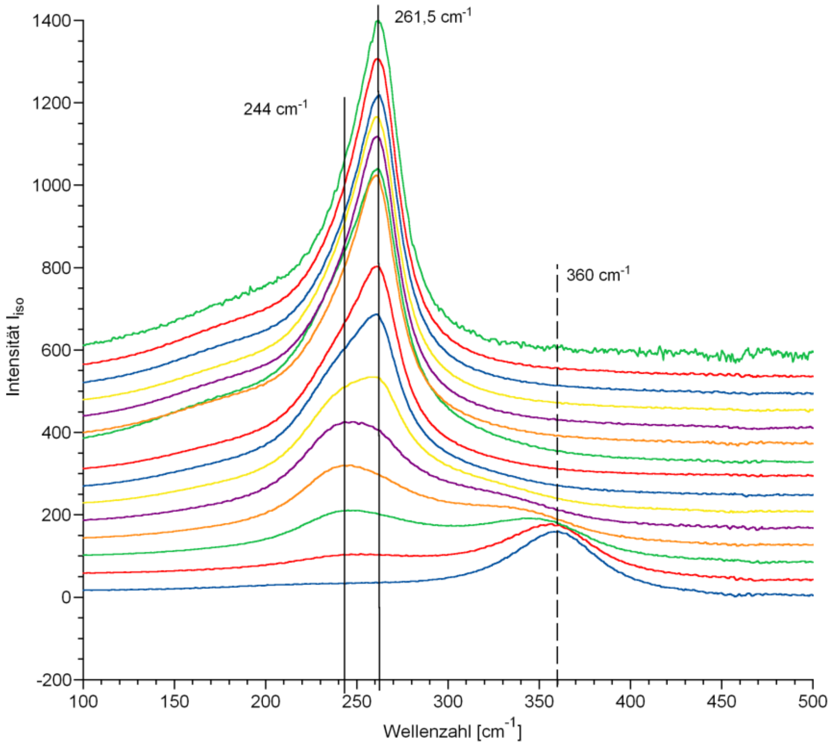

Fig. 3.16 Raman spectra of $Cd(ClO_4)_2$ solutions with increasing LiCl concentration

3.4.3 Investigation of the background bands of chloride and water

Preparation of the solutions: LiCl solutions with $NaClO_4$ as internal standard

Nine solutions were prepared, the composition of which is shown in Tab. 13.10 (p. 478). $NaClO_4$ served as the internal standard (IS). The solutions were prepared by weighing out stock solutions and solids. For this purpose, LiCl (Sigma; SigmaUltra; min. 99% LiCl) and water (tridest.) were weighed in. 10 ml volumetric flasks were used for the solutions. The accuracy of the volume was 0.02 %.

Raman spectra of the LiCl solutions and results

The isotropic Raman spectra (in R format) are shown in Fig. 3.17 are shown. At 255 cm^{-1}, the total symmetric vibration of the $Li(OH_2)_4^+$ species can be observed (v_1 modes of LiO_4; cf. Fig. 3.17). At lower water/ LiCl ratios (water : LiCl >1 : 10), an additional vibrational mode, namely that of the stretching vibrational mode of Li-Cl, is visible in the spectra at 365 cm^{-1}. It is most intense at the lowest molar water to LiCl ratio (R_W =4.13). Conversely, only the hydrated species, $Li(OH_2)_4^+$, is observed in the solutions with high R_w values.

It should be mentioned that three additional $LiClO_4$ solutions were measured in which the v_1 mode of LiO_4 can be observed very well. In the perchlorate solutions, the translational vibration band is very weak at approx. 185 cm^{-1}.(influence of the perchlorate). Consequently, the mode at 250 cm^{-1} is very well observed. Furthermore, the perchlorate is a very weak base and does not penetrate into the first coordination sphere of the lithium.

The most pronounced modes of LiCl solutions (around 180, 210 and 370 cm^{-1}) do not fall into those ranges that are important for evaluating the Cd and Zn spectra.

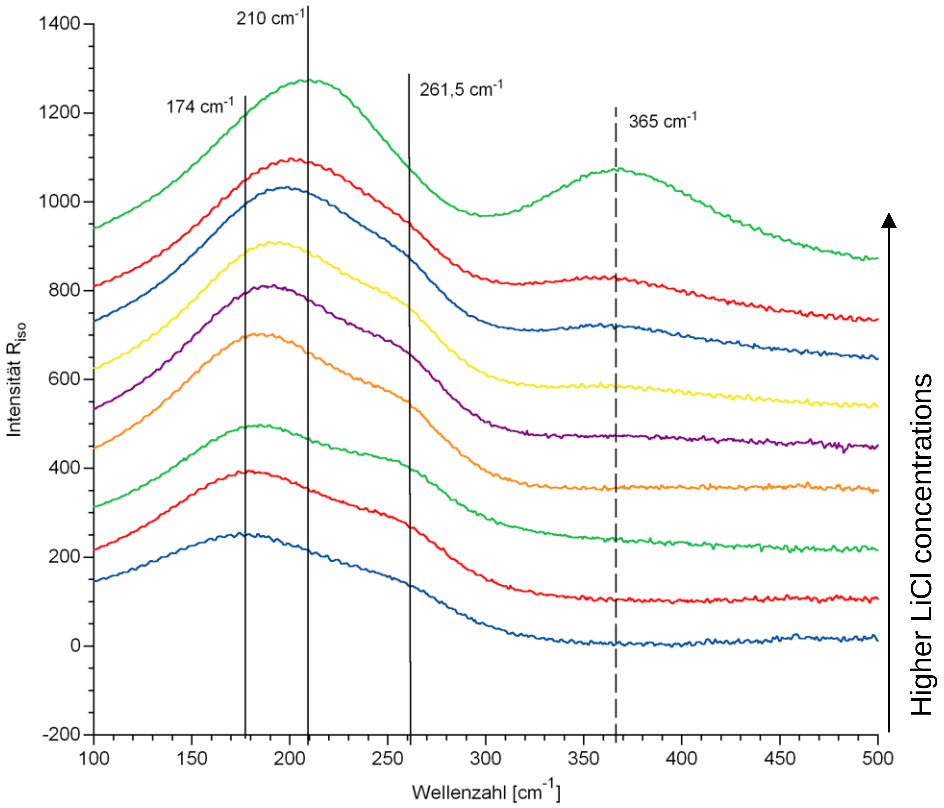

Fig. 3.17 Raman spectra of LiCl- solutions

3.5 Raman spectra of zinc in solutions of NaCl, KCl, $MgCl_2$, and $CaCl_2$

3.5.1 Measurements in the system $Zn(ClO_4)_2$ – NaCl – H_2O

13 Solutions were prepared whose composition is shown in Tab. 13.5 (p. 475). The solutions were prepared by weighing stock solutions and solids. NaCl (Merck; for analysis; > 99.5 % NaCl), water and Zn-perchlorate stock solution (2.463 mol/L; density at 23C ° = 1.4735 g/ml) were weighed in. 10 ml volumetric flasks were used for this purpose. The accuracy of the volume is 0.02 %. The spectra are similar in shape and position to those already recorded in the system $Zn(ClO_4)_2$-LiCl-H_2O. The results of the first five measurements are shown in Fig. 3.18.

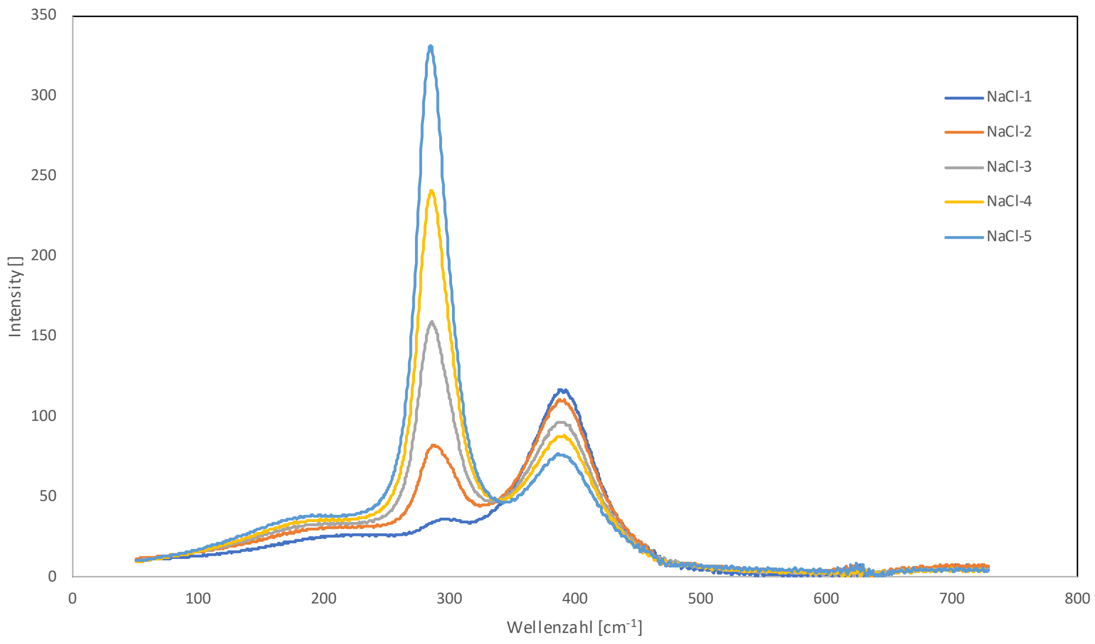

Fig. 3.18 Raman spectra of mixed NaCl-$Zn(ClO_4)_2$ solutions (measurements 1 to 5)

3.5.2 Measurements in the system $Zn(NO_3)_2$ – KCl – H_2O

Ten solutions were prepared whose composition is shown in Tab. 13.6 (p. 476). Due to the low solubility of $KClO_4$, a $Zn(NO_3)_2$ stock solution had to be used. $Zn(NO_3)_2{\cdot}6H_2O$ (Alfa Aesar, ultrapure, 99.99 % Zn base) was used to prepare the $Zn(NO_3)_2$ stock solution. The concentration of the stock solution was 2.070 mol/l and its density at 23 °C was 1.3588 g/ml. The solutions were prepared by weighing stock solutions and solids. For this purpose, KCl (Merck; for molecular biology; > 99.5 % KCl), tridest. Water and Zn-nitrate stock solution were weighed in. 10 ml volumetric flasks were used for the solutions. The accuracy of the volume was 0.02 %. A white unidentified precipitate precipitated from solution no. 10 after about 30 minutes. The solution was discarded. The spectra are similar in shape and position to those already recorded in the previous system $Zn(ClO_4)_2$ - LiCl - H_2O.

3.5.3 Measurements in the system $Zn(ClO_4)_2$ -MgCl-H_2O

23 solutions were prepared, the composition of which is shown in Tab. 13.6 (p. 476). The solutions were prepared by weighing in stock solutions and solids. For this purpose, $MgCl_2{\cdot}6H_2O$ (Merck; Fractopur; > 99.5 % Mg basis), water (tridest.) and Zn-perchlorate

stock solution (2.463 mol/l; density at 23 °C = 1.4735 g/ml) were weighed in. 10 ml volumetric flasks were used for the solutions. The accuracy of the volume was 0.02 %.

In contrast to the systems with alkali chlorides, another peak occurs in $MgCl_2$ solutions at about 365.5 cm^{-1}. It can be assigned to the ν_1-mode of the magnesium hexaaqua complex $[Mg(H_2O)_6]^{2+}$ (MgO_6, cf. Rudolph et al., 2003).

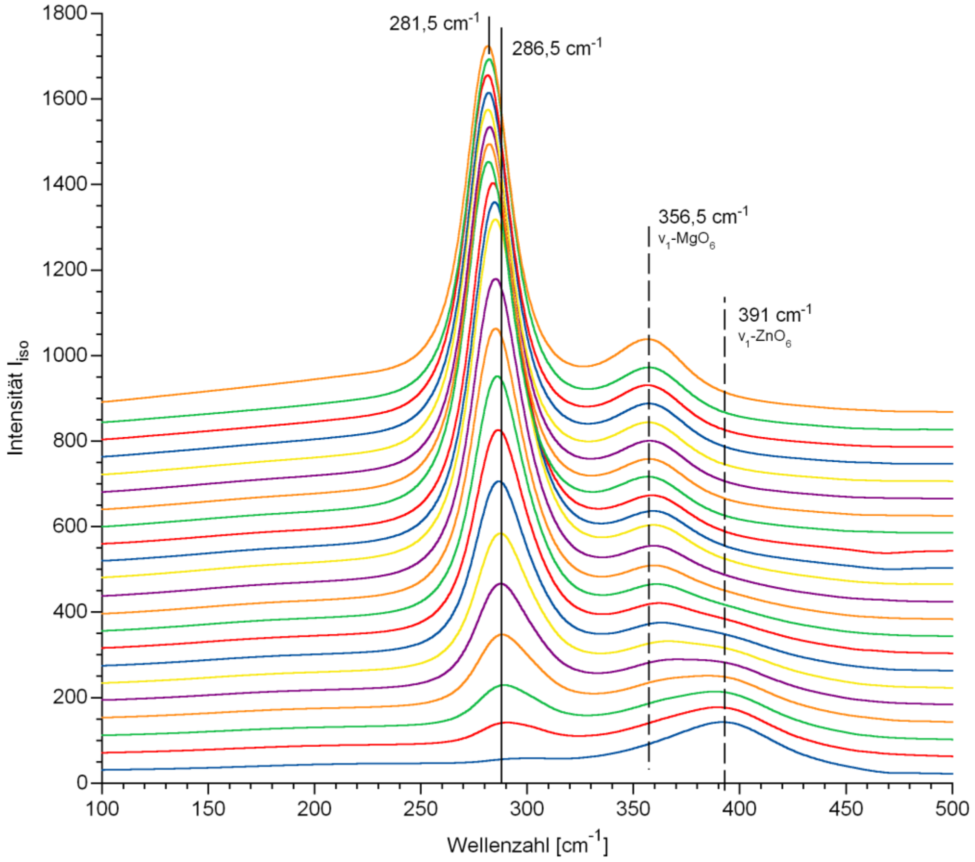

Fig. 3.19 Raman spectra of solutions of the system $Zn(ClO_4)_2 – MgCl_2 – H_2O$

3.5.4 Measurements in the system $Zn(ClO_4)_2$-$CaCl_2$-H_2O

Nine solutions were prepared, the compositions of which are shown in Tab. 13.7 (p. 476). The solutions were prepared by weighing in stock solutions and solids. $CaCl_2 \cdot 2H_2O$ (Merck; for molecular biology; > 99.5 % Ca basis), water (tridest.) and Zn-perchlorate stock solution (2.463 mol/l; density at 23 °C = 1.4735 g/ml) were weighed in. 10ml volumetric flasks were used for the solutions. The accuracy of the volume was 0.02 %. A vibrational band of the calcium hexaaqua complex is not observed, therefore the observed spectra are similar to those in the $Zn(ClO_4)_2$ – NaCl – H_2O and $Zn(NO_3)_2$ – KCl – H_2O systems.

3.6 Raman spectra of cadmium in solutions of NaCl, $MgCl_2$, $CaCl_2$ and KCl

3.6.1 Measurements in the system $Cd(ClO_4)_2$ – NaCl – H_2O

Twelve solutions were prepared by weighing solids and stock solutions (NaCl, Merck for analysis; > 99.5 %; water (tridest.); Cd-perchlorate stock solution, 2.464 M, density at 23 °C = 1.5384 g/ml). The compositions are shown in Tab. 13.8 (p. 477). 10 ml volumetric flasks were used for the solutions. The accuracy of the volume was 0.02 %. The spectra are similar to the measurements in the system $Cd(ClO_4)_2$ – LiCl – H_2O mentioned above.

In Fig. 3.20 the isotropic spectra of the $Cd(ClO_4)_2$ solutions with the highest NaCl/ $Cd(ClO_4)_2$ ratios are shown. A very broad mode at ca. 190.5 cm^{-1} may be attributed to the hindered translations of the strong hydrogen bonds of the water with the electrolyte (Cd^{2+}- Cl^- - H^+ - $O(Na^+)$). It was not observed in LiCl solutions of similar concentrations. Position and shape of the spectra did not change between 2.8 and 4.4 mol/l NaCl. It can therefore be assumed that already at 2.8 mol/l NaCl all the cadmium has been transferred to the highest chlorinated complex.

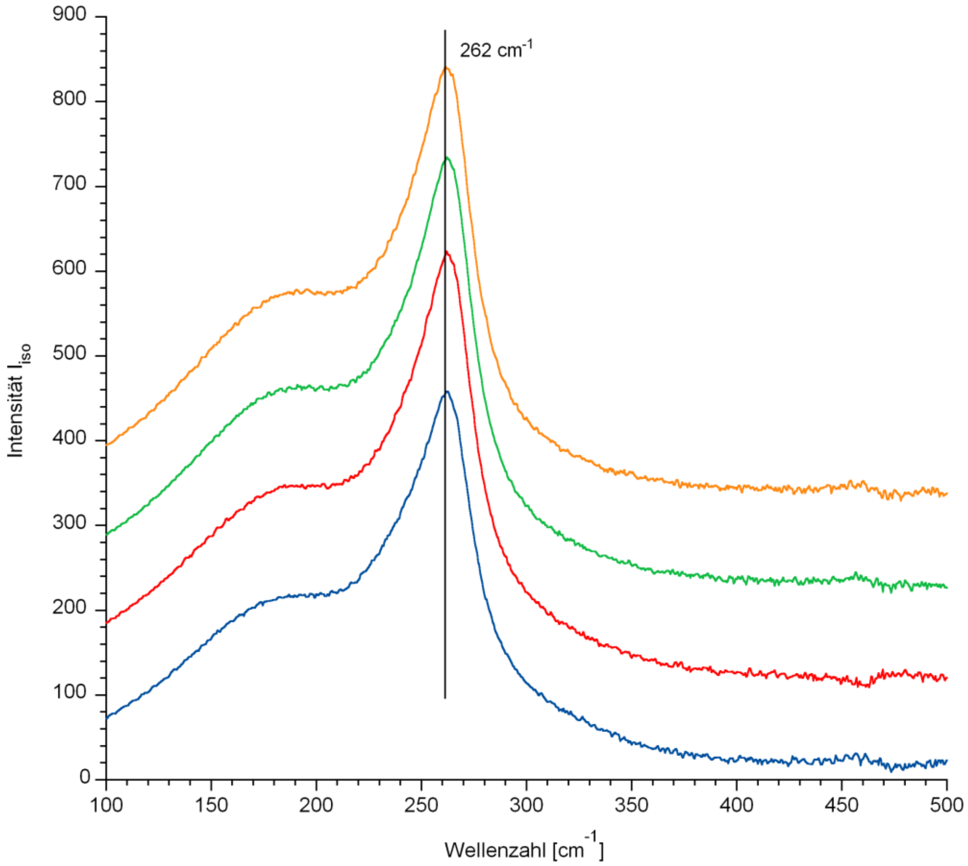

Fig. 3.20 Raman spectra of the four most concentrated solutions of the system $Cd(ClO_4)_2$ – NaCl – H_2O

3.6.2 Measurements in the system $Cd(ClO_4)_2$ – $MgCl_2$ – H_2O

Solutions were prepared whose compositions are shown in Tab. 13.9 (p. 478). The solutions were prepared by weighing in stock solutions and solids. For this purpose, $MgCl_2 \cdot 6H_2O$ (Merck; Fractopur; > 99.5 % Mg basis), water (tridest.) and Cd-perchlorate stock solution (2.464 mol/l; density at 23 °C =1.5384 g/ml)) were weighed in. 10 ml volumetric flasks were used for the solutions. The accuracy of the volume was 0.02 %. As with the analogous Zn system, the ν_1-MgO_6 band (356.5 cm^{-1}), which is very close to the main vibration of the cadmium hexaaqua complex (ν_1-CdO_6: 360 cm^{-1}), is noticeable here at higher Mg concentrations (Fig. 3.21).

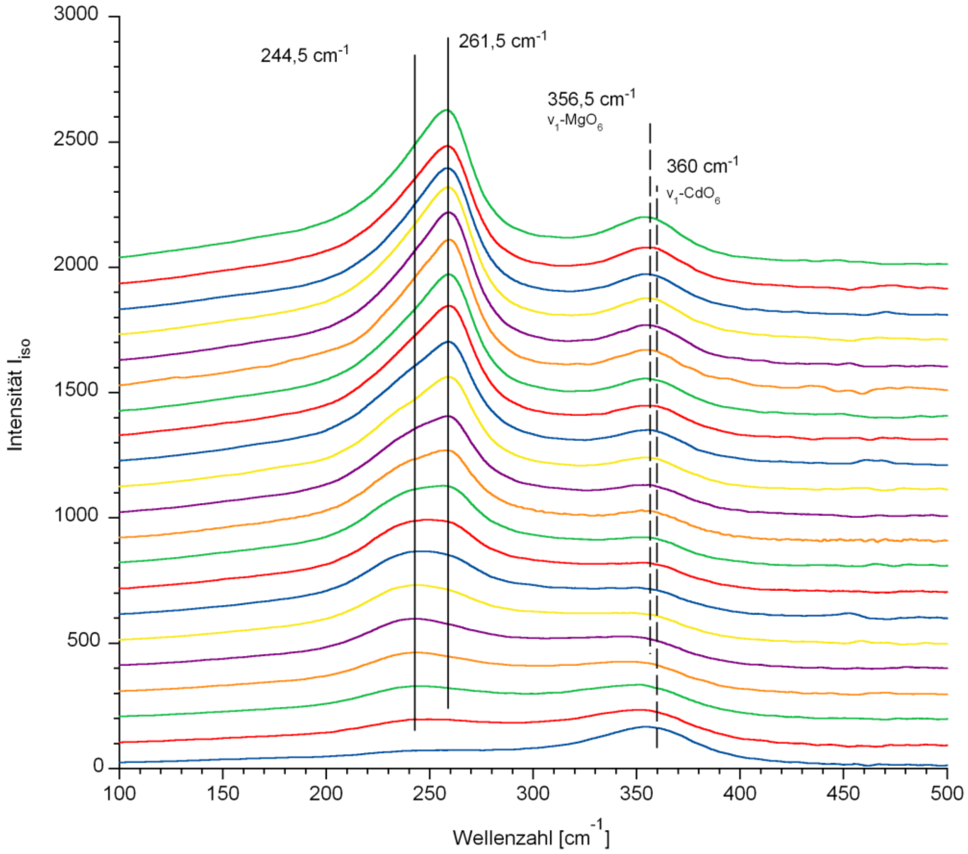

Fig. 3.21 Raman spectra of solutions of the system $Cd(ClO_4)_2 – MgCl_2 – H_2O$

3.6.3 Measurements in the system $Cd(ClO_4)_2$-$CaCl_2$-H_2O

9 solutions were prepared, the compositions of which are shown in Tab. 13.10 (p. 478). The solutions were prepared by weighing in stock solutions and solids. For this purpose, $CaCl_2 \cdot 2H_2O$ (Merck; Fractopur; > 99.5 % Mg basis), water (tridest.) and a Cd-perchlorate stock solution (2.464 mol/l; density at 23 °C =1.5384 g/ml)) were weighed in. 10 ml volumetric flasks were used for the solutions. The accuracy of the volume was 0.02 %. The recorded spectra corresponded in order and shape to those in the system with LiCl. However, the three solutions with the highest calcium concentration showed a shift of the peak from the maximum at 261.5 cm^{-1}, as found in NaCl and LiCl solutions, to 257 cm^{-1}. So, it seems that the spectrum is extended by another peak.

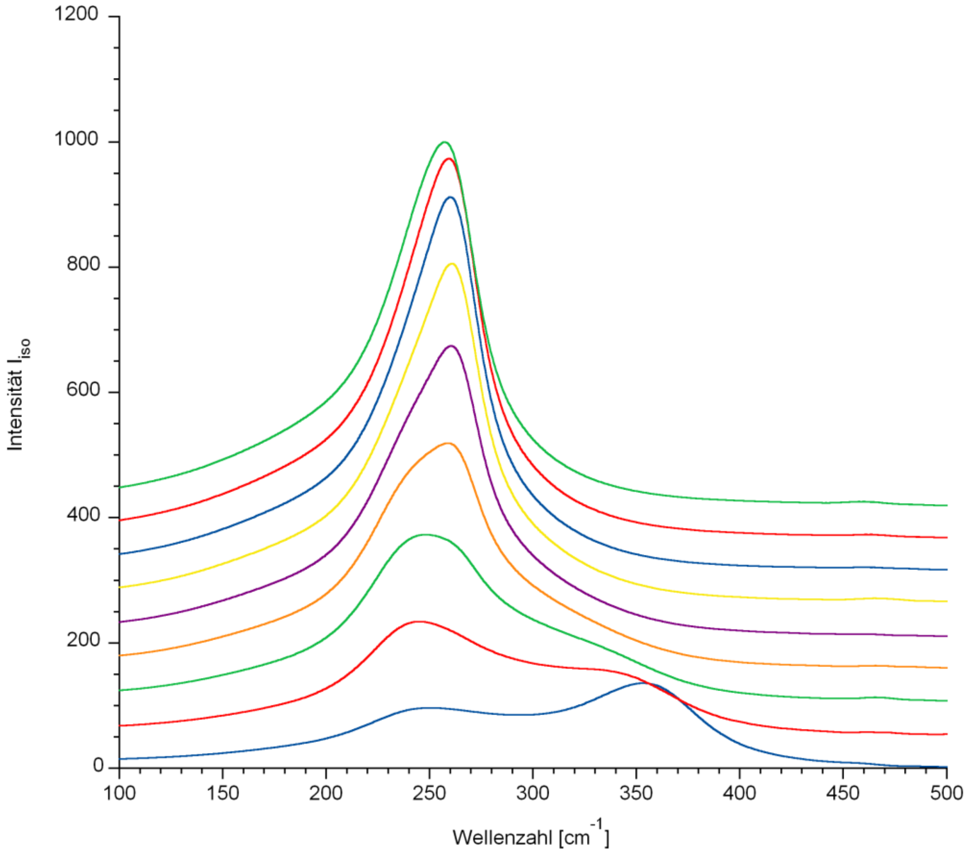

Fig. 3.22 Raman spectra of $Zn(ClO_4)_2$ solutions with increasing $CaCl_2$ concentrations

3.6.4 Measurements in the system $Cd(ClO_4)_2$ – KCl – H_2O

The preparation and measurement of these solutions was omitted, as the poor solubility of $KClO_4$ prevented a closer examination.

4 Factor analytical separation of superimposed spectra

4.1 Introduction

Glossary

$A_{w,m}$	Signal strength (at wavelength w and measurement m)
a, $\vec{a}$	measured value vector of a measurement
c, $\vec{c}$	Vector of the species concentrations of a measuring solution
$\varepsilon_{w,s}$	Absorption or extinction coefficient (for species s and wavelength w)
A	Measurement matrix
E	Matrix of absorption coefficients
C	Matrix of species concentrations
Ce	Matrix of abstract species concentrations

Indices

m, mess	index for measurements
s, spez	Species index
w, well	index for wavelengths

Constants

M	Total number of measurements
S	Total number of species

Spectroscopic methods are particularly suitable for the identification and quantification of complexes in aqueous solutions. In contrast to electroanalytical methods, they provide not only one piece of information per system (e.g., an electrochemical potential), but a whole bundle of information in the form of absorptions or intensities at different frequencies (the solution spectra). This makes it much easier to derive a model for species distribution and species activities. If two or more solution species have very different and also known spectra, their concentrations can be easily determined by applying Lambert-Beer's law.

$$a_{well} = \sum_{spez} \varepsilon_{well,spez} c_{spez} \tag{4.1}$$

Difficulties regularly arise when the individual species spectra required for evaluation are not known *a priori* and cannot be observed separately due to strong spectral overlap. In that case, they must be identified and separated using mathematical methods. While the separation of two species spectra is still relatively easy to perform, considerable problems arise with three or more strongly overlapping spectra.

The use of factor analytical methods has proven to be a helpful approach in recent years. They are based on a mathematical-statistical analysis of the measured value matrix. The aim is to identify and quantify (species concentrations) their essential main components (species spectra). The following section explains the *Evolving Factor Analysis* method we use.

4.2 Mathematical treatment of spectrometric measurements

Each measurement spectrum can be described as a vector **a,** which consists of the signal strengths a (absorptions or intensities) at the frequencies *well*[4] (or w):

$$\vec{\boldsymbol{a}} = [a_1, \dots, a_{well}, \dots, a_w]^{\mathrm{T}} \qquad (4.2)$$

With a total of M measurements (numerator: mess[5]), a measurement spectrum matrix **A** can be created from all measurement spectra $\mathbf{a}_{\mathrm{mess}}$

$\boldsymbol{A} = [\vec{a}_1, \dots, \vec{a}_{mess}, \dots, \vec{a}_M]^{\mathrm{T}}$(4.3)For both UV absorption and Raman measurements, if the path length *l* of the exciting or absorbed light through the solution is uniform, the signal strength (absorption *a* or intensity *i*) results from the product of the species concentration and a molar species- and wavelength-specific coefficient. For absorption measurements this is a specific absorption or extinction coefficient, for Raman measurements a specific light scattering coefficient j.

$$a_{well,spez} = \varepsilon_{well,spez} c_{spez} \qquad (4.4)$$

$$i_{well,spez} = j_{well,spez} c_{spez} \qquad (4.5)$$

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[4] „well“ for „Wellenlänge“ (German for wavelength)

[5] „mess“ for „Messung“ (German for measurement)

Since the formalism is the same for both measurement types, the explicit treatment of the Raman variant is omitted in the following.

The combined absorption coefficients for all S species (numerator: *spez*[6]) and W wavelengths (numerator: *well*) span the matrix **E**[S,W].

All species concentrations are summarised in the vector **c**.

$$\vec{\boldsymbol{c}} = \left[c_1, \dots, c_{spez}, \dots, c_S\right]^{\mathrm{T}} \tag{4.6}$$

If several species are present, the observed absorption at the wavelength *well* is always to be considered as the sum of the individual absorptions of all species:

$$a_{well} = \sum_{\mathrm{spez}} \varepsilon_{\mathrm{well,spez}} c_{\mathrm{spez}} \tag{4.7}$$

If we combine these equations for the absorption at all wavelengths, we obtain the following expression in a shortened matrix notation:

$$\mathbf{A} = \mathbf{EC} \tag{4.8}$$

The absorption matrix thus results from the product of the matrices of the absorption coefficients and the species concentrations.

The art of spectra deconvolution consists of finding a physically meaningful combination of the initially unknown matrices **E** and **C** that explains the measured spectra **A**.

4.3 Determination of the number of spectroscopically active species

The first important question to be clarified deals with the number of absorbing species. Chemical considerations are an important basis. Let us take the complex formation of cadmium in chloride solutions as an example. In the literature, complexes with up to six ligands have been postulated (e.g., KORSHUNOV et al., 1951). Until recently, voltammetric or potentiometric measurement results were interpreted in such a way that at least four

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[6] „spez“ for „Spezies“ (German for species)

complexes with $n_{Cl} = 1...4$ were to be expected. The same view prevails for zinc. Unfortunately, the Raman spectroscopic results are not unambiguous, since the bands of the different cadmium and zinc species overlap very strongly. But there are serious indications that one or even two previously postulated complexes are very unstable and do not contribute significantly to speciation (BREDIG and VAN ARTSDALEN, 1956). An *a priori* determination therefore does not seem possible.

Factor or principal component analysis has proven to be a suitable tool for determining the number of species S. Its basic principle is to find the mutually independent components (species spectra and species concentrations) in the absorption matrix **A.**

A number of different approaches have been developed for this purpose (cf. e.g., Malinowski 1977, MALINOWSKI 1977, GAMPP et al. 1985ff., MALINOWSKI 1991, MEINRATH 1997), which served as the basis for the algorithm implemented in the WOTAN programme.

With the help of an eigenanalysis, the absorption matrix can be decomposed into a product of two matrices that contain the concentrations as well as the individual spectra in abstract form:

$$\underset{W\times M}{\mathbf{A}} = \underset{W\times M}{\hat{\mathbf{E}}}\,\underset{M\times M}{\hat{\mathbf{C}}} \qquad (4.9)$$

$\underset{W\times M}{\hat{\mathbf{E}}}$ contains the orthogonal column eigenvectors, and $\underset{M\times M}{\hat{\mathbf{C}}}$ the likewise orthogonal row eigenvectors. "Abstract form" means that the matrices $\underset{W\times M}{\hat{\mathbf{E}}}$ and $\underset{M\times M}{\hat{\mathbf{C}}}$ already contain all necessary information about species spectra and -concentrations, but unfortunately not yet in a physically meaningful form. In fact, the spectra of different species are usually not "orthogonal" but correlate with each other to a greater or lesser extent. Only suitable transformations turn the orthogonal eigenvectors into vivid concentrations and spectra.

The first step of the factor analysis is the decomposition of the orthogonal covariance matrix into abstract factors that are also eigenvectors. The SVD algorithm (single value decomposition, cf. PRESS et al. 1992) is used for this in the WOTAN programme. It separates the data matrix A in the following way:

$$\underset{W\times M}{\mathbf{A}} = \underset{W\times M}{\mathbf{U}}\,\underset{M\times M}{\mathbf{S}}\,\underset{M\times M}{\mathbf{V}} \qquad (4.10)$$

The columns of the matrix **U** contain the eigenvectors of $\mathbf{AA}^T$, while the columns of **V** contain the eigenvectors of the covariance^T matrix **AA**. **S** is a diagonal matrix whose diagonal elements represent the roots of the eigenvalues or singular values.

The following relations apply:

$$\underset{W\times M}{\hat{\mathbf{E}}} = \underset{W\times M}{\mathbf{U}}\,\underset{M\times M}{\mathbf{S}} \qquad (4.11)$$

and

$$\underset{M\times M}{\hat{\mathbf{C}}} = \underset{M\times M}{\mathbf{V}} \qquad (4.12)$$

The column vectors in $\hat{\mathbf{E}}$ as well as the row vectors in $\hat{\mathbf{C}}$ are orthogonal eigenvectors of the data matrix **A**. A pair of column vectors / row vectors represents a factor. The matrix **S** contains the square roots of the eigenvalues, whereby the column vectors belonging to column a in $\hat{\mathbf{E}}$ and the row vectors in $\hat{\mathbf{C}}$ have the same eigenvalues. The eigenvalues express the proportion of the total variance of the data set for which the respective eigenvectors are responsible. The peculiarity is that not all eigenvectors or all rows and columns in and $\hat{\mathbf{E}}$ and $\hat{\mathbf{C}}$ are needed to reflect the significant information in **A**. Using statistical methods, it can be easily demonstrated that the number of eigenvectors to be considered can usually be reduced to a small number S. S corresponds to the number of distinguishable, significantly absorbing species in the system, i.e., whose absorption is greater than the measurement uncertainty. The remaining factors only express the measurement noise and can be neglected for the reproduction of the absorption matrix. Thus, the matrices $\underset{WxM}{\hat{\mathbf{E}}}$ and $\underset{MxM}{\hat{\mathbf{C}}}$ reduce to $\underset{WxS}{\hat{\mathbf{E}}}$ and $\underset{SxM}{\overline{\mathbf{C}}}$. The above equation thus reduces to

$$\underset{W\times M}{\overline{\mathbf{A}}} = \underset{W\times S}{\overline{\mathbf{E}}}\,\underset{S\times M}{\overline{\mathbf{C}}} = \underset{W\times S}{\overline{\mathbf{U}}}\,\underset{S\times S}{\overline{\mathbf{S}}}\,\underset{S\times M}{\overline{\mathbf{V}}} \qquad (4.13)$$

without significant information being lost on the side of the absorption matrix. Fig. 4.1 illustrates the connection once again.

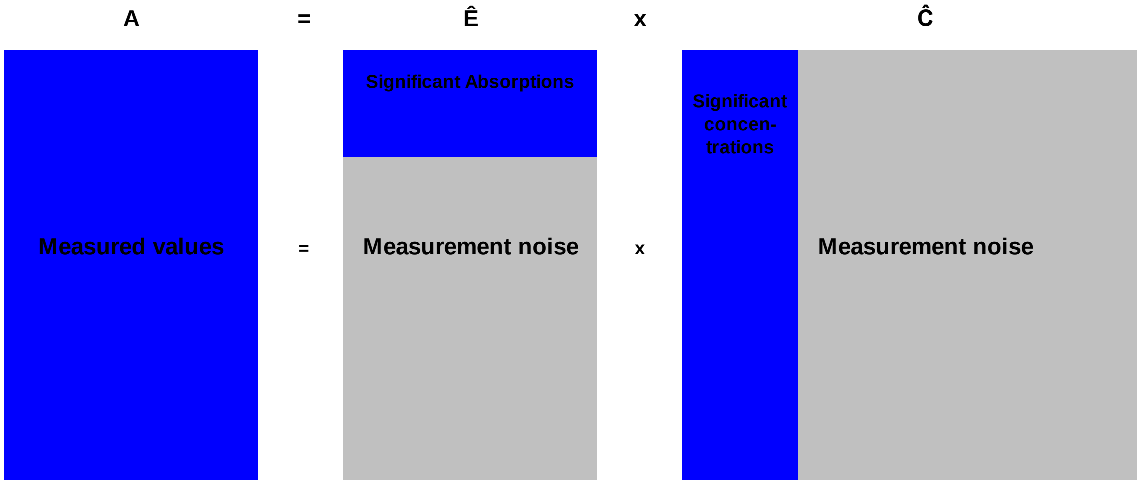

Fig. 4.1 Reduction of the abstract absorption and concentration matrices to their respective significant portions

How many significant factors are contained in a measurement matrix can be determined with the help of suitable statistical parameters. They are essentially based on comparing a known measurement scattering or one determined from the measurement matrix itself with the mean deviation of the regression model. The n=1...N eigenvectors from $\hat{\mathbf{E}}$ and the corresponding abstract concentrations from $\hat{\mathbf{C}}$ serve as regression model. The model is increased step by step by one eigenvector until the calculated deviation (measured value minus calculated value) falls below a certain threshold. A good overview of possible procedures can be found in MALINOWSKI (1991). In Wotan, the χ^2-criterion (BARTLETT, 1950), the error functions of MALINOWSKI (1977) and the "eigenvalue-one criterion" (MALINOWSKI, 1991) were implemented. All methods have in common that the determination of the number of significant factors is not very sharp. According to our own experience, deviations of ± 1 in the number of significant factors must always be expected. In these cases, the calculated residual error of the optimisation can be used as an additional criterion. If an additionally allowed species does not lead to an improvement of the model, this species has to be considered superfluous - at least for the explanation of the measurement spectra. The species could still exist, but its spectrum differs too little from other significant species.

After determining the number of significant factors, the matrices $\hat{\mathbf{E}}$ and $\hat{\mathbf{C}}$ are reduced to the noise-free $\overline{\mathbf{E}}$ and $\overline{\mathbf{C}}$. Both contain the sought species concentrations and individual spectra, but still only in abstract form. The aim of the further procedure is now to transform these matrices so that they contain physically meaningful information.

4.4 Transformation of abstract eigenvectors into physically meaningful spectra vectors: Evolving Factor Analysis (EFA)

If a set of measurement spectra contains an inner sequence, such as increasing ligand concentrations or steadily increasing pH, the *evolving factor analysis* (EFA) *is a* suitable evaluation method. It was described by Gampp et al. (1985 ff.). Its essential advantage over other methods is the absence of a predefined chemical model. No assumptions have to be made regarding the shape of the species spectra (Gauss/Lorentz), the type of species involved, or the physico-chemical relationships between the species concentrations. Instead, the method uses the empirical observation that the change in ligand concentration has a steady influence on the number and concentration of species present; the species concentrations either always increase, always decrease or pass through exactly one maximum. Gampp et al. (1985ff .) were able to show that there is a connection between such typical concentration courses and the development of the eigenvalues. For this purpose, the measurement spectra are sorted according to the ligand concentrations and the factor analysis is carried out step by step:

1. Start with the two solutions with the lowest ligand concentration and determine the eigenvalues of the covariance $\mathbf{A}^{\mathbf{T}}\mathbf{A}$ matrix. Then the solution with the next highest ligand concentration is added and the determination of the eigenvalues is repeated. Continue in this way step by step until all measurements are included (forward EFA).
2. In the second step, this procedure is carried out in reverse, i.e., starting with the solutions of highest ligand concentration (reverse EFA) (Fig. 4.2 above).

3. Now the development of the eigenvalue j from the forward procedure and the eigenvalue S+1-j from the backward procedure are plotted on top of each other. For five relevant species, for example, these are the eigenvalues 2 (forward) and the eigenvalues 4 (backward). The two values belonging to each other at a measuring point are compared and the smaller value is adopted (Fig. 4.2 centre). In this way, a profile is obtained step by step for each eigenvector (Fig. 4.2 below).

4. The profiles form the initial values for the abstract species concentrations c_e. All abstract concentrations form the matrix $\underset{\mathbf{S\times(M-2)}}{\mathbf{Ce}}$. Note that no value can be obtained for the first and the last measurement. In the EFA, they represent two stand-alone vectors for which neither eigenvalue nor eigenvector can be determined. Compared to the concentration matrix **C,** the matrix **Ce** therefore lacks the first and the last column. The absorption matrix $\underset{\mathbf{W\times(M-2)}}{\mathbf{Ax}}$, reduced in the same way, belongs to the matrix **Ce**.

5. To stabilise the calculations, the introduction of a discrimination matrix D has proved useful. Its dimension corresponds to that of the concentration $\underset{S\times(M-2)}{\mathbf{Ce}}$ matrix . It contains 1 at all positions where the determined eigenvalue is above a critical significance level and is therefore considered significant, otherwise it contains a zero. GAMPP et al. (1986) proposed the eigenvalue of the eigenvector S + 1 (i.e., the first non-significant eigenvector) of the covariance $\mathbf{A}^{\mathbf{T}}\mathbf{A}$ matrix as the significance level T.

$$d_{s,m} = \begin{cases} 1 & ce_{s,m} > T \\ 0 & ce_{s,m} < T \end{cases} \qquad (4.14)$$

6. Each profile (each row in **Ce**) is now normalised so that its maximum corresponds to unity. The elements *ca* of the profile-normalised matrix **Ca**(SxM-2) are thus obtained:

$$ca_{s,m} = \frac{ce_{s,m}}{max(ce_{s,1},\dots,ce_{s,m},\dots,ce_{s,M})} \qquad (4.15)$$

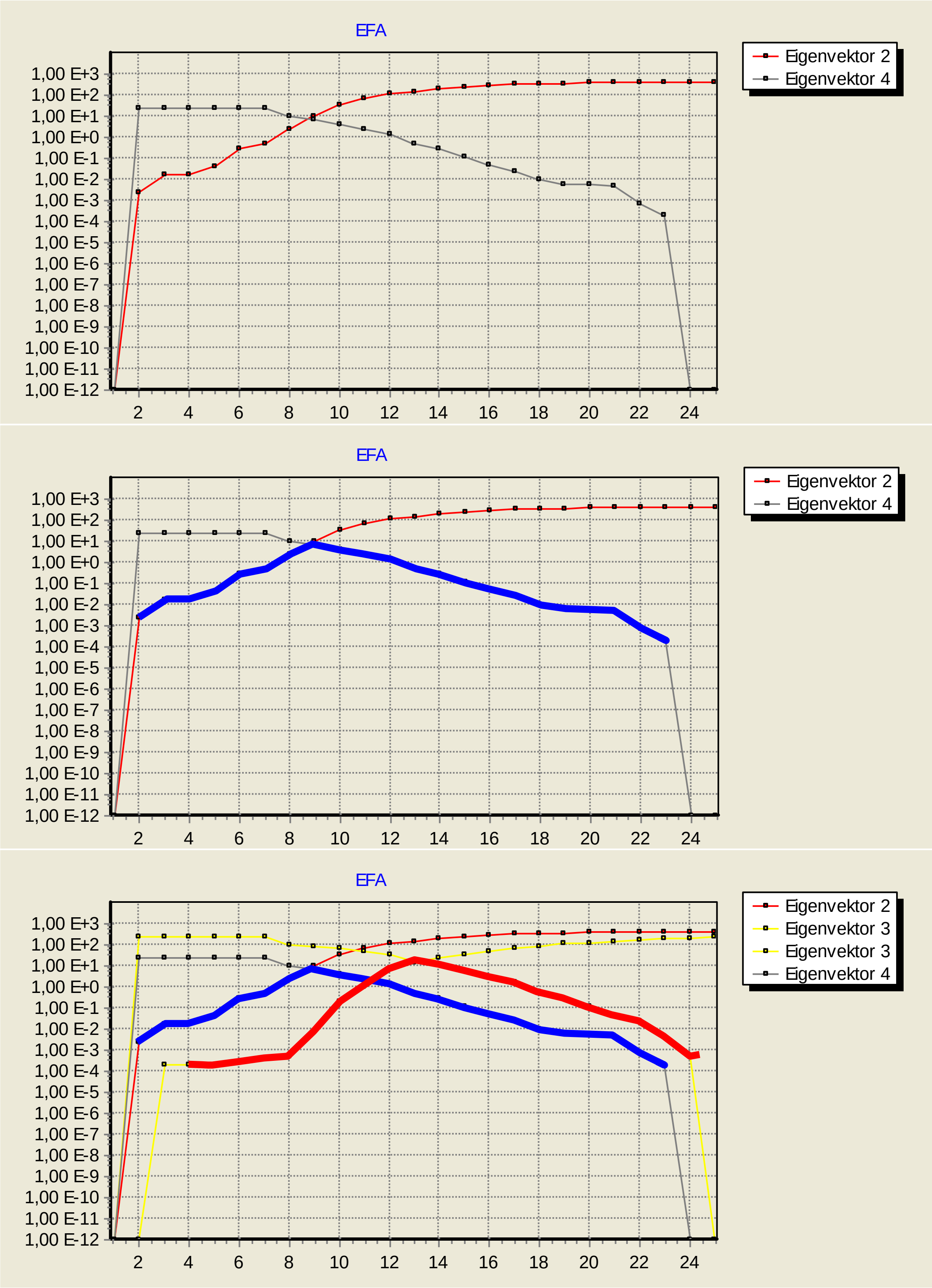

Fig. 4.2 Evolving Factor Analysis: combination of eigenvectors from forward and backward EFA to estimate concentration profiles

7. The molar concentrations $cn_{s,m}$ of the species s at the measurement m in the matrix **Cn** can be obtained from the matrix **Ca** with the help of the known total concentrations c_{tot}

$$cn_{s,m} = \frac{ca_{s,m}}{\sum_s ca_{s,m}} c_{tot,m} \qquad (4.16)$$

8. The obtained concentration matrix **Cn** is a good starting point for the following optimisations. From this the coefficient matrix **E** can be calculated according to

$$\mathbf{Ax} = \mathbf{ECn} \qquad (4.17)$$

$$\mathbf{E} = \mathbf{AxCn}^T \left(\mathbf{CnCn}^T\right)^{-1} \qquad (4.18)$$

9. In order to determine the missing concentrations of the first and last measurement, the newly obtained coefficient matrix **E** is used:

$$\mathbf{A} = \mathbf{EC} \qquad (4.19)$$

$$\left(\mathbf{E^T E}\right)^{-1} \mathbf{E^T A} = \mathbf{C} \qquad (4.20)$$

10. The concentration matrix is cleaned by removing all concentration side maxima as well as negative concentrations.

11. The residual matrix R, which describes the deviation between calculated and measured signal strengths, is obtained from the following difference:

$$\mathbf{R} = \mathbf{A} - \mathbf{EC} \qquad (4.21)$$

The total deviation is expressed with the error sum of squares FQS. It is calculated from the sum of the squares of all elements of R:

$$\mathrm{FQS} = \sum_w \sum_m r_{w,m}^2 \qquad (4.22)$$

12. In parallel, the noise strength RS is calculated. It describes which part of the measurement signals cannot be described by the significant eigenvectors:

$$\underset{\mathbf{W\times M}}{\mathbf{Rs}} = \underset{\mathbf{W\times M}}{\mathbf{A}} - \underset{\mathbf{W\times S}}{\overline{\mathbf{U}}}\ \underset{\mathbf{S\times S}}{\overline{\mathbf{S}}}\ \underset{\mathbf{S\times M}}{\overline{\mathbf{V}}} \qquad (4.23)$$

$$\mathrm{RS} = \sum_{w}\sum_{m} \mathrm{rs}_{w,m}^{2} \qquad (4.24)$$

The error sum of squares cannot become smaller than the noise strength. Now follows the actual optimisation loop. The aim is to minimise the error sum of squares FQS. First, the current optimisation state is saved at loop pass n. It contains the matrix **Ca**$_n$. The species concentrations ca_i are normalised to the known total concentration of the metal core c_k:

$$\mathrm{ca}_i := \frac{\mathrm{ca}_i}{\sum_s v_{k,s}\mathrm{ca}_s} c_{k,tot} \qquad (4.25)$$

The new absorption matrix is calculated as follows:

$$\mathbf{A} = \mathbf{ECa} \qquad (4.26)$$

$$\mathbf{E}_{n+1} = \mathbf{ACa}_n{}^T \left(\mathbf{Ca}_n \mathbf{Ca}_n^T\right)^{-1} \qquad (4.27)$$

The new absorption matrix is cleaned up by setting all negative absorption coefficients to zero. At this point, the programme allows the consideration of fixed species spectra. If these are available individually from measurements or are already available in the course of other evaluations, they are used in E_{n+1} instead of the calculated values.

In the next step, the species concentrations are optimised again. For each measurement, the discrimination matrix defined above is used to determine which species have a significant share in the total absorption. In the absorption matrix E, all columns are removed that stand for non-significant species or are not significant in the respective measurement. The following applies:

$$\hat{e}_{w,s}(m) = e_{w,s} d_{s,m} \qquad (4.28)$$

Starting from equation (4.13) with the noise-free factor matrix product $\overline{\mathbf{U}}\overline{\mathbf{S}}\overline{\mathbf{V}}$

$$\underset{\mathbf{W}\times\mathbf{M}}{\overline{\mathbf{A}}} = \underset{\mathbf{W}\times\mathbf{S}}{\overline{\mathbf{E}}}\ \underset{\mathbf{S}\times\mathbf{M}}{\overline{\mathbf{C}}} = \underset{\mathbf{W}\times\mathbf{S}}{\overline{\mathbf{U}}}\ \underset{\mathbf{S}\times\mathbf{S}}{\overline{\mathbf{S}}}\ \underset{\mathbf{S}\times\mathbf{M}}{\overline{\mathbf{V}}} \qquad (4.29)$$

the reduced and discriminated absorption matrix **Ê(m)** is used to calculate the corresponding species concentrations for each individual measurement:

$$\mathbf{Ca} = \left(\hat{\mathbf{E}}(\mathbf{m})^{\mathbf{T}}\hat{\mathbf{E}}(\mathbf{m})\right)^{-1}\hat{\mathbf{E}}(\mathbf{m})^{\mathbf{T}}\overline{\mathbf{U}}\overline{\mathbf{S}}\overline{\mathbf{V}} \quad (4.30)$$

From the calculated concentration matrix, only the values belonging to the measurement *m* are used.

After all measurements have been processed in this way, a renewed and mostly also improved concentration matrix **Ca** is available. It is again cleaned from all negative values. For all measurements that, starting from the concentration maximum, were beyond measurements with previously calculated negative concentration values, the species concentrations are set to zero. With the help of the calculated absorption matrix $\hat{\mathbf{A}}$

$$\hat{\mathbf{A}} = \mathbf{ECa} \quad (4.31)$$

the residual maximum of the optimisation loop *n* is calculated:

$$\mathrm{R(n)} = \mathrm{A} - \mathrm{ECa} \quad (4.32)$$

The optimisation is completed when the error sum of squares

$$\mathrm{FQS(n)} = \sum_{w}\sum_{m}\mathrm{r(n)}_{w,m}^{2} \quad (4.33)$$

is no longer getting smaller but bigger again.

5 Factor analytical deconvolution of spectra of solutions containing lead chloride

5.1 Previous UV spectroscopic investigations of solutions containing lead chloride

Lead chloro complexes were first postulated by VON ENDE (1901) based on solubility measurements. Measurements of the UV spectra of solutions containing lead chloride were first carried out and described in detail by FROMHERZ and LIH (1931). Their conclusions are largely in agreement with the statements of later authors (CAVIGLI 1950, HAIGHT and PETERSON 1965, VIERLING 1971, YURCHENKO et al. 1976, SEWARD 1984, BYRNE et al. 1981, BYRNE and MILLER 1984). According to them, the spectrum of the free lead ion (more precisely of the aquo-complex) consists of one band with a maximum at 209 nm. The addition of chloride leads to the consecutive formation of two new bands at about 227 nm and 245 nm. At higher chloride concentrations, the solution spectra change continuously in such a way that the absorption maxima slowly shift in the direction of longer wavelengths. Individual bands cannot be clearly identified, but at the highest chloride concentration the formation of a cut-off spectrum is observed at about 272 nm. With increasing chloride concentration, only partially observable short-wave bands also appear (maxima around 180 to 200 nm), whose observation is made very difficult by the strong absorption of the chloride ion (charge transfer band). The longer wavelength band is caused by the transition from the electronic ground state $^1S_0 \rightarrow {}^3P_1$, the shorter wavelength band is caused by $^1S_0 \rightarrow {}^3P_2$.

Based on the previous work, four species spectra with one main band each can be clearly identified. The identity of the first three bands is undisputed in the literature: 209 nm (Pb^{2+}), 226 nm ($[PbCl]^+$) and at 245 nm ($[PbCl_2]^0$). The narrow and high boundary band with the maximum at 272 nm must come from an excitation of the most strongly chlorinated lead complex. FROMHERZ and LIH (1931) concluded from the narrow half-value width and the concentration-independent position of this band that this must be a coordinatively saturated complex that interacts only weakly with the environment. They identified it as $[PbCl_4]^{2-}$. Some authors argued that $[PbCl_6]^{4-}$or even $[PbCl_7]^{5-}$ was the highest chlorinated complex in aqueous solution (e.g., PAPOFF et al. 1955; HAIGHT and PETERSON 1965). However, these are only postulates without spectroscopic evidence.

MIRONOV (1961) was already able to show by means of potentiometric measurements that the type of metal cations noticeably influences the position of the complex equilibria.

Byrne and Miller (1984) investigated this effect for H^+, Na^+, Ca^{2+} and Mg^{2+} and quantified it with the help of specific ion interaction coefficients. However, their measurements only reached up to 1 mol/l ionic strength and do not allow conclusions to be drawn about the conditions in higher concentrated solutions.

As Hagemann (1999) was able to show in agreement with Fromherz and Lih (1931), the UV spectra of solutions containing lead chloride can be satisfactorily described with the aid of a set of five 2-parameter Gaussian curves. The individual spectra were assigned to the species Pb^{2+}, $[PbCl]^+$, $[PbCl_2]^0$, $[PbCl]_3^-$ and $[PbCl_4]^{2-}$ (Tab. 5.1). They each consist of a long-wave band with peak maxima at 209 to 272 nm and a short-wave band, of which only a part of the long-wave flank extends into the measurable UV range (from 190 nm).

Tab. 5.1 Absorption maxima and half-widths of the long-wave lead complex bands (Hagemann, 1999)

Species	λ_{max} [nm]	$\tilde{\nu}_{1/2}$ $[cm]^{-1}$	λ_{max} $[l*mol^{-1}*cm^{-1}]$
Pb^{2+}	209.1	1812	9010
$[PbCl]^+$	226.4	1996	9020
$[PbCl]_2^0$	244.9	1774	9160
$[PbCl]_3^-$	261.8	1476	9200
$[PbCl]_4^{2-}$	272.3	1057	16000

The determination of the positions of the individual spectra was carried out by optimising the band parameters for five Gaussian curves with the corresponding short-wave band edges. Models with four species were not sufficient to explain the measurement spectra. 6 species models led to very arbitrary band positions and were difficult to optimise. It was already clear at that time that the fit procedure used reached its limits, especially at medium and high chloride concentrations. Thus, the position of the long-wave bands of the species $[PbCl_3]^-$ could not be determined with certainty. Depending on the data selection and optimisation path, the peak maximum fluctuated between values of 260 and 265 nm. 261.8 nm was the most favourable value in many optimisations (Tab. 5.1). Further and improved information should therefore be obtained from the measured spectra with the help of factor analysis.

5.2 Factor analytical spectrum deconvolution

5.2.1 First evaluation: determination of the number of lead chloro species

With the factor-analytical spectrum deconvolution described above, the measured data from HAGEMANN (1999) was re-examined. In that work, the spectra of lead chloride in dilute to concentrated solutions of the salts NaCl, KCl, $MgCl_2$ and $CaCl_2$ were examined.

Several models were tested, some with five, some with six species and based on different sets of solution spectra. Models with seven species cannot be optimised. The species spectra shown in the Tab. 5.2 are obtained when all solution spectra are evaluated simultaneously. The first column shows the results of the spectral separation procedure used in HAGEMANN (1999). In that study, an attempt was made to build up the solution spectra by a set of Gaussian bands whose parameters (half-width, position, height) were optimised. The two right columns show the results of the factor analysis assuming five or six species and using all available solution spectra. As can be seen, the results of HAGEMANN (1999) and the factor analysis (5 species) differ mainly in the positioning of the main bands for $[PbCl_2]^0$ and $[PbCl_3]^-$. HAGEMANN (1999) already noted that the position of the bands cannot be determined unambiguously and depends strongly on the respective selection of the solution spectra used. As a result, significant differences between calculated and measured spectra occur for solutions with a medium chloride content. If, for example, the evaluation is restricted to NaCl solutions (Tab. 5.3, right column), the calculated bands for $[PbCl_2]^0$ and $[PbCl_3]^-$ and even for $[PbCl]^+$ are shifted to the shorter wavelength side. The bands are also more symmetrical and the fit for all solution spectra is optimal. If spectra from chloride-rich solutions are added, especially $MgCl_2$ and $CaCl_2$ solutions, all optimised bands move to longer wavelengths and the bands become asymmetrical. An optimal fit of all solution spectra is not possible with a uniform set of five species. Especially at medium chloride concentrations, significant deviations between calculated and measured spectra become visible.

The optimisation improves if the solutions with the highest chloride concentrations (> 5 mol/l) are excluded (Tab. 5.3, central column). As before with NaCl solutions, a satisfactory modelling is obtained. It is interesting that the 5 species model and the 6 species model calculate similar peak maxima when the 5-species model is limited to NaCl solutions (up to about 5 mol/l).

Tab. 5.2 Absorption maxima and half-widths of the long-wave lead complex bands I

Model	**Model with 5 species (HAGEMANN 1999)**		**Model with 5 species (this work)**		**Model with 6 species (this work)**	
Species	**λ_{max} [nm]**	**ε_{max} [l·mol^{-1}·cm^{-1}]**	**λ_{max} [nm]**	**ε_{max} [l·mol^{-1}·cm^{-1}]**	**λ_{max} [nm]**	**ε_{max} [l·mol^{-1} cm^{-1}]**
Pb^{2+}	209.1	9010	**208.8**	**8655**	at 209	~ 9000
$[PbCl]^{+}$	226.4	9020	**226.2**	**6311**	225.4	5661
$[PbCl]_2^{0}$	244.9	9160	**251.0**	**7126**	243.6	5582
$[PbCl]_3^{-}$	261.8	9200	**265.6**	**9773**	260.7	8463
$[PbCl]_4^{2-}$	272.3	16000	**272.45**	**17786**	269.3	11430
Species 6 $[PbCl_6]^{2-}$?					272.7	18686
			FQS=0.78		FQS=0.27	

Tab. 5.3 Absorption maxima and half-widths of the long-wave lead complex bands II

Model	**Solution NaCl 1-12, KCl 1-9**		**All solutions up to 5.2 mol/l Cl^-, up to $CaCl_2$ (No. 24)**		**NaCl solutions only**	
Species	**λ_{max} [nm]**	**ε_{max} [l·mol^{-1}·cm^{-1}]**	**λ_{max} [nm]**	**ε_{max} [l·mol^{-1}·cm^{-1}]**	**λ_{max} [nm]**	**ε_{max} [l·mol^{-1}·cm^{-1}]**
Pb^{2+}	208.7	8709	~209.0		208.7	8678
$[PbCl]^{+}$	224.7	5333	224.9	5362	224.5	5080
$[PbCl]_2^{0}$	244.1	6061	245.9	6389	244.5	6651
$[PbCl]_3^{-}$	-	-	263.6	7907	262.9	7834
$[PbCl]_4^{2-}$	-	-	270.4	12325	269.95	11348

Tab. 5.4 Absorption maxima and half-widths of the long-wave lead complex bands III

Model	**solutions > 5 mol/l Cl 2 Species**		**solutions < 5.2 mol/l Cl 6 Species**	
Species	**λ_{max} [nm]**	**ε_{max} [$l \cdot mol^{-1} \cdot cm^{-1}$]**	**λ_{max} [nm]**	**ε_{max} [$l \cdot mol^{-1} \cdot cm^{-1}$]**
Pb^{2+}	-	-	~ 209	
$[PbCl]^{+}$	-	-	224.5	5191
$[PbCl]_2^{0}$	-	-	241.6	5409
$[PbCl]_3^{-}$	270.0	11178	257.6 267.7*	6814 10415
$[PbCl]_4^{2-}$	272.2	15620	271.2	12217

* Purely formal assignment, no spectroscopic proof

The comparison makes clear that a single set of five individual spectra is not sufficient to satisfactorily explain the measurement spectra of all lead chloride solutions:

- Depending on the maximum concentration of the last solution considered, the position of the last long-wave band of the last species is determined at 270 - 272.3 nm. The more highly concentrated solutions were involved in the optimisation, the more the band moves to higher wavelengths. The same applies to the long-wave band of the fourth species.

- Assuming five absorbing species and taking all recorded solution spectra into account, the calculated long-wave bands of the second and third species show a clear asymmetry. The bands appear to be stretched in towards each other. For solution spectra containing these two species in approximately the same concentration, the error between calculated and measured spectrum is particularly high.

- Especially in the medium concentration range, there are clearly perceptible deviations between the calculated and the measured solution spectra. The spectrum of the third species seems to be placed too far in the long-wave range.

- These difficulties do not arise if only moderately concentrated solutions are considered (as e.g., in Millero and Byrne 1984, Luo and Millero 2007, Byrne et al. 2010). On the contrary, the complex $PbCl_4^{2-}$ is also omitted there. Models based on a limited set of concentrations (e.g., Woosley and Millero 2013, Xiong et al. 2013) therefore do not correctly reflect the chemism in concentrated salt solutions.

- Much more symmetrical bands and a considerably better reproduction of the measurement spectra are obtained when six species are assumed. The position of the calculated long-wave main bands for the first three species agrees quite well with the values obtained when only low concentration solutions are considered. The position of the bands of the last species is similar to that obtained when only the highest concentrated solutions are evaluated.

- An isosbestic point occurs in the most concentrated solutions. For magnesium chloride solutions (5-species model) it is at 267.0 nm and $\varepsilon = 10800$ cm^{-1} mol^{-1} (to be observed between 7.02 and 8.8 mol/l Cl). For calcium chloride solutions it is slightly shifted: 267.3 nm and $\varepsilon = 10800$ cm^{-1} mol^{-1}. (visible between 7.16 and 10.4 mol/l). The value for the isosbestic point calculated in the 5-species model is 266.6 nm and $\varepsilon = 11010$ cm^{-1} mol^{-1}. In the 6-species model it is calculated at 267.42 nm and $\varepsilon = 11076$ cm^{-1} mol^{-1}.

The observations could be explained by one of the following three models:

A. Six species are present instead of the previously assumed five. The additional sixth species is a structural isomer of one of the already accepted species ($[PbCl]^+$ to $[PbCl_4]^{2-}$).

B. Six species are present instead of the previously assumed five. The additional sixth species is $[PbCl_5]^{3-}$ or $[PbCl_6]^{4-}$.

C. The position and shape of the bands is increasingly concentration-dependent.

The variants are discussed below.

5.2.2 Additional structural isomer (A)

It is assumed that six species are present instead of the previously assumed five. This is either a species beyond $[PbCl_4]^{2-}$ or a structural isomer of one of the lower chlorinated complexes. Let us first consider the latter. Conceivable would be, for example, a pair of species

$$\underset{\text{octahedral}}{PbCl_3(H_2O)_3]^-} \equiv \underset{\text{tetrahedral}}{[PbCl_3(H_2O)]^-} + 2H_2O \qquad (5.1)$$

The tetrahedral structure is proven for complexes of the type $[MCl_4]^{2-}$ (M = Cd^{2+}, Hg^{2+}) (AHRLAND 1973). SEWARD (1984) concluded in analogy to this that the transition from octahedral to tetrahedral structure also takes place with Pb(II) during the formation of the trichloro complex:

$$[PbCl_2(H_2O)_3]\ ^0 + Cl \equiv [PbCl_3(H_2O)]^- + 2H_2O \qquad (5.2)$$

octahedrahedral

According to NIKOL et al. (1992), the complex $[PbCl_3]^-$ ion has a trigonal-pyramidal structure. The structural difference between the first chloro complexes and the complex $[PbCl_4]^{2-}$ is shown by the height and width of the long-wave band (Tab. 5.4): It is considerably narrower and much higher than that of the species Pb^{2+}, $[PbCl]^+$ and $[PbCl_2]^0$ – an indication of higher symmetry and less band broadening due to interaction with the environment. In contrast, AHRLAND (1973) pointed out that the transition from octahedral to tetrahedral structure in some soft-core d^{10}-complexes (e.g., Tl(III) chloro complexes) may well be distributed over several complexation steps, so that certain complexes exist in two structures side by side. In such a case, very broad bands would be expected, as different structures would result in different, overlapping absorption spectra. The observable absorption spectrum would then be an unknown combination of the individual spectra of two isomers. The "mixed" absorption spectrum only has a constant position if the mass ratio of the two isomers to each other does not change.

The equilibrium between two structural isomers (as an example the third complex) obeys the following formula

$$\frac{[PbCl_3(H_2O)_3]^-}{[PbCl_3(H_2O)]^-}\,\frac{\gamma_{okt}}{\lambda_{tet}} = K \cdot a_W^2 \qquad (5.3)$$

If we assume that the ratio of the activity coefficients of the two isomers changes only slightly, the position of the equilibrium depends only on the square of the water activity. Let us take the measurements in $CaCl_2$ solutions as an example: The square of the water activity decreases between 0.23 and 5 mol/l $CaCl_2$ concentration from 0.95 to 0.25. If one assumes that the activity coefficients of $[PbCl_3(H_2O)_3]^-$ und $[PbCl_3(H_2O)]^-$ develop approximately the same in the mentioned concentration range, the concentration ratio of the isomers can change by a factor of four after all. Depending on how much the spectra of the isomers differ from each other, a considerable change in the absorption spectra could result. The extent to which this affects the solution spectra cannot be estimated at present.

5.2.3 A complex $[PbCl_5]^{3-}$ or $[PbCl_6]^{4-}$ (B)

The assumption of six species leads to a model that describes the absorption spectra much better than a 5-species model. The addition of a seventh species, on the other hand, worsens the model considerably. Fig. 5.3 and Tab. 13.1 ff. (p. 471) show a calculated species distribution if it is assumed that six species are present in the system Pb-M-Cl-H_2O. The additional species could be $[PbCl_5]^{3-}$ or $[PbCl]_6^{4-}$.

$[PbCl_5]^{3-}$in solids

A species $[PbCl_5]^{3-}$ has so far only been detected in a solid, in which the complex anion is shielded by a very large organometallic complex (KALF and ENGLERT 2006).

$[PbCl_6]^{4-}$in solids

The hexachloro complex $[PbCl_6]^{4-}$, on the other hand, has been found in several solids: Cs_4PbCl_6, K_4PbCl_6 and in an organometallic complex (cf. also BERGERHOFF and SCHMITZ-DUMONT 1956, BERGERHOFF 2001). According to MØLLER (1960A), CYGLER and GRABOWSKI (1976) and PETROV et al. (1987), the compound Cs_4PbCl_6 contains an isolated almost ideally octahedral ion $[PbCl_6]^{4-}$. The bond length Pb-Cl in Cs_4PbCl_6 is 2.93 Å (MØLLER 1960A). Similar results were obtained for solid hexakis (2-chloroethylammonium)hexachloroplumbate(II)chloride (GESELLE and FUESS 1995). According to Møller (1960b), Cs_4PbCl_6 forms already at 20 °C in a CsCl concentration of 6.7 mol/kg, i.e., at chloride concentrations as they occur in concentrated $MgCl_2$ or $CaCl_2$ solutions, but not in NaCl and KCl solutions.

A compound K_4PbCl_6 is also known, but it apparently only forms in melts (HILDEBRAND and RUHLE 1927). It does not crystallise from concentrated KCl solution. The observation of a compound $Mg_2PbCl_6 \cdot 13H_2O$ (OTTO and DREWES 1890) in concentrated $MgCl_2$ solutions could also indicate a complex $[PbCl_6]^{4-}$ if one interprets the molecular formula as $[Mg(H_2O)_6]_2^{4+} \cdot PbCl_6^{4-} \cdot H_2O$. In the investigations of HAGEMANN(1999), a composition $Mg_3PbCl_8 \cdot 19H_2O$ was found instead. This contradiction cannot be resolved at present.

For the reflection spectrum of a CsCl-$PbCl_2$ mixture, PATHAK and SEN (1975) found a maximum at about 282 nm (4.4 eV). Thin-film preparations of Cs_4PbCl_6 showed an absorption maximum at 284-285 nm (KONDO et al. 2001a, YUNAKOVA ET AL. 2015, AKKERMAN et al. 2017). In contrast, TSAI and COONEY (1976a) reported a maximum of the reflection spectrum at 293 nm.

Pb complex in doped NaCl, KCl and RbCl crystals and in $CsPbCl_3$

KONDO et al. (2001a, 2001b) investigated the absorption behaviour of a $PbCl_2$ film on CsCl applied at low temperatures. According to the authors, after heating to 400 K, this had partially reacted with CsCl to form $CsPbCl_3$. However, the peak at about 272 nm (4.55eV) was not assigned to reacted $PbCl_2$. Only further heating led, it was assumed, to Cs_4PbCl_6 and an absorption peak at 285 nm (4.35eV). Although there is no proof that Cs_4PbCl_6 was actually formed, the agreement with other measurement results (see above) shows that it is probably this compound. Furthermore, it is unclear to what extent the solid-state spectra can give clear indications of the species present in aqueous solutions, or whether the species present in the strong crystal field of the solids may show slightly different spectra. Interesting is the identification of a second band in the far UV range with a maximum at about 196 nm (with FESEFELDT band at about 225 nm, with HILSCH and POHL at 193 -198 nm).

NaCl, KCl and RbCl crystals doped with Pb^{2+} show absorption bands at 273 nm (KÄDING 1932, FUKUDA 1964) - significantly lower than in Cs_4PbCl_6. The species occurring in the crystals is probably identical to the species occurring in concentrated solutions of the salts mentioned. For here as there, a band is observed at 272 - 274 nm, but the band is somewhat narrower in solids. This shows that even in the strong crystal field of NaCl or KCl there is hardly any shift of the highest absorption band of the highest complex compared to concentrated chloride solutions. The type of alkali ions has little influence on the position of the absorption bands in solid alkali chlorides (HILSCH and POHL 1928, FESEFELDT 1930, FROMHERZ 1931, BOHUN and TRNKA 1964, ZUBER and WEIL 1991). In emission bands, on the other hand, a perceptible shift of the bands towards longer wavelengths can be observed when the atomic weight of the alkali ion increases (BOHUN and TRNKA 1964).

HILSCH and POHL (1928) as well as FESEFELDT (1930) investigated the UV absorption of pure, crystalline lead chloride and found two bands at 271 and 219 nm . Thus, a similarly coordinated complex also occurs here.

BOHUN et al. (1965.1970) found that in KCl doped with $PbCl_2$, lead is found at the cation sites and must therefore be coordinated octahedrally with six chloride ions. From this, they concluded that $PbCl_6^{4-}$ ions must be present in KCl. However, this contradicts the spectroscopic measurements, which show a clear difference between doped KCl crystals and Cs_4PbCl_6.

$[PbCl_6]^{4-}$ in solution

Møller (1960a) assumed on the basis of spectroscopic evidence that $[PbCl_6]^{4-}$ must also occur in solution, but further evidence is lacking. Tsai and Cooney (1976a) assumed that $[PbCl_6]^{4-}$ does not occur in solution because the solution spectra they measured showed an absorption maximum of at most 271 nm, but solid Cs_4PbCl_6 had a maximum at 293 nm. As already described above, however, several other authors report significantly lower values (around 282-285 nm).

For a hypothetical $PbCl_6^{2-}$ in aqueous solution, a bond length for Pb-Cl of 2.966 Å was calculated for an octahedral complex using *ab initio* methods (Freza et al. 2013). This corresponds to the bond length in the solid state (see above).

An orienting UV measurement (this study) in a 11.1 mol/kg CsCl solution (7.4 M) showed a peak maximum at about 276.9 nm, i.e., still significantly higher than the maxima[7] observed so far in NaCl, KCl, $MgCl_2$, $CaCl_2$ solutions (Hagemann 1999, Avramenko and Bilyj 1960: up to 272 nm). The value is also higher than the value calculated for a 6-species model for the fifth complex species. This is not necessarily contradicting, because the strong overlapping of the absorption spectra of the individual species made a clear evaluation of the measured solution spectra difficult. It is even possible that assuming one species absorbing at 285 nm, a model with seven species (incl. $PbCl_5^{3-}$) becomes necessary. This can only be further clarified by additional measurements on solutions with very high chloride content.

It would therefore be obvious that in highly concentrated chloride solutions, especially in the presence of stabilising cations such as Cs^+, Ca^{2+} and Mg^{2+}, at least partial formation of $[PbCl_6]^{4-}$ occurs. The species could possibly also occur in the form of a ternary complex of the type $M_n[PbCl_6]^{n \cdot a-4}$. Ternary chloro complexes have not been described for lead or other metal cations, but for hydroxo and carbonato complexes of other heavy cations, e.g., Tc^{IV}, Zr^{IV}, Nd^{III} (Altmaier et al. 2008; Neck et al. 2009; Yalçintaş et al. 2016). Calcium does not form an "inner sphere" complex with chloride, but above a concentration of 6 mol/kg $CaCl_2$ a weak contact pair $[Ca(H_2O)_5Cl]^+$ is predominant. (Rudolph and Irmer 2013). This could contribute to a stabilisation of the chloro complex $[PbCl_6^{4-}]$ if a simultaneous coordination to Pb^{2+} takes place.

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[7] Measurement in the GRS laboratory

In summary, it can be said that the existence of $PbCl_6^{4-}$ in solids has been proven. In highly concentrated chloride solutions higher than 6 mol/kg the species is at least possible based on experimental findings and theoretical considerations.

5.2.4 Variable bands (C)

It is assumed that the position and shape of the bands are increasingly dependent on concentration. KORTÜM (1936,1962) was already able to show in a review article, which unfortunately received far too little attention, that Lambert-Beer's law on the proportionality between absorbent concentration and extinction no longer applies strictly even with small changes in the solution medium. The deviations called "salt effect" depend on the absorption band as well as on the type of background salt. Similar to HALBAN and EBERT (1924) and HALBAN and EISENBRAND (1928) with picrates and nitrates, SCHEIBE (1926a, 1926b) also found drastic concentration influences on the position of the iodide absorption band when using concentrated magnesium and calcium chloride solutions. While its maximum in water is found at 220 nm, it is found in 4.5 molar $MgCl_2$ or $CaCl_2$ solution at 227.3 nm. A shift of 2 nm is found at 2.32 mol/l $MgCl_2$ or $CaCl_2$. The effect thus seems to increase at higher concentrations. SCHEIBE attributes this to the strongly decreasing content of free water in the solution. In 4.5 molar $CaCl_2$ solutions, there are only three molecules of water per dissolved ion. This strongly influences the solvation and thus also the orbital structure of the iodide ion. In the case of potassium nitrate, similarly strong effects are found in $CaCl_2$ and $SrCl_2$ solutions, but curiously almost not in $MgCl_2$ solutions.

Considering that the fourth lead species plays a significant role in the 5-species model from 0.23 mol/l up to the experimental maximum concentration of $CaCl_2$ (5.2 mol/l), an analogous influence on the position of the long-wave band of the fourth species would not be surprising. On the other hand, the observation of an isosbestic point in solutions of the highest chloride solutions is a proof that two species with distinct spectra a present. A continuous shift of the peak without an isosbestic point would be expected in case of a variable band. So, this thesis seems to be unlikely.

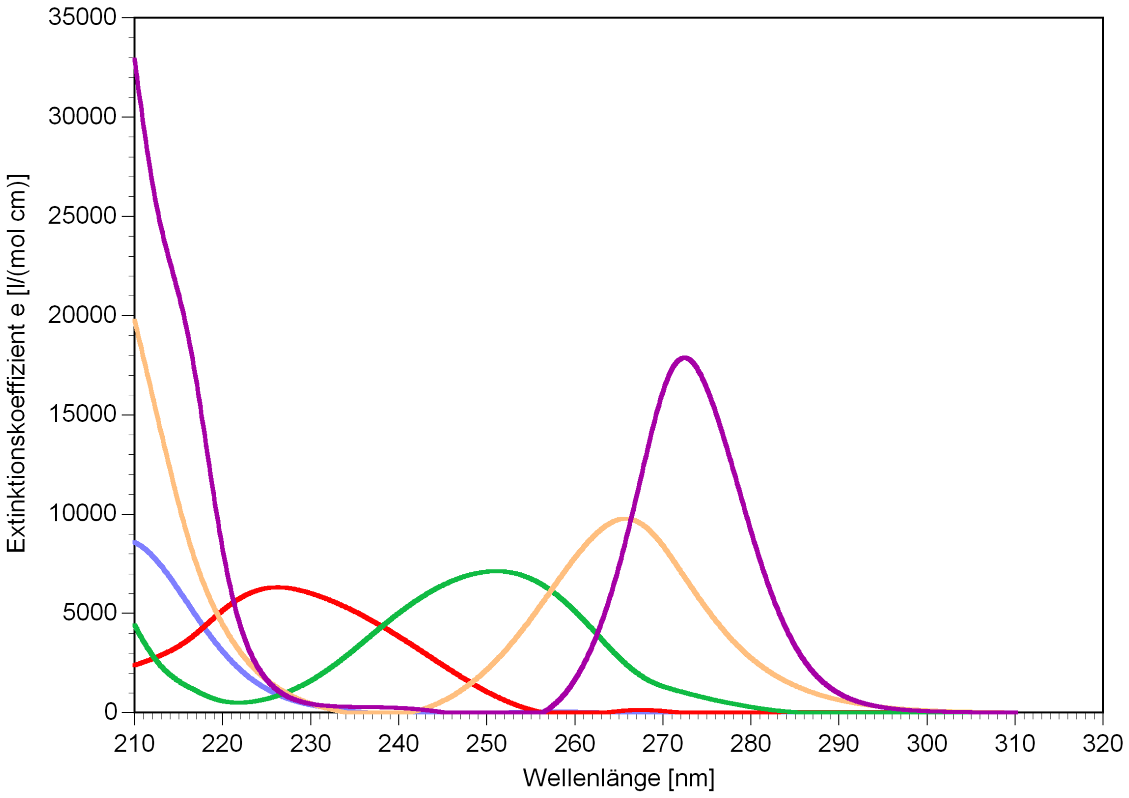

Fig. 5.1 Species spectra of lead chloro complexes in the 5-species model

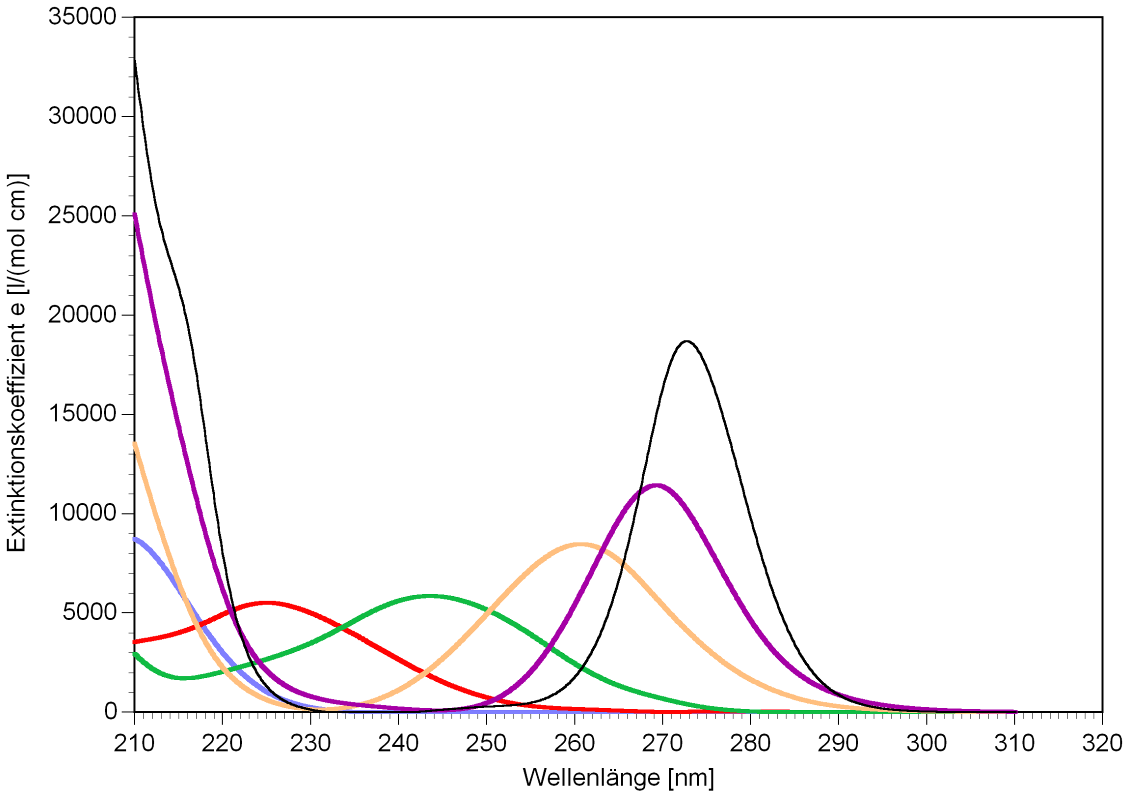

Fig. 5.2 Species spectra of lead chloro complexes in the 6-species model

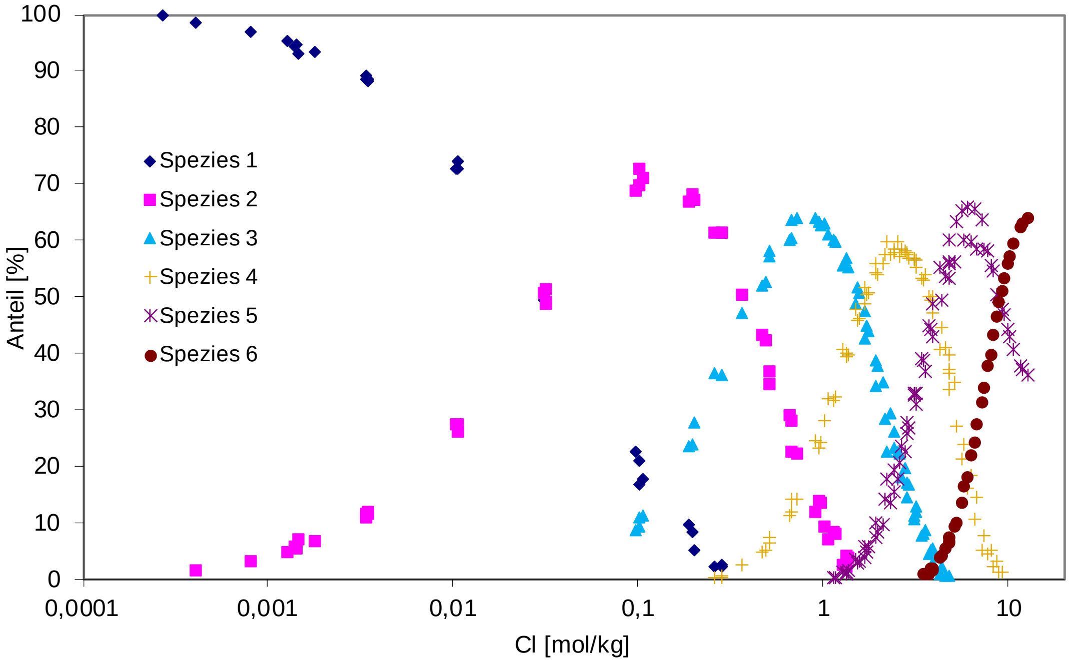

Fig. 5.3 Concentration distribution of a 6-species model

Conclusion

With a five-species model and concentration-independent species spectra, the measurement spectra found cannot be adequately explained. Three variants (structural isomers, a fifth complex, strongly concentration-dependent species spectra) were discussed. None of them can be completely ruled out at this stage, but the existence of $PbCl_6^{4-}$ in solids shows that further chloro complexes in solution beyond $PbCl_4^{2-}$ are at least possible. Additional information, but probably no final clarification, could be provided by experiments with constant chloride concentration but increasing inert salt concentration (e.g., with metal perchlorates), measurements in systems with high, constant ionic strength as well as spectroscopic investigations on solutions and solids. Due to the currently unclear information situation, we have decided not to make any changes to the speciation model of HAGEMANN (1999) or HERBERT et al. (1999) at present.

6 Factor-analytical deconvolution of Raman spectra of solutions containing cadmium and zinc chloride

6.1 Solutions containing cadmium chloride and the formation of cadmium chloro complexes

In the absence of other ligands, cadmium is present as an octahedral hexaaqua complex $[Cd(H_2O)_6]^{2+}$ (RUDOLPH and IRMER 1994; RUDOLPH 1998). The UV absorption bands of the cadmium and zinc chloro complexes lie largely in the vacuum UV range. Only their slopes extend into the range around 200 nm (DOEHLEMANN and FROMHERZ 1934). They do not allow a quantitative analysis. Direct Raman spectroscopic observations to elucidate complex formation were first made by VENKATESWARAN (1935). Due to the weakness of the excitation, the author could not provide clear evidence for chloro complexes. No Raman bands were also found by ROLFE et al. (1954) when investigating the system $CdCl_2$ - KCl - H_2O.

DELWAULLE (1955) found a band at 250 cm^{-1}, which she assigned to the species $[CdCl_4]^2$. A more detailed characterisation was achieved by DAVIES and LONG (1968), who located two band maxima at about 260 cm^{-1} ($\nu_1(a_1)$ pol) and 94 cm^{-1} (depol). Deviating from this finding and in contradiction to almost all comparably heavy tetrachloro complexes, LATYŠEVA and ANDREEVA (1971) and KHRIPUN et al. (2001) based on this assume an octahedral aquacomplex $[Cd(H_2O)_2Cl_4]^{2-}$. This is also contradicted by the measurements of ADAMS et al. (1963) on anhydrous tetraethylammonium tetrachloro cadmium $((C_2H_5)_2N)_2CdCl_4$. The compound shows a band maximum at the same position as the chloride-rich cadmium-containing solutions. Therefore, there must also be an equally structured and anhydrous complex in solution.

Factor analysis of XANES measurements in NaCl/HCl solutions of up to 18 m chloride delivered only two independent components (BAZARKINA et al. 2010a). These may be mixtures of octahedral and tetrahedral species. The maximum ratio of Cl/Cd was four, but the formation of $[CdCl_5(H_2O)_n]^{3-}$ could not be excluded.

Between the forms $[Cd(H_2O)_6]^{2+}$ and $[CdCl_4]^{2-}$, there are probably three other complexes with one to three chloride ions. There is uncertainty about the stability and structure of these complexes.

It is certain that there is a change from an octahedral to tetrahedral structure between the second and the third complex. This can be concluded from the extraordinarily high reaction enthalpy during this step (AHRLAND 1973), which includes a dissociation of three water molecules:

$[CdCl_2(H_2O)_4]^0 + Cl\text{-} \rightarrow [CdCl_3(H_2O)]^- + 3\ H_2O$

The stability of the third complex seems to be rather weak (BAZARKINA et al. 2010b). The planar $[CdCl_3]^-$ complexes in KCl-$CdCl_2$ melts postulated by BUES (1955) in the course of Raman spectroscopic measurement data are rejected by BREDIG and VAN ARTSDALEN (1956). The latter pointed out that the parts of the spectrum designated as $[CdCl_3]^-$ bands can easily be $^-$interpreted as superpositions of bands of the species $[CdCl_2]^0$ and $[CdCl_4]^2$. Measurements of the freezing point depression of $NaNO_3$ melts with small amounts of added $CdCl_2$ and KCl/$CaCl_2$ also point to Cd^{2+}, $[CdCl_2]^0$ and $[CdCl_4]^{2-}$ as the only species present. Models with $[CdCl_3]^-$ are not able to explain the measured data. The pyramidal $[CdCl_3]^-$ ions postulated later by TANAKA et al. (1963) must also be rejected in a similar way. One reason for the difficulty in interpreting the Raman spectra may have been the very poor signal-to-noise ratio encountered in early measurements. Furthermore, due to strong superpositions and very unevenly distributed intensities, the number of clearly separated bands that should result from the selection rules for the molecular vibrations for the potential complex structures is not found.

In concentrated cadmium chloride solutions, only one band is found by Raman spectroscopy, which cannot be assigned to the chloro complexes mentioned so far. It is assigned to the vibration of a $(CdCl_2)_n$ polymer (DAVIES and LONG, 1968).

In concentrated aqueous solutions of KCl, $CaCl_2$ and $MgCl_2$ but not of NaCl, solids are formed that, at least stoichiometrically contain a $CdCl_6$ unit: K_4CdCl_4, $Mg_2CdCl_6{\cdot}12H_2O$, $Ca_2CdCl_4{\cdot}12H_2O$ (see 7.9 ff). The compound K_4CdCl_4 is the prototype of a whole class of solids. It was shown to contain octahedral $[CdCl_6]^{4-}$ ions (BERGERHOFF and SCHMITZ-DUMONT 1956, BERGERHOFF, 2001). The shift of the peak maximum in Raman measurements in concentrated $CaCl_2$ solutions (section 3.6.3) could indicate that this complex also forms in solution. On closer inspection, a similar change in the main peak can also be observed in the most concentrated $MgCl_2$ solution.

6.2 Raman spectroscopic quantification of complex formation

Numerous papers have appeared in the literature dealing with the complexation of cadmium in chloride solutions. In the IUPAC database of PETTIT and POWELL (2001), over 86 sources are listed that contain information on formation constants of cadmium chloro complexes. Without having experimental evidence for their existence, the respective measured data (potentiometric, polarographic, solubilities, etc.) were "fitted" using five species. The remarks in the previous chapter certify that considerable doubts exist about the stability of $[Cd(H_2O)_xCl_3]^-$ and perhaps of $[Cd(H_2O)_5Cl]^+$ as well.

The first task of our own Raman spectroscopic measurements was therefore to elucidate the number of significant species in cadmium chloride solutions. The Raman spectra of 11 solutions of the system $Cd(ClO_4)_2$-NaCl-H_2O and 15 solutions of the system $Cd(ClO_4)_2$-LiCl-H_2O served as a basis. Perchlorate was required in each case as an internal reference. Only the isotropic spectra in which the strong background signal of the water does not occur are used for evaluation. In pure cadmium perchlorate solutions without added chloride, the solution spectrum in the range from 50 to 700 cm^{-1} shows a polarised band at 360 cm^{-1}, which can be attributed to the totally symmetrical cadmium hexaaqua complex (RUDOLPH 1998). With the addition of small amounts of chloride, the height of this band decreases and another broad peak appears on its flank at about 245 cm^{-1}. On further addition, the peak of this new band first broadens and a slightly offset narrow, slightly asymmetric but intense band develops at about 262 cm^{-1}, which has previously been identified as the vibrational band of the tetrahedral ion $[CdCl_4]^{2-}$ (DAVIES and LONG 1968).

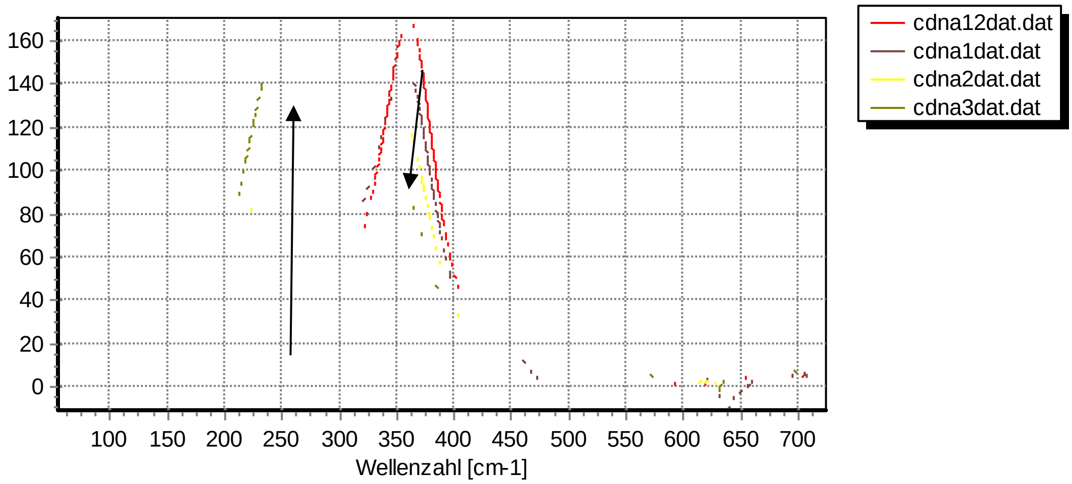

Fig. 6.1 Raman spectra of $Cd(ClO_4)_2$ solutions (about 1 mol/l) with addition of 0 - 1.2 mol/l NaCl or LiCl

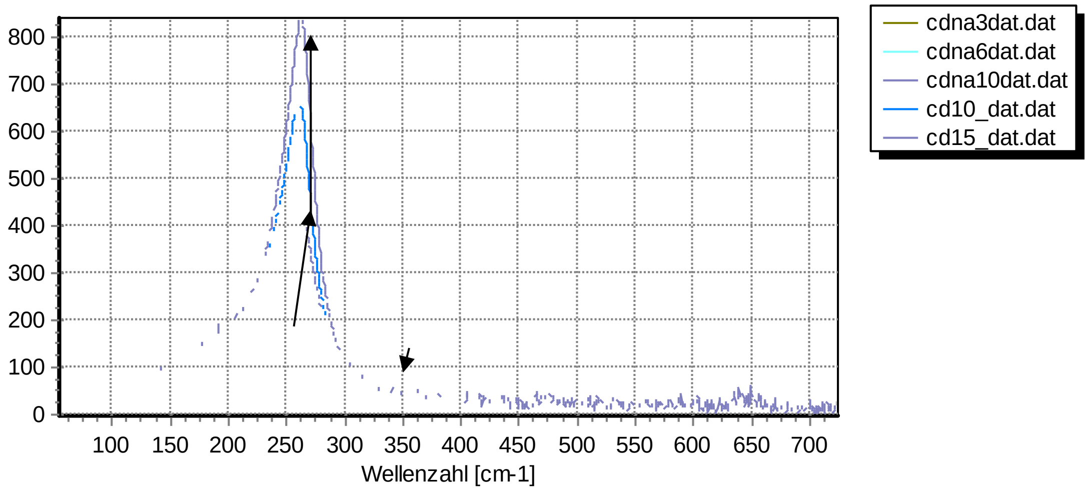

Fig. 6.2 Raman spectra of $Cd(ClO_4)_2$ solutions (about 1 mol/l) with addition of 1.2 - 6.3 mol/l NaCl or LiCl

The factor-analytical treatment of the recorded spectra indicated the presence of three distinguishable species. The inclusion of a fourth species leads to strongly correlated and distorted species spectra. In no case, solution spectra showed even a hint of another band indicating the presence of further significant species. This leaves three species, which were interpreted as $[Cd(H_2O)_6]^{2+}$, $[CdCl_2(H_2O)]^0$ and $[CdCl_4]^{2-}$ on the basis of the previous findings. It cannot be excluded that $[CdCl(H_2O)_5]^{2+}$ was present but could not be distinguished from $[Cd(H_2O)_6]^{2+}$ analogous to the situation with zinc.

For the spectrum of the chloride-free cadmium hexaaqua complex $[Cd(H_2O)_6]^{2+}$, the solution spectrum of the preparation CdLi1 was normalised to the concentration of 1 mol/l cadmium. As a result of the factor analysis, we obtained the three polarised species spectra shown in Fig. 6.3. The position of the spectrum of the cadmium hexaaqua complex was already known from earlier work. It essentially consists of a largely symmetrical single peak at 360 cm^{-1}. Some information was also already known about the position of the last spectrum of the tetrachloro complex. It shows a high-intensity peak with a maximum at 262 cm^{-1}. It appears asymmetric due to a not exactly localisable, weak and broad side band at about 180 cm. The calculated Raman spectrum of the dichloro complex appears even more structured. In addition to its maximum at 242 cm^{-1}, two further subordinate side bands can be identified at about 280 and 330 cm^{-1}. It cannot be ruled out that these are factor-analytical artefacts resulting from the strong superposition and thus correlation of the species spectra.

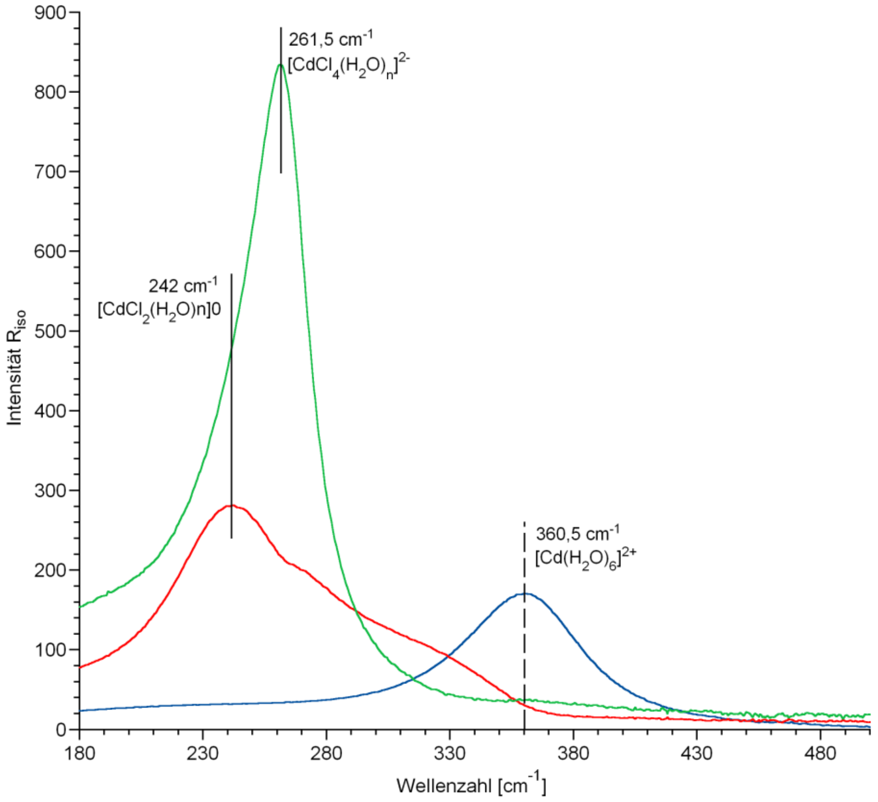

Fig. 6.3 Factor-analytically determined isotropic Raman spectra of three cadmium species

A closer look at the calculated solution spectra shows that especially in the range of 330 cm^{-1} there is a noticeable difference between calculated and experimental values

(Fig. 6.4) for solutions with a chloride/cadmium ratio below 2. Under similar concentration ratios, a single peak can be detected for zinc in two measurements and in the similar wavenumber range. Although it can be localised, it remains too weak for factor-analytical evaluation. We assume that for both cadmium and zinc a monochloro complex with a narrow existence area and a weaker band is noticeable. A quantification is not possible due to the weakness of the signal, but probably also not necessary since it will soon be replaced by the dichloro complex.

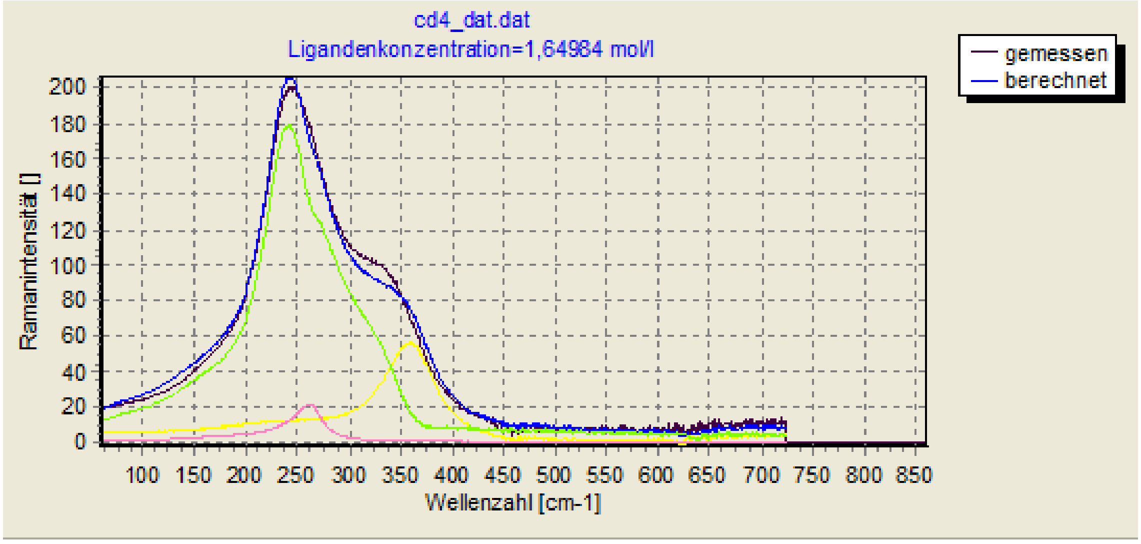

Fig. 6.4 Polarised Raman spectrum of the solution CdLi4: deviations between calculated and measured spectrum at 330 cm^{-1}If the calculated species spectra are used as a basis, we obtain the spectra shown in Tab. 13.14 (p. 481) and Fig. 7.1. From the results it is clear that complex formation starts very early in the considered solutions. The cadmium dichloro complex has a very wide range of existence in the investigated solutions. It already forms in solutions with the lowest chloride addition (0.3 mol/kg) and is still detectable in the solutions with the highest chloride content (7.9 mol/kg).

6.3 Factor analytical evaluation of Raman spectra of solutions containing zinc chloride

6.3.1 State of knowledge so far

Zinc probably forms four chloro complexes $[ZnCl_n]^{2-n}$ with chloride (n= 1...4). At least, attempts have been made in the past to explain potentiometric data (including SILLÉN and LILJEQUIST 1944; ŠČUKAREV et al. 1956), ion exchange experiments (SHORT and

MORRIS 1961), solubility measurements (RUAYA and SEWARD 1986), ^{67}Zn NMR studies (MACIEL et al. 1977) and extraction data (SCIBONA et al. 1966) with the help of a five-species model. More recent critical evaluations such as APARICIO and ELIZALDE (1996) also assume the existence of all four possible chloro complexes without further consideration. In contrast, FERRI and SALVATORE (1988c) showed that potentiometrically determined activity coefficients of zinc in 3 to 5 molar perchlorate solutions with up to 3.3 M chloride can be explained with only two complexes, $[ZnCl_2]^0$ and $[ZnCl_4]^{2-}$.

The spectroscopic proof of the existence and structure of the individual species still causes difficulties. UV spectroscopy is not a suitable method because the absorption bands lie in the vacuum UV and are superimposed by the chloride bands. Only at the highest chloride concentrations weak edges are found, which extend to wavelengths of about 200 nm. A quantitative evaluation is not possible (DOEHLEMANN and FROMHERZ 1934). Ultrasonic spectroscopy (TAMURA 1977) and dielectric spectroscopy (KAATZE et al. 1987) proved to be insufficiently sensitive.

Further information is provided by Raman spectroscopy, X-ray scattering, XAFS measurements, and ab initio calculations on the relative stability of hypothetical complex structures.

The first Raman spectroscopic investigations date back to the 1930s (DAMASCHUN, 1932; HIBBEN, 1932; VENKATESWARAN, 1935; HIBBEN, 1937). Apart from the assignment of the bands, all the essential characteristics of the Raman spectra of solutions containing zinc chloride are already described here: a band around 390 cm^{-1}, which corresponds to the free zinc ion or aqua complex, a band around 280 cm^{-1}, which occurs in concentrated $ZnCl_2$ solutions with further chloride addition and another band at 285 cm^{-1}, which is assigned to a negatively charged complex ion (DAMASCHUN, 1932, postulated $[ZnCl_6]^{4-}$).

DELWAULE (1955) investigated the Raman oscillations of zinc chloride, bromide and iodide in various solvents. The position of the bands changed only slightly. In acetone, octanol and butanol, $ZnCl_2$ does not dissociate, so that only one band can be seen at 305 cm^{-1}.

MORRIS et al. (1963) confirmed the results of DELWAULLE (1955), but now additionally found a strongly polarised but very weak band at 286 cm^{-1} in tri-n-butyl phosphate extracts, which they assigned to the complex $[ZnCl_3]^-$.

IRISH et al. (1963) made the first attempt to order and interpret the results available to date. In particular, they tried to assign specific molecular vibrations to the Raman bands found in order to determine the type of complexes that occur. From their results, they concluded the existence of four species: $[Zn(H_2O)_6]^{2+}$, $[ZnCl]^+$, $[ZnCl_2]^0$(aq), and an octahedral $[ZnCl_4(H_2O)_2]^{2-}$, although the evidence for $[ZnCl]^+$ is very weak.

According to the interpretation of IRISH (1967), the comparison of the spectra of $ZnCl_4^{2-}$ with $ZnI_4^{2-}$and $ZnBr_4^{2-}$ indicates that the usually assumed tetrahedral structure cannot be correct. Only two absorption lines are observed, whereas a tetrahedral structure would expect four lines. In particular, the chloro complex should show a better separation of the ν_2 (bending) and ν_2 bands compared to the bromo and chloro complexes because of the lower mass of the chloride, but this is not the case. A suitable structure would be octahedral: $[ZnCl_4(H_2O)_2]^{2-}$. This is still possible for chloride, but not for the larger ions bromide or iodide.

QUICKSALL and SPIRO (1966) were able to show that both in solids (Cs_2ZnCl_4) and in solution there is tetrahedral $[ZnCl_4]^{2-}$ and not an octahedral $[ZnCl_4(H_2O)_2]^{2-}$ as IRISH (1963) suggested.

GILBERT (1967) interpreted his Raman measurements with LiCl solutions to the effect that at concentrations below 4 mol/kg $[ZnCl_4]^{2-}$ is present next to $[ZnCl]^+$, whereas at concentrations above 4 mol/kg $[ZnCl_2]^0$ is present next to $[ZnCl_4]^{2-}$. Similar results were found by SHURVELL and DUNHAM (1976) who, above a chloride concentration of 3.01 mol/l and a constant Zn concentration of 1.505 mol/l, observed in a factor analysis only two zinc chloro complexes identified as $[ZnCl_4]^{2-}$ and $[ZnCl_2]^0$.

KANNO and HIRAISHI (1980) also found mainly two species in Raman measurements in concentrated (gel-like) solutions of ZnCl-LiCl mixtures: $[Zn(H_2O)_6]^{2+}$and $[ZnCl_4]^{2-}$.

MARLEY and GAFFNEY (1990) found, in addition to $[ZnCl_4]^{2-}$and $[ZnCl_2]^0$, $[ZnCl_3]^-$ at 286 cm^{-1} and, at higher temperatures, $[ZnCl]^+$ at 328 cm^{-1}. Their evaluation shows contradictions, however, as they attribute a dominant or negligible role to $[ZnCl]^+$ at 25 °C, depending on the graphical representation.

PARCHMENT et al. (1996) as well as HARRIS et al. (2003) undertook ab initio calculations to estimate the most likely stable conformations of the four chloro complexes. According to them, the complexes with one and two chlorine atoms are to be regarded as octahedral, the complexes with three or four chlorine atoms probably as tetrahedral. The complexes with n = 2, 3, 4 should be stable, but not $[ZnCl]^+$(aq). Interesting for Raman spectroscopy is the statement that the predicted Raman vibrational frequencies for $[Zn(H_2O)_6]^{2+}$ and $[Zn(H_2O)Cl]^+$ differ only very little from each other (about 5 cm^{-1}). In this case, it could be that complex formation in solution already occurs when there is still no clearly visible change in the band at 390 cm^{-1}. However, the measurements so far gave no indication of a signal lying close to the $[Zn(H_2O)_6]^{2+}$ band.

MAEDA et al. (1996) investigated the formation of zinc chloride solution using both Raman spectroscopy and X-ray scattering. Based on the results in solutions and solids of the type $LiCl-ZnCl_2-H_2O$, they deduced the presence of the complexes $[ZnCl_2]^0$, $[ZnCl_3]^-$ and $[ZnCl_4]^{2-}$. According to their results, $[ZnCl_3]^-$ is predominant in solutions with a high $ZnCl_2$ content (e.g., 5 M) but limited additional chloride content (LiCl up to 5 M) whereas $[ZnCl_4]^{2-}$ is not detectable. It was not possible to clarify whether $[ZnCl]^+$ also occurs. In in their opinion, Raman spectra of the species $[ZnCl]^+$ and $[ZnCl_2]^0$ do not differ or the concentration $[ZnCl]^+$ was too small in the solutions for X-ray scattering to be detected.

WERTZ and BELL (1973a, 1973b) provided supplementary studies with the help of X-ray diffraction (XRD) investigations on solutions. According to this, the two complexes $[ZnCl_4]^{2-}$ and $[ZnCl_2(H_2O)_2]^0$ have a pseudotetrahedral structure. Other complexes (mono- or trichloro-complex) cannot have a significant part in the speciation.

According to the XAFS studies by MAYANOVIC et al. (1997,1999) and D'ANGELO et al. (2011), zinc in concentrated chloride solutions (6 m NaCl) is mainly present as a tetrahedral $[ZnCl_4]^{2-}$ complex without the participation of coordinated water. In $ZnCl_2$ solutions up to 0.2 M, no complex formation occurs. At higher chloride concentrations, a continuous increase in the number of coordinated chlorine atoms is observed.

A XANES investigation by LIU et al. (2007) yielded little new information, as the species $[ZnCl_n(H_2O)_{6-n}]^{2-n}$ (n=1-3), which were considered octahedral, yielded practically identical spectra. Only the tetrahedral complex $[ZnCl_4]^{2-}$ could be quantified.

Ab initio calculations by PYE et al. (2007) suggested that the $[ZnCl_2]^0$ complex in solution is an octahedral tetraaqua ion with the two chlorine atoms in cis position (in vacuum a tetrahedral diaqua complex would be more stable). The trichloro complex containing one additional water molecule, is tetrahedral.

Later, MEI et al. (2015) assumed on the basis of ab initio calculations in combinations with XAS measurements that there is no stable octahedral complex beside $[Zn(H_2O)_6]^{2+}$.

The relevance of the complexes $[ZnCl(H_2O)_5]^+$ and $[ZnCl_3(H_2O)_n]^-$ remains unclear. It obviously depends on the specific experimental conditions (at least at 25 °C). Their detection is made more challenging by the fact that the spectra of the octahedral complexes differ only slightly in Raman, XANES and X-ray scattering measurements. In general, it is noticeable that there are partly different assumptions about the complex at which the transition to the tetrahedral structure occurs. This concerns $[ZnCl_2]^0$ but also $[ZnCl_3]^-$. This is significant for the evaluation of the measurement results.

However, it seems that in solutions with low $ZnCl_2$ concentration but high ionic strength, the two species form only in a subordinate proportion. In solutions of low ionic strength and low zinc content, the first chloro-complex could have some relevance. The relevance of $[ZnCl_3]^-$ remains unclear.

6.3.2 Raman measurements: Number of factors and assignment of spectra

The starting point for determining the number of factors was a set of spectra obtained from the measurements of the $Zn(ClO_4)_2$-NaCl and $Zn(ClO_4)_2$-LiCl series (Tab. 13.15). These two series each have the widest range of Cl/Zn ratios. The evaluation was carried out for the wavenumber range 100 to 700 cm^{-1}. All spectra were normalised with respect to their zinc perchlorate concentration. The spectrum $Zn(ClO_4)_2$-LiCl-2 was excluded because of the strong noise of the measurement signal. The measurement series $Zn(ClO_4)_2$-$MgCl_2$ (Tab. 13.6) was initially not used because of the interfering MgO_6 band (see above). The $Zn(ClO_4)_2$-$CaCl_2$ series (Tab. 13.7) was also not considered at first because it turned out that the position of the peak maximum at the highest $CaCl_2$ concentration was shifted by 2 cm^{-1} compared to the value determined from the other systems. The measurements from the system $Zn(NO_3)_2$-KCl (Tab. 13.6) were not used at first because it was not clear what influence the deviating background medium (nitrate) had on the position of the zinc chloro complex bands. Only the first spectrum at c_{KCl}= 0 was taken into account, since the species spectrum of $[Zn(H_2O)_6]^{2+}$ had the same position and shape.

The number of factors (=single species spectra) minimally needed to construct the measurement spectra was determined by applying the Evolving Factor Analysis several times, each time with a different number of possible factors. This showed that the total error resulting from the squared differences between calculated and measured spectra becomes minimal when three factors are allowed. It proved to be helpful to set the spectrum of the free zinc ion from the measurement $Zn(ClO_4)_2$- LiCl-1 with $c_{LiCl} = 0$ as the spectrum of the first factor. Otherwise, a spectrum with partially negative intensities was obtained for the first species.

Models with four or more species showed an order of magnitude higher error sum of squares, models with two species had only twice the error sum of squares but were not able to satisfactorily reproduce the spectra of solutions of medium chloride content.

Based on the findings obtained so far also by other measurement methods, it is assumed that the three species found in the Raman measurements are $[Zn(H_2O)_6]^{2+}$, $[ZnCl_2(H_2O)_{2/4}]^0$ and $[ZnCl_4]^{2-}$.

6.3.3 Position and shape of the Raman spectra of $[Zn(H_2O)_6]^{2+}$ and zinc chloro complexes

In Fig. 6.5 the isotropic species spectra determined by factor analysis are shown. In addition to the known spectrum of $[Zn(H_2O)_6]^{2+}$ at 388.5 cm^{-1}, the peak maxima for $[ZnCl_2(H_2O)_2]^0$ at 286 cm^{-1} and of $[ZnCl_4]^{2-}$ at 281 cm^{-1} were found (Tab. 6.1). It cannot be excluded that the maximum of $[ZnCl_4]^{2-}$ is at even lower wavenumbers than calculated with the factor analysis. At least one sample ($Zn(ClO_4)_2$-LiCl-16) showed a maximum at 280.5 cm^{-1}. To clarify this question, additional measurements at even higher Li/Zn ratios would be necessary.

A peak at 295 cm^{-1} could be observed with solution $Zn(ClO_4)_2$- NaCl-1. Apart from this measurement, it was also weakly observed in the solution $Zn(ClO_4)_2$ - NaCl-2. In the following measurements it was completely covered by the strong band at 286 cm^{-1}. It is possible that this is a weak indication of the species $[ZnCl(H_2O)_5]^+$. However, a characterisation and quantification were not possible with the help of the factor analysis. On the other hand, MAEDA et al. (1996) pointed out that the Raman spectra of $[ZnCl]^+$ and $[ZnCl_2]^0$ are indistinguishable. In this case, the reported amount of $[ZnCl_2]^0$ would have to be regarded as a sum that includes $[ZnCl]^+$.

Tab. 6.1 Position of the Raman bands of zinc species in LiCl and NaCl solutions

Species	Maximum $[cm]^{-1}$
$[Zn(H_2O)_6]^{2+}$	388.5
$[ZnCl_2(H_2O)_n]^0$	286
$[ZnCl_4]^{2-}$	281

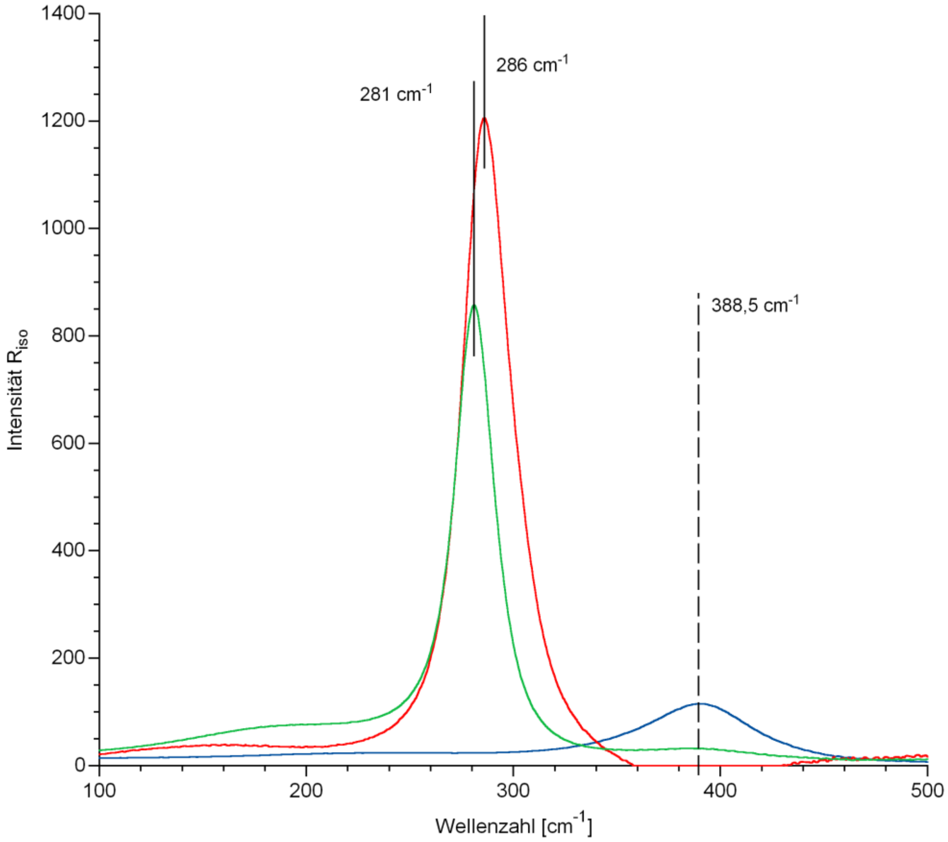

Fig. 6.5 Calculated isotropic Raman spectra of zinc species

6.3.4 Zinc speciation in LiCl and NaCl solutions

On this basis, the concentration distribution was calculated for the individual zinc species (Tab. 13.11, S.479). Fig. 6.6 shows on the right a plot of the zinc speciation versus the total LiCl concentration and the free chloride concentration after taking into account the chloride bound in the zinc chloro complexes. The concentration of $[Zn(H_2O)_6]^{2+}$ decreased continuously and disappeared completely at about 5-6 mol/l LiCl. From about 1 mol/l LiCl concentrations, the neutral $[ZnCl_2(H_2O)_n]^0$ molecule became noticeable, whose share in the total speciation did not exceed 30 %. From about 3 mol/l LiCl, it can be mathematically proven that from 5 mol/l LiCl the species $[ZnCl_4]^{2-}$ predominates and at about 7 mol/l LiCl it is practically exclusively present.

The scatter in the curves is due to the variable $Zn(ClO_4)_2$ concentrations. Therefore, with the same LiCl concentrations, different concentrations of free chloride (Fig. 6.8) and changing zinc speciation are possible. Fig. 6.6 shows on the right the zinc speciation as a function of the calculated free chloride concentration. If the derivations are correct, a dramatic change in speciation occurs between about 1.5 and 2 mol/l free chloride. The zinc present in solution binds most of the added chloride in the form of chloro complexes (even more evident in Fig. 6.8). Only from concentrations of about 5 mol/l LiCl does the free chloride concentration begin to rise again.

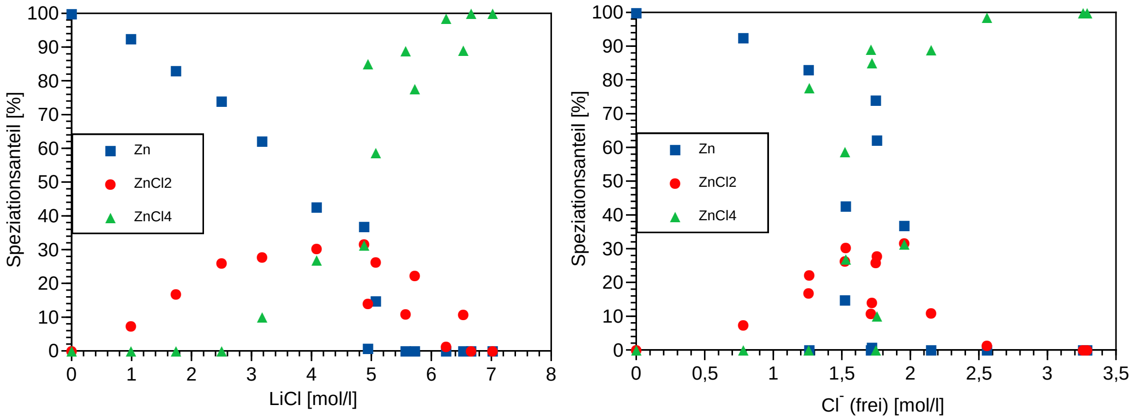

Fig. 6.6 Speciation distribution of zinc in LiCl solutions

If the peak maximum of the spectrum of $[ZnCl_4]^{2-}$ should indeed be shifted further towards 280 cm^{-1} as indicated above, this would lead to a broadening and strengthening of the calculated region of existence of $[ZnCl_2(H_2O)_4]^0$.

The results are largely identical in NaCl solutions (Fig. 6.7). The zinc speciation determined is shown in Tab. 13.12 (p. 479).

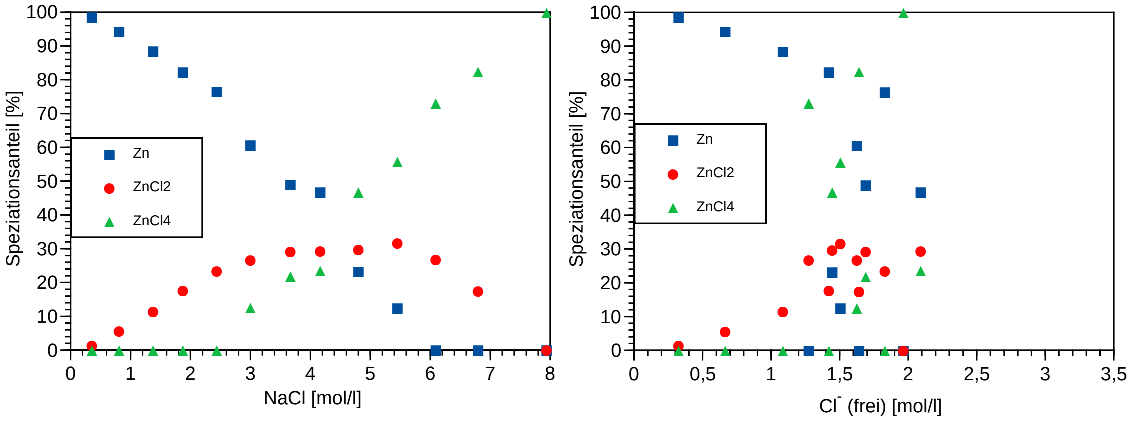

Fig. 6.7 Speciation distribution of zinc in NaCl solutions

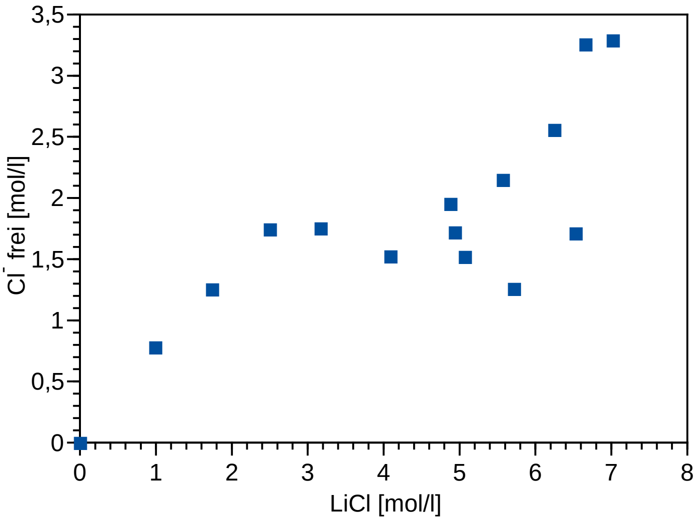

Fig. 6.8 Dependence of the free chloride concentration on the total LiCl content (Zn_{total} = 0.7 - 1.5 mol/l)

6.3.5 Zinc speciation in $CaCl_2$ solutions

The Raman spectra in the most concentrated $CaCl_2$ solutions shifted by about 2 cm^{-1} in the direction of large wavenumbers compared to the measurements in LiCl and NaCl solutions. If one takes the species spectra determined in NaCl and LiCl solutions as a basis, then from a $CaCl_2$ concentration of 3 mol/l onwards, 20% of the zinc seems to be constantly bound in $[ZnCl_2]^0$. This analysis is contradicted by the experience that the degree of complexation basically increases with increasing chloride concentration. Also, in $CaCl_2$ solutions it is to be expected that with increasing chloride concentration the formation of the tetrachloro complex $[ZnCl_4]^{2-}$ is preferred over the dichloro complex $[ZnCl_2]^0$.

It was therefore assumed that a shift of the band occurred in concentrated $CaCl_2$ solutions. The position and shape of the species spectra were redone for $CaCl_2$.

As in the previous evaluation, the spectrum $Zn(ClO_4)_2$- LiCl-1 was set as the spectrum of the ion $[Zn(H_2O)_6]^{2+}$. In addition, the spectrum of the highest concentrated solution Zn - Ca - Cl - 1 was taken as the spectrum of the species $[ZnCl_4]^{2-}$. We consider this assumption to be justified, since the spectra of the three highest concentrated solutions with c_{CaCl2} = 3- 4 mol/l practically did not change any more and can thus be regarded as limit spectra. Under these circumstances we obtained the maxima listed in Tab. 6.2. On this basis, data in Tab. 13.13 (p. 480) and Fig. 6.9 were calculated. Similar to the LiCl and NaCl systems, the concentrations of Zn^{2+} and $[ZnCl_4]^{2-}$ reach parity at about 4 mol/l Cl concentration, but the proportion of neutral $[ZnCl_2]^0$ turns out to be lower (max. 13 %), which qualitatively agrees well with the predictions.

Tab. 6.2 Maxima of the Raman bands of zinc species in $CaCl_2$ solutions

Species	**$CaCl_2$: Maximum $[cm]^{-1}$**	**LiCl, NaCl: maximum $[cm]^{-1}$**
$[Zn(H_2O)_6]^{2+}$	388.5	388.5
$[ZnCl_2(H_2O)_n]^0$	289	286
$[ZnCl(H_2O)_n]_4^{2-}$	282.5	281

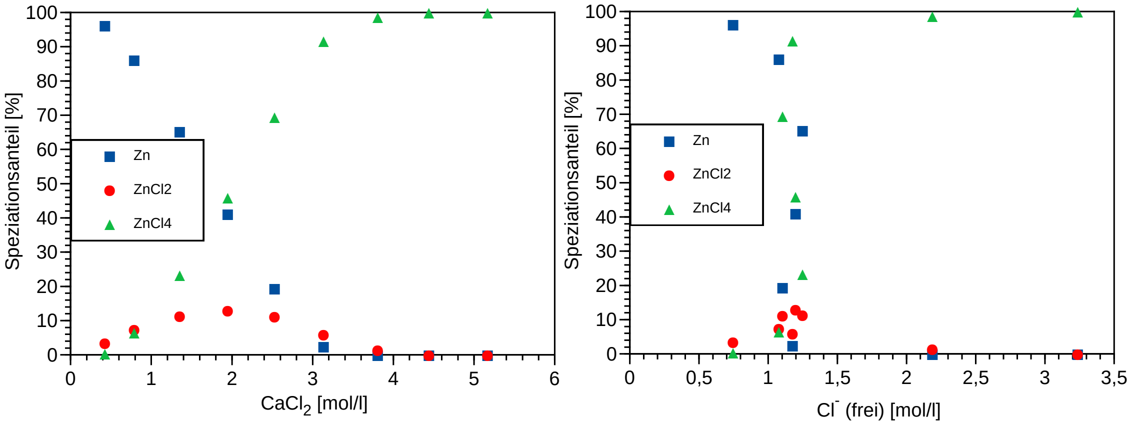

Fig. 6.9 Speciation distribution of zinc in $CaCl_2$ solutions

6.3.6 Zinc speciation in $MgCl_2$ and KCl solutions

As already explained above, the measurements in $MgCl_2$ solutions cannot be evaluated at present. There is a lack of sufficient data for a quantitative correction of the measured spectra with regard to the MgO_6 band. In the KCl solutions, it remains unclear what influence the modified medium (zinc nitrate) had on the position of the Raman bands. Also, the selected KCl concentrations were not high enough to determine the position of a border spectrum in these solutions. Therefore, an evaluation had to be omitted.

7 Thermodynamic model for cadmium in saline solutions

7.1 Development of a parameter set for cadmium under consideration of complex formation

7.1.1 Consideration of complex formation

Previous work has shown that the solubility equilibria of concentrated salt solutions containing cadmium can only be modelled to a limited degree without explicitly taking complex formation into account. FILIPPOV et al. (1987) succeeded in describing the system Cd, Na || Cl, SO_4-H_2O by introducing additional interaction parameters, which in a certain way should also express the complex formation. A corresponding attempt for the analogous system Cd, K || Cl, SO_4-H_2O failed (RUMYANTSEV, personal communication). Similar experiences were made by HERBERT and MÖNIG (1996), who tried, for the first time, to develop a parameter set for cadmium in solutions of the oceanic system. However, the lack of suitable data in many subsystems was also an obstacle. The data gaps they identified could be closed by using solubility measurements and isopiestic investigations in this study. Cadmium also forms complexes with sulphate. However, earlier work showed that an explicit consideration of the sulphate complexes is not necessary in the modelling (HERBERT and MÖNIG, 1996).

7.1.2 Parameter set explicitly considering chloro-complexes

The Raman measurements carried out in this project allowed for the first time a spectroscopically justifiable quantification of the chloro complex formation of the cadmium. On the basis of the Tab. 13.14 for the system $Cd(ClO_4)_2$-NaCl-H_2O as well as further potentiometric and isopiestic data for the systems $CdCl_2$ and $CdCl_2$-NaCl-H_2O, a parameter set for cadmium and its chloro complexes in NaCl solutions was developed with the aid of the program Wotan (HAGEMANN, 1999).

The following assumptions were made:

- Up to a total Cd concentration of 2 mol/kg, the interaction between different Cd species is negligible. Of the studies listed in Tab. 7.1 only measurement data with less than 2 mol/kg cadmium were considered.

- In dilute solutions, $CdCl_2$ behaves like $SrCl_2$. The interaction coefficients were therefore taken from $SrCl_2$ (KIM and FREDERICK, 1988).

Tab. 7.1 Measurement data considered for the determination of ion interaction parameters

System	**Data type**	**Source**
$CdCl_2$-H_2O	potentiometric	REILLY and STOKES (1970)
$CdCl_2$-H_2O	isopiestic	ROBINSON (1940)
$CdCl_2$-H_2O	isopiestic	PAN and NI (1968)
$CdCl_2$-H_2O	potentiometric	QUINTIN (1936)
$CdCl_2$-H_2O	potentiometric	GETMAN (1928)
$CdCl_2$-H_2O	potentiometric	GETMAN (1931)
$CdCl_2$-NaCl-H_2O	Solubility/isopiestic	LILIČ and MOGILEV (1967)
$CdCl_2$-NaCl-H_2O	isopiestic	FILIPPOV and VIVČARIK (1978)
$CdCl_2$-H_2O	potentiometric	HORSCH (1919)
$CdCl_2$-H_2O	potentiometric	VISIĆ and MEKJAVIĆ (1989)
$CdCl_2$-H_2O	potentiometric	TREUMANN and FERRIS (1958)
$CdCl_2$-H_2O	potentiometric	HEFLEY and AMIS (1965a.1965b)
$CdCl_2$-H_2O	isopiestic	RARD and MILLER (1985)
$CdCl_2$-NaCl-H_2O	Solubility	BASSET et al. (1939)
$CdCl_2$-NaCl-H_2O	Solubility/isopiestic	FILLIPPOV et al. (1991)
$CdCl_2$-H_2O	isopiestic	FILIPPOV et al. (1975)

The model developed in this way is able to reproduce the speciation of cadmium in concentrated NaCl and LiCl solutions very well (Fig. 7.1 f.). Unfortunately, no agreement could be found for the activity coefficients in dilute $CdCl_2$ solutions (Fig. 7.3). Here, modelling without complexes delivers better results. The calculated mean activity coefficients for $CdCl_2$ remained too high down to concentrations of 0.0001 mol/kg. At these concentrations, element-specific differences no longer have an effect. $SrCl_2$, $MgCl_2$, and $FeCl_2$ solutions all show the same activity coefficients. The large number of matching experimental data makes measurement errors completely improbable. There is a systematic deviation that can only be explained by a significantly earlier onset of complex formation.

From the difference between the calculated and the measured activity coefficients, the proportion of complexed cadmium can be derived. The results are shown in Fig. 7.4 shown. As can be seen, complex formation starts very early. Already at 0.1 mol/kg $CdCl_2$ more than 50% of the cadmium is bound in the form of chloro complexes. From the data, a complex formation constant β_1 ($[CdCl]^+$) of about 100 can be derived. This agrees very well with literature data (Tab. 7.4 mean value around 91). Unfortunately, these findings cannot be matched with the conclusions from Raman spectroscopy. A complex $[CdCl]^+$ could not be detected and accordingly does not occur in the derived speciation model. Cd^{2+} is the predominant species up to a chloride concentration around 1 mol/kg.

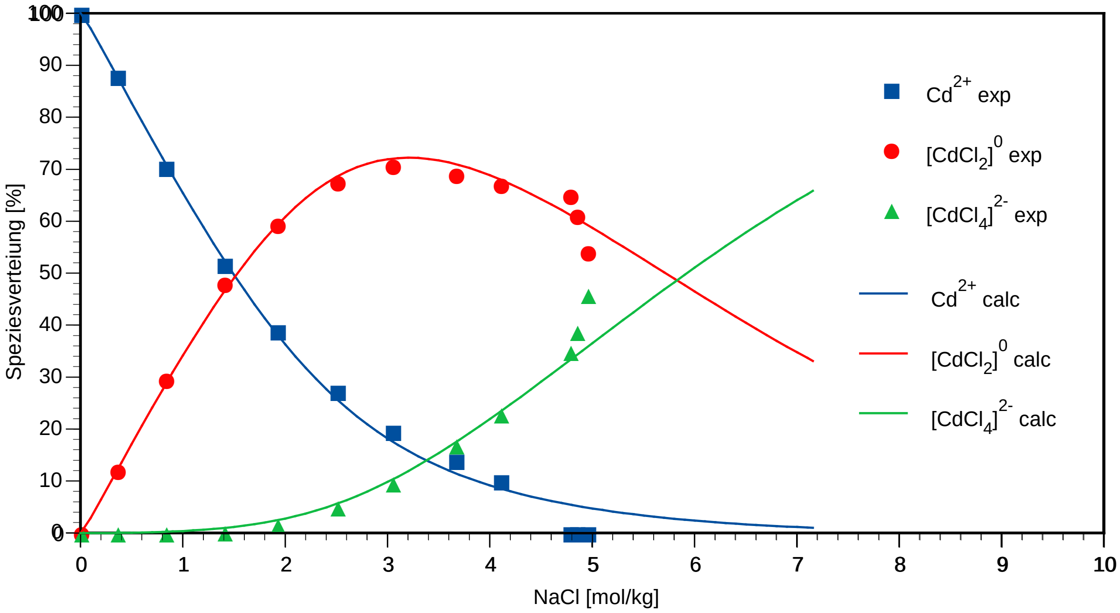

Fig. 7.1 Experimentally determined (Raman) and calculated chloro complex formation in the system $Cd(ClO_4)_2$-NaCl-H_2O at 25°C (c[$Cd(ClO_4)_2$] = 1.2 mol/kg)

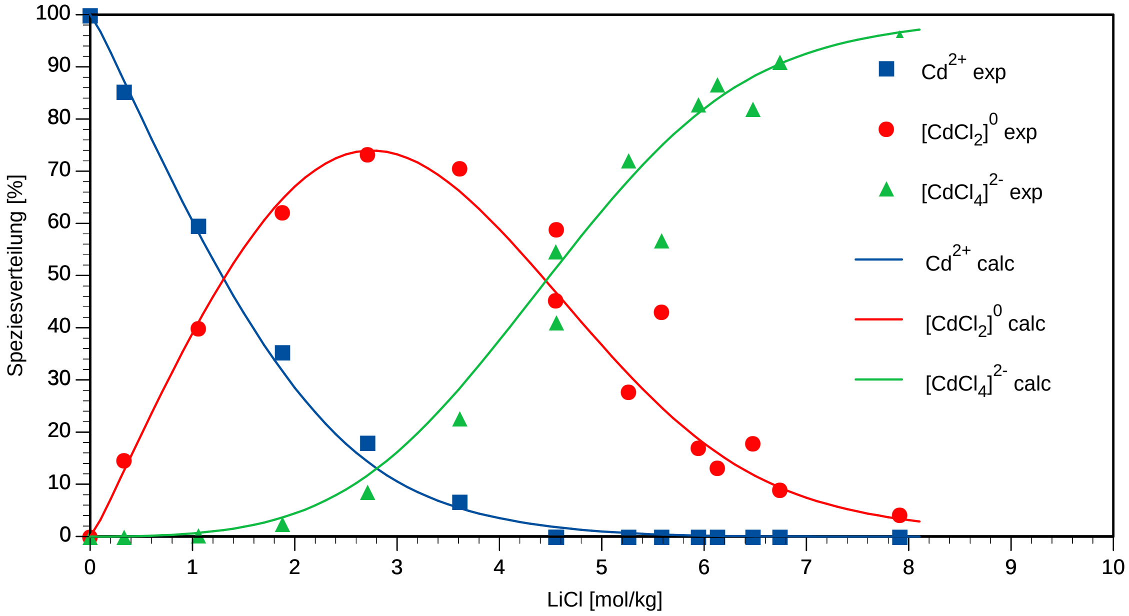

Fig. 7.2 Experimental (Raman) and calculated species distribution in the system $Cd(ClO_4)_2$-LiCl-H_2O at 25°C

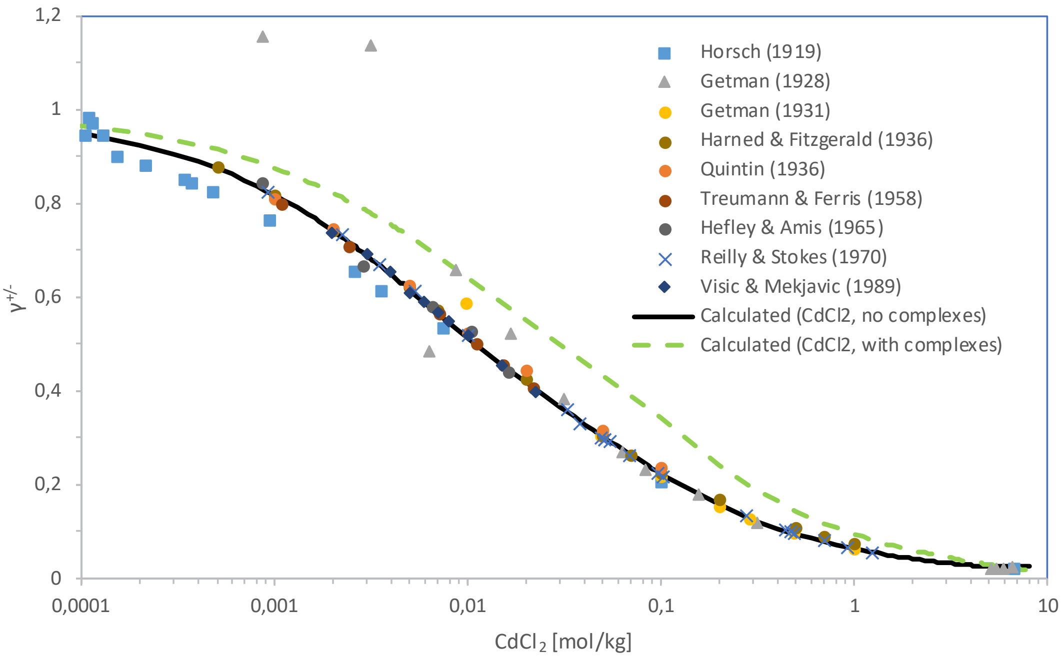

Fig. 7.3 Experimental and calculated activity coefficients in the system $CdCl_2$ - H_2O

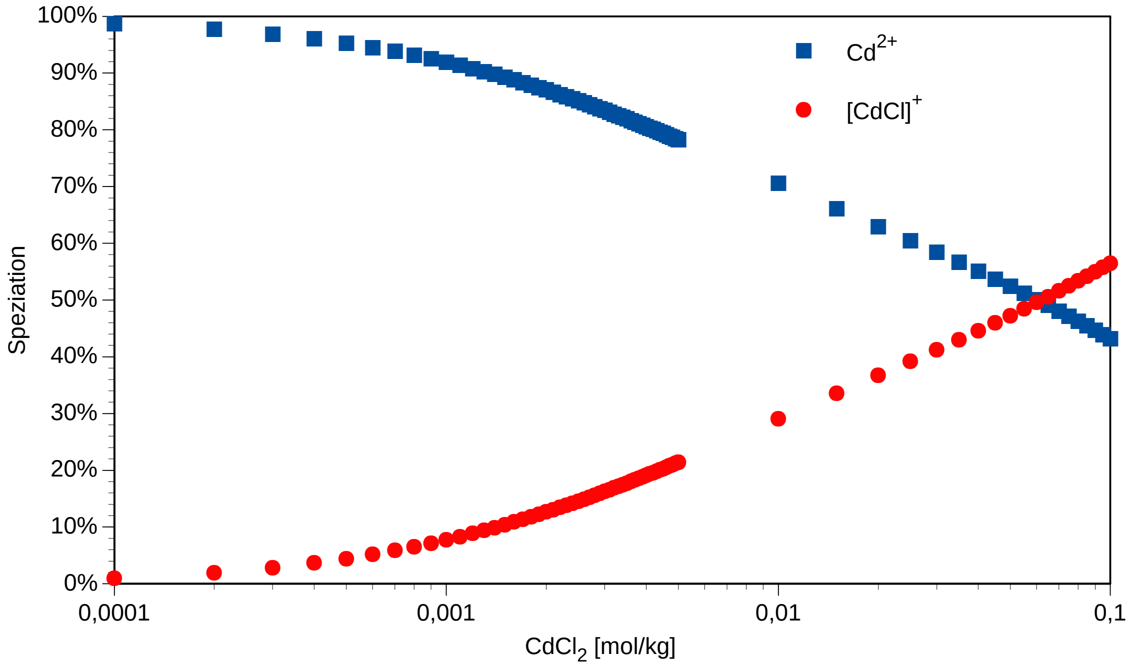

Fig. 7.4 Derived speciation for small $CdCl_2$ concentrations

How can the different results be interpreted? The factor analysis of the Raman spectroscopy did not reveal any indications of the species $[CdCl]^+$. It is conceivable that the two species $[Cd(H_2O)_6]^{2+}$ and $[CdCl(H_2O)_5]^+$ have very similar Raman spectra and are therefore indistinguishable. Possibly, additional measurements with solutions of small chloride concentrations (0.001 to 0.1 mol/l) could provide interesting information. However, at this stage it is not possible to develop a parameter set with explicit inclusion of the cadmium chloro complexes.

7.2 Development of a parameter set for cadmium without consideration of complex formation

As a pragmatic way out of this situation, a parameter set was developed that shows good performance at least for the cadmium concentrations relevant for environmental problems. It cannot be, however, applied to in mixed salt solutions with $CdCl_2$ concentrations above 2 mol/kg. The derivation of the parameters is described in the following sections. The derived parameters are shown in Tab. 7.14 and Tab. 7.15. Because of the importance of potentiometric investigations, a critical evaluation of the available data on the standard electrode potential of cadmium amalgam and important reference electrodes is given first.

7.3 Necessary electrode potentials for the evaluation of potentiometric investigations

7.3.1 The chloride electrodes Hg|Hg_2Cl_2|Hg_2^{2+} and AgCl|Ag

The standard potential of the calomel electrode Hg_2^{2+} | Hg_2Cl_2 | Hg was investigated in detail by GRZYBOWSKI (1958) and determined[8] to be 0.26813 V. For the potential of the silver-silver chloride electrode, BATES and BOWER (1954), BATES et al. (1956) and HETZER et al. (1964) found 0.22234 V. The reproducibility of the electrode potential cannot be reduced to less than ± 0.2 mV even after the most careful preparation (BATES and MACASKILL 1978). Therefore, it is still recommended to normalise the electrode using an assumed activity coefficient of 0.904 for 0.01 m HCl (BATES et al. 1956).

7.3.2 The sulphate electrodes Hg_2^{2+} | Hg_2SO_4 | Hg and Pb^{2+} | $PbSO_4$ | Pb(Hg, 2 phases)

Until today, considerable uncertainties exist about the standard electrode potential of the mercury(I) sulphate electrode Hg_2^{2+} | Hg_2SO_4 | Hg. ALBRIGHT et al. (2000) pointed out that the more recent measurements, estimates and derivations concentrate on values around 0.61224 to 0.61257 V (esp. RONDININI ET AL., 1988; MUSSINI ET AL., 1989; CLEGG ET AL., 1994; RARD and CLEGG, 1995, but also COVINGTON et al, 1965). HAMER and WU (1995) emphasised with their investigations that the electrode potential should be several mV higher. In broad agreement with the early work of HARNED and HAMER (1935), they suggest the value 0.61544 V. ALBRIGHT et al. (2000) themselves derived an intermediate value of 0.61360 V. The question cannot be answered conclusively. In this paper, the electrode potential is set at 0.61257 V according to the latest experimental investigations (RONDININI et al., 1988; MUSSINI ET AL., 1989) and in agreement with COVINGTON et al. (1965).

The lead sulphate-lead amalgam electrode Pb^{2+} | $PbSO_4$ | Pb (Hg, 2 phases) was characterised by FUSI and MUSSINI (1997). As a result of extensive data comparison and their own experiments, they determined -0.35272 V as the standard potential. For the electrode Pb^{2+} | Pb they obtained -0.35857 ± 0.0006 V.

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[8] According to READ (1960), MARCUS (1980) recommended the very close value 0.26828 ± 0, 0002V. The small difference has no significant influence on the evaluations made here.

Tab. 7.2 Standard electrode potentials of important electrodes and electrodes chains

Type	Value [V]	Source
Zn(Hg 2 phases) | $ZnCl_2$(m) | AgCl | Ag	0.98428 ± 0.00015	LUTFULLAH et al. (1976), confirmed by RARD and MILLER (1989)
Cl^- | AgCl | Ag	0.22234	BATES and BOWER (1954)
Cl^- | Hg_2Cl_2 | Hg	0.26813	GRZYBOWSKI (1958)
SO_4^{2-} | Hg_2SO_4 | Hg	0.61257	RONDININI et al. (1988)
SO_4^{2-} | $PbSO_4$ | Pb(Hg, 2 phases)	-0.35272 ± 0.00002	FUSI and MUSSINI (1997)
SO_4^{2-} | Pb	-0.35857 ± 0.00060	FUSI and MUSSINI (1997)
Zn | Zn(Hg, 2 phases)	0.0006	COHEN (1900)
Zn(Hg,sat) | Zn^{2+}	0.76194	derived
Zn | Zn^{2+}	0.76251	derived
Zn(Hg.2 phases) | $ZnCl_2$(m) | Hg_2Cl_2 | Hg	1.03007	derived
Zn | $ZnCl_2$(m) | Hg_2Cl_2 | Hg	1.03064	derived

7.3.3 The cadmium amalgam electrode

For the evaluation of the potentiometric measurements, a uniform value for the standard electrode potential of the most frequently used electrode Cd(Hg,Cd-saturated) | $CdCl_2$(m) | AgCl | Ag is required. The determined values are summarised in Tab. 7.4. HARNED and FITZGERALD (1936) already pointed out that complex formation ($CdCl^+$) is to be expected already at small cadmium chloride concentrations. The value of QUINTIN (1936) does not contain a corresponding consideration and is therefore excluded. The results of HEFLEY and AMIS (1965a, 1965b) stand out both because of their great uncertainty and because of the very strongly deviating complex formation constant determined by them (Tab. 7.4). 0.5738 ± 0.0006 V is obtained as the mean value. If 0.22234 V is assumed as the potential of the AgCl | Ag electrode (HETZER et al. 1964, BATES and BOWER 1954, BATES et al. 1956), the half-cell potential of Cd(Hg,sat) |Cd^{2+} would be 0.3514V. LONGHI et al. (1979) pointed out that strictly speaking this is not a standard electrode potential, but only a reference potential of the cadmium-saturated amalgam electrodes. The standard electrode potential would refer to an amalgam electrode with $x_{Cd} \rightarrow 0$. This nomenclatural discussion is irrelevant for the evaluation.

The data of LUCASSE (1929) and FEAKINS et al. (1973) cannot be evaluated because no information is available on the type of Cd amalgam used. HARNED and FITZGERALD (1936) only had smoothed data printed in their publication, the measured data are not available. GÓMEZ HERRERA et al. (1944) only gave molarities for the solutions they investigated, the conversion of which into molarities would lead to additional uncertainties. The most recently published measurement data by STOKES (1990) refer to a measuring cell with a concentration of 1.000 mol/kg $CdCl_2$, whose cell voltage is not specified. The evaluation requires the reference to an activity coefficient of cadmium chloride calculated for these concentrations, which can be taken from other compilations. We refrain from including these data.

GETMAN (1928.1931a) worked with the cells Cd(Hg,Cd-10%) |$CdCl_2$(m) |Hg_2Cl_2|Hg and Cd|$CdCl_2$(m) |Hg_2Cl_2|Hg. His measured values are always given for the latter cell type. For the electrode potential of the half-cell Cl^-|Hg_2Cl_2|Hg, 0.26813 V is assumed (GRZYBOWSKI 1958), and 0.04742 V for the half-cell Cd|Cd(Hg,Cd-10%) (GETMAN, 1928). Consequently, the measuring cell Cd|$CdCl_2$(m) |Hg_2Cl_2|Hg would have a standard cell voltage of 0.6670 V.

HORSCH (1919) used an amalgam electrode containing only 4.6 wt.-% cadmium. By comparative measurements, GETMAN (1931) determined the potential of the half-cell Cd(Hg, 4.6 wt.-%)|Cd to be 0.0534 V, so that 0.5678 V follows as the standard electrode potential. The measured values obtained by Horsch at very low concentrations are somewhat doubtful since the solubility of the silver chloride ($K_{sp} = 1.77 \cdot 10^{-10}$) begins to have an effect.

The measured values of HARNED and FITZGERALD (1936) above 0.1 mol/kg appear too high in comparison with isopiestically obtained data (ROBINSON 1940; STOKES 1990) and are rejected.

Tab. 7.3 Potentiometric measurements on cadmium chloride solutions

Cadmium electrode	**Counter electrode**	**Source**
Cd amalgam (4.6%)	AgCl|Ag	Horsch (1919)
Cd amalgam (10%)	HgCl|Hg_2	Getman (1928)
Cd amalgam (%?)	AgCl|Ag	Lucasse (1929)
Cd metal	HgCl|Hg_2	Getman (1931)
Cd amalgam (sat)	AgCl|Ag	Quintin (1936)
Cd amalgam (sat)	AgCl|Ag	Harned and Fitzgerald (1936)
Cd amalgam (10%)	HgCl|Hg_2	Ishikawa and Takai (1937)
Cd amalgam (sat)	AgCl|Ag	Treumann and Ferris (1957)
Cd amalgam (sat)	AgCl|Ag	Hefley and Amis (1965a, 1965b)
Cd amalgam (sat)	AgCl|Ag	Reilly and Stokes (1970)
Cd amalgam (%?)	AgCl|Ag	Feakins et al. (1973)
Cd amalgam (sat)	AgCl|Ag	Višić and Mekjavić (1989)
Cd amalgam (sat)	AgCl|Ag	Stokes (1990)

Tab. 7.4 Standard electrode potential of the electrode Cd(Hg, 11wt . -% Cd = sat = 2-phase) |$CdCl_2$(m) |AgCl|Ag

Value [V]	**Complex formation constant β_1 used ($CdCl^+$)**	**Source**
0.5776	-	Quintin (1936)
0.573	91	Harned and Fitzgerald (1936)*
0.5745 ± 0.0002	90 ± 4	Treumann and Ferris (1957)*
0.57162 ± 0.0013	14	Hefley and Amis (1965a)
0.5739	85 ± 1	Reilly and Stokes (1970)*
0.57368	100	Višic and Mekjavić (1989)*
0.5738 ± 0.0006	**91 ± 6**	**Mean value (from *)**

Tab. 7.5 Standard potentials of important electrodes and electrodes containing cadmium

Type	**Value [V]**	**Source**
Cd(Hg, 11 Gew.-% Cd = sat = 2 phases) | $CdCl_2$(m) | AgCl | Ag	0.5738 ± 0.0006	This work
Cd | Cd(Hg, Cd-10%)	0.04742	GETMAN (1928)
Cd | Cd(Hg, Cd-4.5%)	0.0534	GETMAN (1931)
Cd(Hg,sat) | Cd^{2+}:	0.35146	derived
Cd(Hg,Cd-10%) | $CdCl_2$(m) | Hg_2Cl_2 | Hg	0.61959	derived
Cd(Hg,Cd-4.5%) | $CdCl_2$(m) | AgCl | Ag	0.5678	derived
Cd | $CdCl_2$(m) | Hg_2Cl_2 | Hg	0.66701	derived
Cd | Cd^{2+}	0.3989	derived
Cd(Hg, sat) | Cd^{2+},SO_4^{2-} | $PbSO_4$ | Pb(Hg, sat)	-0.0013	derived

7.4 The binary system $CdCl_2$-H_2O

7.4.1 Vapour pressure measurements

Direct vapour pressure measurements (ISHIKAWA and TAKAI, 1937; LILIČ and MOGILEV, 1967) as well as isopiestic measurements are available for the system (ROBINSON, 1940; FILIPPOV and VIVČARIK, 1978; PAN and NI, 1968; ŠUL'C et al., 1971; RARD and MILLER, 1985; FILIPPOV et al., 1991, own measurements cf. Tab. 2.27). The vapour pressure measurements of ISHIKAWA and TAKAI (1937) deviate strongly from the results of the other authors and were not included in the parameter evaluation. The vapour pressure of the saturated solution was published by ISHIKAWA et al. (1932), but without indication of the corresponding concentration. The values of ŠUL'C et al. (1971) were available to us too late and were also not included.

Tab. 7.6 Previous isopiestic measurements on $CdCl_2$ solutions at 25.0 °C

Earlier work	Number of Measuring points	Concentration range [mol/kg]
ISHIKAWA and TAKAI (1937)*	8	0.89 - 6.40
ROBINSON (1940)	39	0.11 - 5.33
LILIČ and MOGILEV (1967)	9	0.37 - 5.48
PAN and NI (1968)	19	0.18 - 5.88
FILIPPOV and VIVČARIK (1978)	11	0.19 - 6.46
RARD and MILLER (1985)	29	1.23 - 5.09
FILIPPOV et al. (1991)	6	1.95 - 6.44
This work	12	1.03 - 6.71

* direct vapour pressure measurements

7.4.2 Potentiometric measurements

A large number of potentiometric measurements are available (Tab. 7.3). Other potentiometric measurements were based on electrode combinations with unknown transition potential (BRESTER 1927; HASS and JELINEK 1932; RILEY and GALLAFENT 1932; NÁRAY-SZABÓ and SZABÓ 1935). They were not taken into account.

On this data basis, the ion interaction coefficients for cadmium chloride were determined (Tab. 7.7). It proved to be advantageous to carry out the calculation in two steps. Based on the isopiestic data available mainly for medium and high concentrations, first $\beta^{(0)}$, $\beta^{(1)}$, and C^{γ} were determined. The potentiometric data were then used for the calculation of $\beta^{(2)}$. By including $\beta^{(2)}$, the early complex formation with chloride is implicitly taken into account. The agreement of the calculated data with the measured values is good to very good up to a concentration of about 2 mol/kg $CdCl_2$, after which significant deviations become noticeable, especially with the more numerous osmotic data (Fig. 7.5, Fig. 7.6).

Tab. 7.7 Binary ion interaction coefficients for cadmium chloride

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	C^{γ}
Cd^{2+} - Cl^-	-0.04008	2.5	-3.1761	12	-44.9301	0.00188

7.4.3 Solubility of $2CdCl_2 \cdot 5H_2O$

At 25 °C, a saturated cadmium chloride solution forms the solid phase $2CdCl_2 \cdot 5H_2O$ = $CdCl_2 \cdot {}^5/_2 H_2O$. It occurs in two modifications, an easily soluble, acicular one, and a less soluble, rhombohedral one. For the solubility of $2CdCl_2$-$5H_2O$, BASSETT et al. (1939), FILIPPOV and VIVČARIK (1978), FILIPPOV et al. (1991) consistently gave 6.57 mol/kg. The solubility constant calculated for this phase at 25 °C is

$$\log K = -4.05$$

This value should be considered approximate as the model was only intended for solutions with a maximum $CdCl_2$ concentration of 2 mol/kg.

At 34 °C, $CdCl_2 \cdot {}^5/_2 H_2O$ changes into the monohydrate $CdCl_2 \cdot H_2O$ (DIETZ, 1899). It can exist as a metastable phase at lower temperatures. From the author's investigations over a wide temperature range, the solubility of the monohydrate at 25 °C can be interpolated. It is about 57.48 wt.-% or 7.373 mol/kg.

BASSETT et al. (1939), on the other hand, found 7.56 mol/kg. Since it cannot be decided which value is to be regarded as more reliable, we initially assume an average value of 7.47 mol/kg. The solubility constant calculated for this phase is at 25 °C:

$$\log K = -1.736$$

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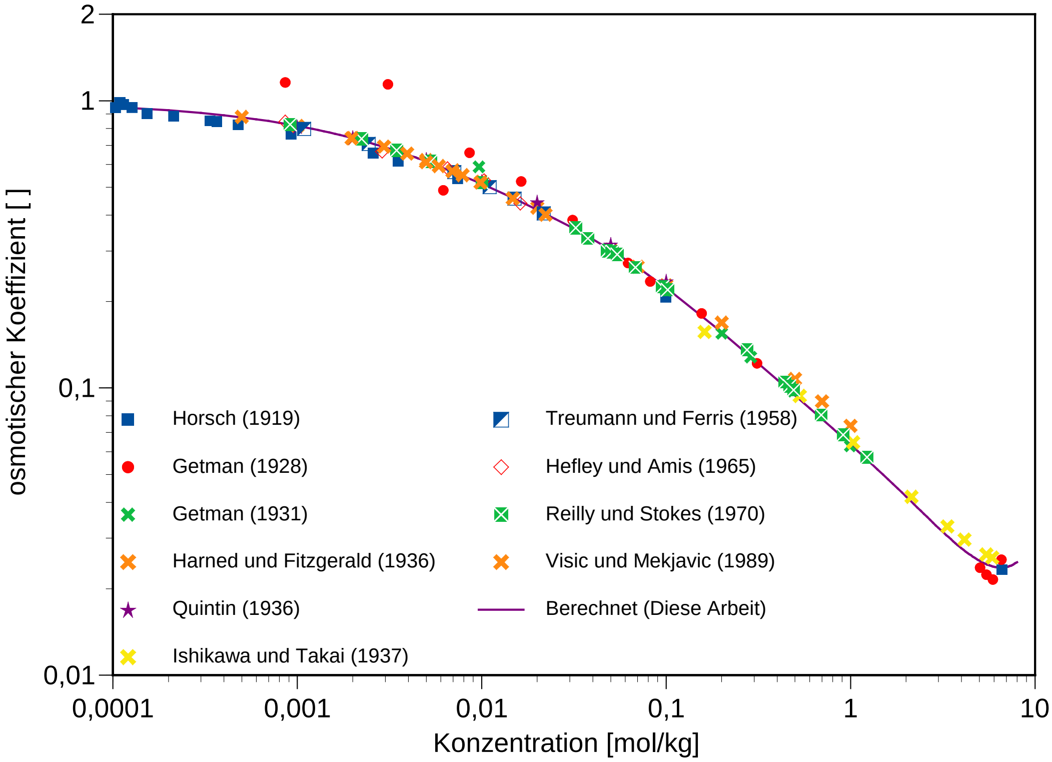

Fig. 7.5 Potentiometrically determined activity coefficients in the system $CdCl_2$ - H_2O

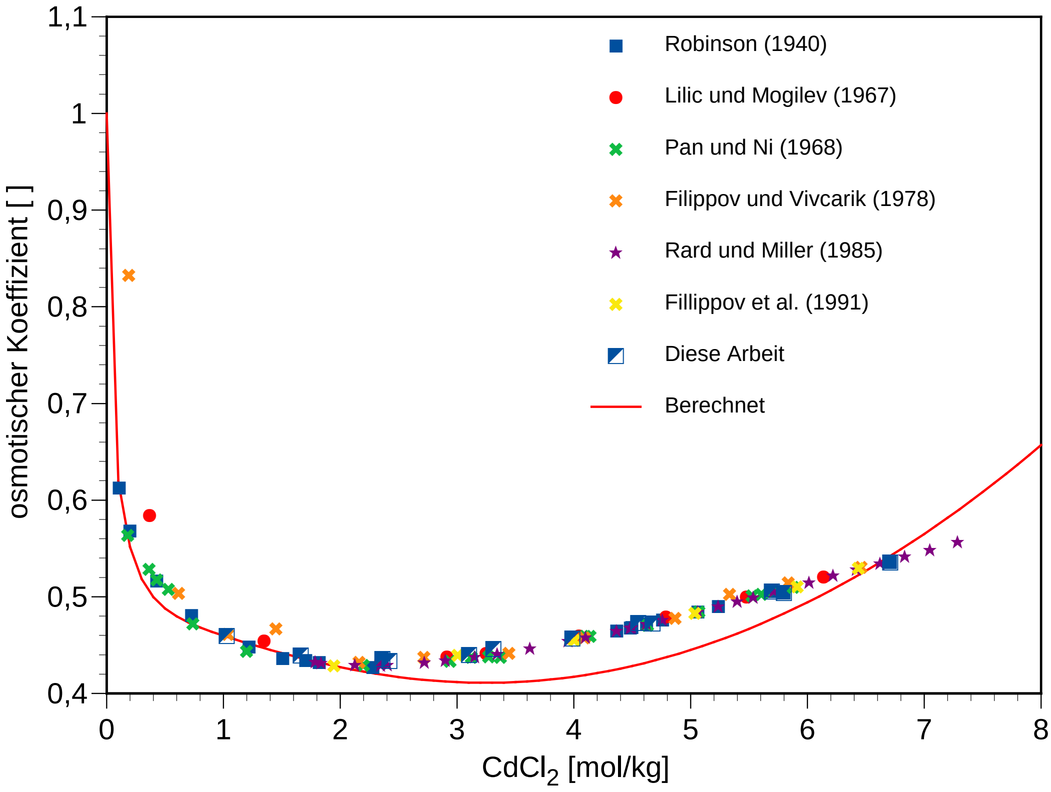

Fig. 7.6 Isopiestically determined osmotic coefficients in the system $CdCl_2$ - H_2O

7.5 The binary system $CdSO_4$-H_2O

7.5.1 Vapour pressure measurements

Isopiestic measurements of the vapour pressure of cadmium sulphate solutions at 25 °C are available from several authors. (Tab. 7.8). In connection with the investigation of ternary systems (see below), some further points were added in this study (Tab. 2.28).

Tab. 7.8 Previous isopiestic measurements on $CdSO_4$ solutions at 25.0 °C

Earlier work	Number of measuring points	Concentration range [mol/kg]
DIESNIS (1935)	1	saturated
ROBINSON and JONES (1936)	62	0.1 - 3.6 (approx.)
FILIPPOV et al. (1973)	9	0.37 - 5.48
FILIPPOV et al. (1985)	19	0.18 - 5.88
MAJIMA et al. (1988)	8	0.20 - 2.70
This work	20	1.39 - 4.82

ROBINSON and JONES (1936) carried out measurements with a total of 62 solutions in the range of about 0.1 to 3.6 mol/kg. Unfortunately, they did not publish the isopiestic concentrations, but only interpolated values at smooth concentrations. Nevertheless, we have taken them into account, because on the one hand they agree very well with the results of FILIPPOV et al. (1985) and the measurements in the present study, and on the other hand they also cover the concentration range from 0.1 to 2 mol/kg $CdSO_4$, for which few other data are available. A comparison of the different series of measurements shows that the data of FILIPPOV et al. (1973) deviate significantly from the other works. They are therefore not taken into account in the parameter evaluation. The evaluation of the vapour pressure measurements of CARPENTER and JETTE (1923) as well as DIESNIS (1935) of saturated cadmium sulphate solutions had to be omitted due to the missing concentration data. The measurement data of MAJIMA et al. (1988) are only available in a Japanese publication, which we were only able to obtain after the parameters had been determined.

7.5.2 Potentiometric measurements

Potentiometric measurements were conducted by GETMAN (1928) and LA MER and PARKS (1931) (Tab. 7.9). Measurements with unknown transition potentials were not considered further in the evaluation (BRESTER 1927; HASS and JELINEK 1932; WOLTEN and KING 1949; MALATESTA et al., 1999). Also not evaluated were the measurements of GÓMEZ HERRERA et al. (1944), who only gave molarities for their solutions.

Tab. 7.9 Potentiometric measurements on cadmium sulphate solutions

Cadmium electrode	Counter electrode	Source
Cd amalgam (10%)	Hg_2SO_4|Hg	GETMAN (1928)
Cd amalgam (sat)	$PbSO_4$|Pb (Hg,sat)	LA MER and PARKS (1931,1933)

The standard electrode potential of the electrode $Cd(Hg, sat)\,|\,Cd^{2+},SO_4^{2-}\,|\,PbSO_4\,|\,Pb(Hg, sat)$ used by LA MER and PARKS (1931) can be calculated from the potential of the half-cells $Cd(Hg, sat)\,|Cd^{2+}$ (0.3514 V) and $SO_4^{2-}\,|\,PbSO_4\,|\,Pb(Hg, sat)$ (-0.35272 ± 0.00002 V, FUSI and MUSSINI, 1997; MUSSINI and MUSSINI, 2002):

$$E_0[Cd(Hg, sat)\,|\,Cd^{2+},SO_4^{2-}\,|\,PbSO_4\,|\,Pb(Hg, sat)] = -0.0013V\,.$$

On this data basis, the ion interaction parameters listed in Tab. 7.10 were determined on this data basis.

Tab. 7.10 Binary ion interaction coefficients for cadmium sulphate

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	C^{γ}
Cd^{2+} - SO_4^{2-}	0.22487	1.4	2.3385	12	-59.824	0.001302

The agreement between measured data and calculated values is very good in all concentration ranges (Fig. 7.7, Fig. 7.8). Only at the highest concentrations above 3 mol/kg smaller deviations in the osmotic coefficient become noticeable.

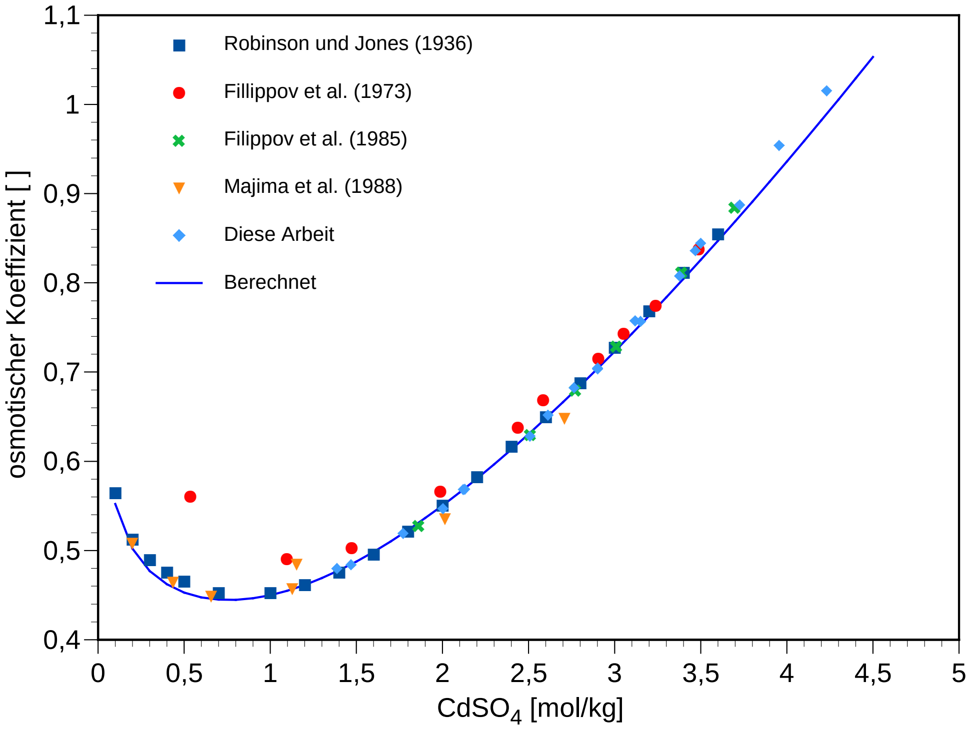

Fig. 7.7 Experimental and calculated osmotic coefficients of cadmium sulphate solutions

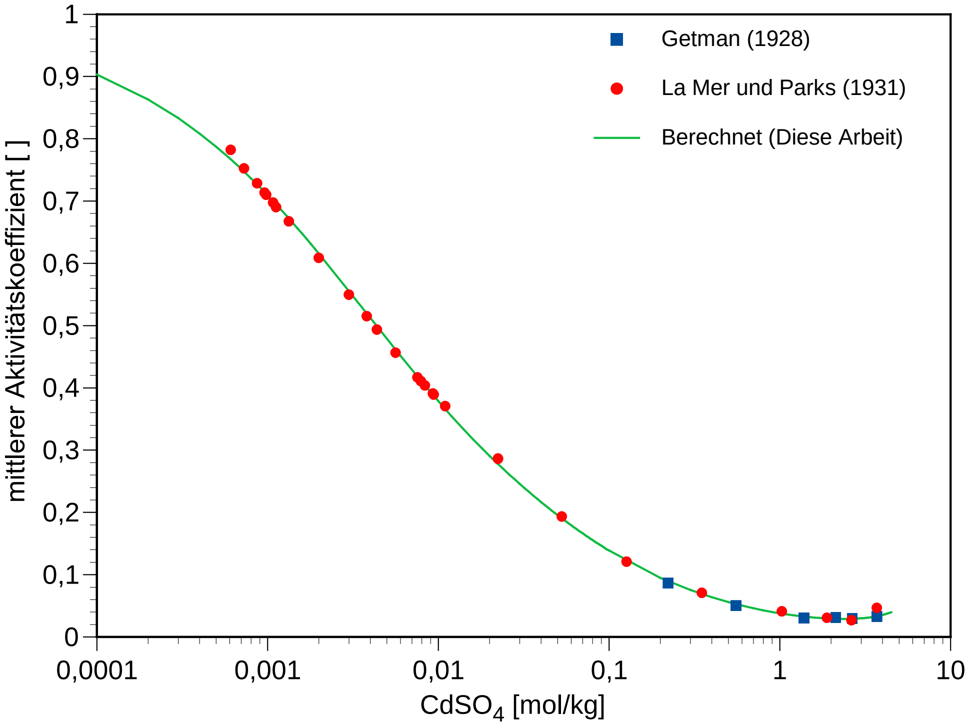

Fig. 7.8 Experimental and calculated mean activity coefficients of cadmium sulphate solutions

7.5.3 Saturated cadmium sulphate solution

At 25 °C a saturated cadmium sulphate solution is in equilibrium with the phase $CdSO_4 \cdot 8/3H_2O$. Its concentration, based on several measurements (Tab. 7.11) is 3.70 ± 0.01 mol/kg. Using the interaction parameters from above, this corresponds to a solubility constant of

$$\log K(3CdSO_4 \cdot 8H_2O) = -5.858$$

Based on the precise measurements of VINAL and BRICKWEDDE (1941), the transition temperature to the monohydrate $\alpha\text{-}CdSO_4 \cdot H_2O$ can be located at 43.4 °C. A slightly different temperature (41.5 °C) was found by BENRATH and THÖNNESSEN, 1932. At 74.5 °C the phase changes to $\beta\text{-}CdSO_4 \cdot H_2O$. Solubility data for 25 °C are not available.

Tab. 7.11 Solubility of $3CdSO_4 \cdot 8H_2O$ at 25.0 °C

Solubility [mol/kg]	Source
3.698	GETMAN (1928)
3.698	LA MER and PARKS (1931)
3.728	BENRATH and THÖNNESSEN (1932)
3.667	VINAL and BRICKWEDDE (1941)
3.690	KARNAUKHOV et al. (1974)
3.708	BALAREV and DOBREVA (1979)
3.702	FILIPPOV et al. (1985)
3.70 ± 0.01	**Mean value**

7.6 The binary system $Cd(ClO_4)_2$-H_2O

The ion interaction coefficients previously published for $Cd(ClO_4)_2$ and $Zn(ClO_4)_2$ (KIM and FREDERICK, 1988) were based on smoothed data in GOLDBERG (1981). We have instead used the original data of PAN and NI (1968), who performed isopiestic experiments in the range 0.13 to 1.9 mol/kg $Cd(ClO_4)_2$. Their parallelly published data on $CdCl_2$ agrees well with the other literature data. Similar experiments were carried out by KÁLMÁN et al. (1970). However, they only published interpolated data converted into activity coefficients, which cannot be assessed without further information.

The water activities of the KCl reference solutions used, given by PAN and NI (1968), were converted with the regression function of ARCHER (1999). It was intended to generate artificial data for the lower concentration range via correlations, similar to $NaClO_4$ or $LiClO_4$. However, it turned out that meaningful correlations could be obtained neither with NaCl nor with equally concentrated $MgCl_2$ solutions. Quotients of the osmotic coefficients ϕ of $Cd(ClO_4)_2$ and NaCl/$MgCl_2$

$$\frac{\varphi_{\mathrm{NaCl}}}{\varphi_{\mathrm{Cd(ClO_4)_2}}} \text{ and } \frac{\varphi_{\mathrm{MgCl_2}}}{\varphi_{\mathrm{Cd(ClO_4)_2}}} \qquad (7.1)$$

did not approach the value of one at cadmium perchlorate concentrations close to zero but deviated from it by 0.02 to 0.04 units. It may be concluded that unrecognised errors have occurred in the determination of the stock solution concentrations. It would therefore make sense to check the measurements of PAN and NI by our own experiments. However, this must be reserved for a future project. Because of the recognised uncertainties, we have refrained from supplementing the measurement data in the lower concentration range. The ion interaction parameters (Tab. 7.14, S.183) allow a very good description of the measured data (Fig. 7.9).

7.6.1 Saturated cadmium perchlorate solution

According to KÁLMÁN et al. (1970), the solubility of $Cd(ClO_4)_2$ is 4.666 mol/kg. However, the isopiestic data points did not come close to this concentration, so that a determination of the solubility constant was omitted.

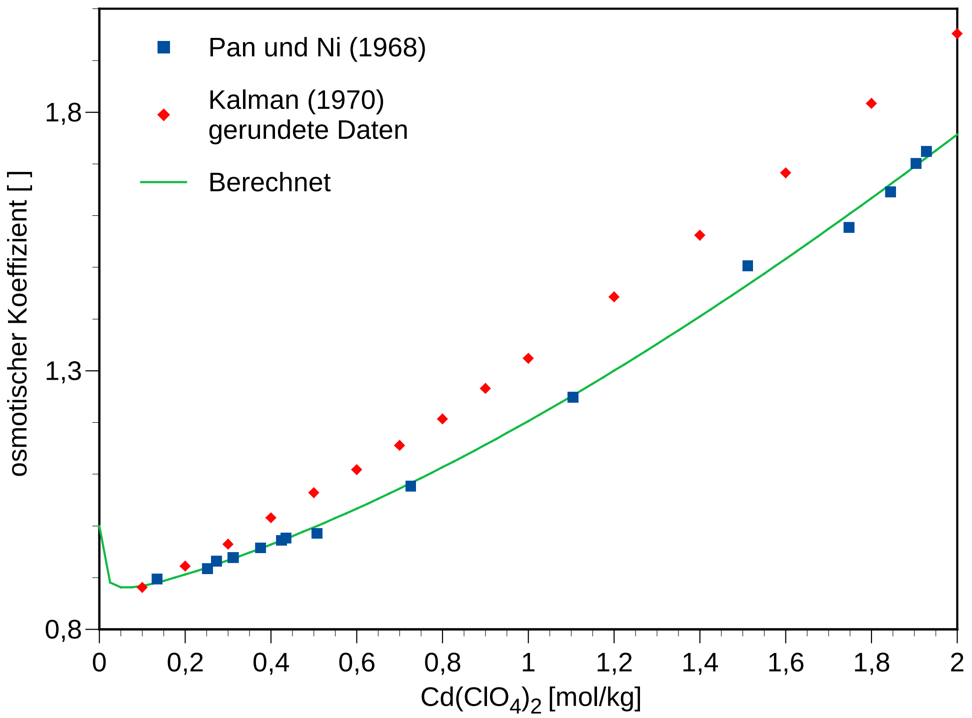

Fig. 7.9 Experimental and calculated osmotic coefficients in the system $Cd(ClO_4)_2$-H_2O at 25 °C

7.6.2 The binary system $Cd(NO_3)_2$ – H_2O

Isopiestic measurements at 25 °C are available from MOTORNAJA et al. (1973), MOTORNAJA and BEN'JASH (1973) and ROBINSON et al. (1942). GOLDBERG (1981) lists further measurements. However, they differ so much in temperature or measured values that they could not be used. With the interaction parameters listed in Tab. 7.12, the experimental data can be well reproduced (Fig. 7.10).

Tab. 7.12 Ion interaction parameters for cadmium nitrate

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	C^{γ}
Cd^{2+} - NO_3^-	0.27940	2	1.77126			-0.00826

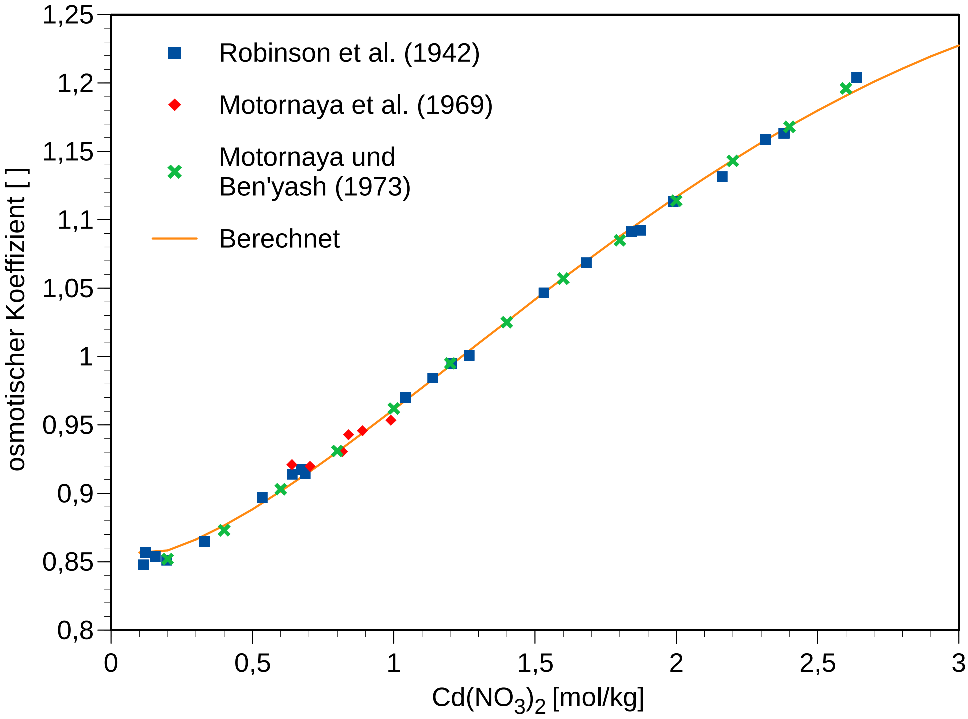

Fig. 7.10 Experimental and calculated osmotic coefficients in the system $Cd(NO_3)_2$-H_2O at 25 °C

7.7 The system $CdCl_2 – CdSO_4 – H_2O$

For this system, solubility measurements were conducted by MOSHINSKI (1975) and FILIPPOV et al. (1991). While FILIPPOV et al. (1991) found a simple eutonic system in which only the two salts $3CdSO_4{\cdot}8H_2O$ and $2CdCl_2{\cdot}5H_2O$ occur, MOSHINSKI observed additional solubility branches of the compounds $CdCl_2{\cdot}H_2O$ and $CdSO_4{\cdot}H_2O$, which have a lower hydrate water content. However, these show a disproportionately higher solubility and are therefore to be regarded as metastable. FILIPPOV et al. (1991) pointed out that this system is a ZDANOVSKIJ system with regard to the water activities, i.e., it has linear isoactivity lines. They proved this by measuring an isoactivity line, whose experimental data, however, were not mentioned in the article. To verify this statement, we have undertaken some additional measurements ourselves. In particular, we found a weak curvature of the isoactivity lines in the more concentrated mixed solutions (Fig. 2.17). The solubility curve in this system can be reproduced very well with the help of the calculated parameters (Fig. 7.11).

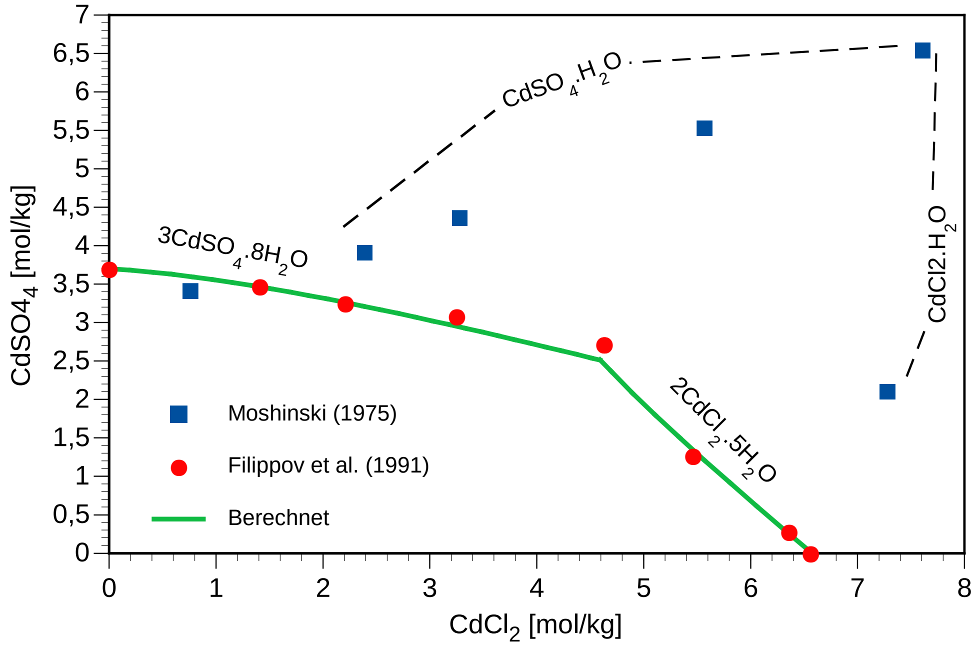

Fig. 7.11 Phase equilibria in the system $CdCl_2$-$CdSO_4$-H_2O at 25°C

7.8 The system $CdCl_2$ – NaCl – H_2O

Three series of solubility measurements with consistent results were available (Bassett et al. 1939, Filippov and Vivčarik 1978, Filippov et al. 1991). According to these authors, cadmium chloride and sodium chloride form two stable double salts at 25 °C: $4CdCl_2 \cdot 3NaCl \cdot 14H_2O$ and $CdCl_2 \cdot 2NaCl \cdot 3H_2O$. Adolff and Hering (1934) found the compound $5CdCl_2 \cdot 4NaCl \cdot 17H_2O$ at 19.3 °C. No further details about the area of existence could be taken from the article. Since Sudhaus (1914) also only detected the double salt $CdCl_2 \cdot 2NaCl \cdot 3H_2O_2$ at 19 -54 °C, the results of Adolff and Hering (1934) are probably incorrect. The system was also investigated by Votinský and Klikorka (1971), but no data could be found in the publication.

The system was also investigated using direct vapour pressure measurements (Lilič and Mogilev 1964, 1967), isopiestic measurements (Filippov and Vivčarik 1978; Filippov et al. 1991), and potentiometric measurements (Brüll 1934c; Reilly and Stokes 1970, Wang et al. 2016[9]). According to Filippov et al. (1991), the measured values from Filippov and Vivčarik (1978) contained a systematic error in the binary system $CdCl_2 \cdot H_2O$.

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[9] The measurements of Wang et al. were only available after the parameter determination was completed and were no longer taken into account.

The authors did not specify the nature of this error; an error in the analysis of the stock solution of $CdCl_2$ would be obvious. However, a systematic difference between the measured values from Filippov and Vivčarik (1978) and Filippov et al. (1991) could not be found. Both series of measurements are therefore used for parameter evaluation.

The early potentiometric measurements of Biron and Afanas'ev (1908) are of more orienting in character and will not be considered further.

Fillippov et al. (1991) successfully attempted to describe the system using additionally introduced Pitzer terms for assumed cadmium chloro complexes.

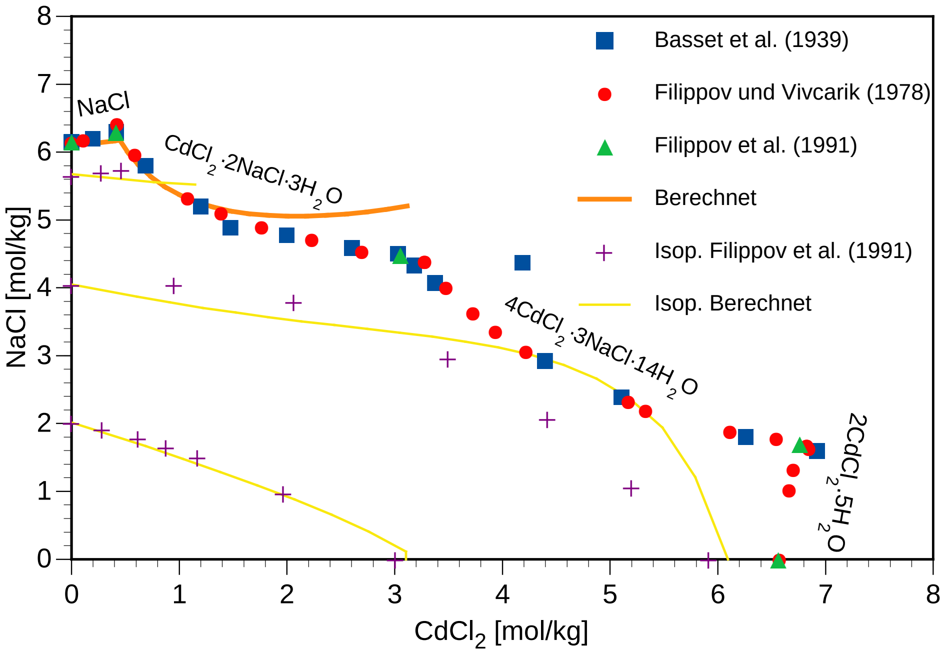

Fig. 7.12 Phase equilibria in the system $CdCl_2$-NaCl-H_2O at 25°C

The determination of the interaction parameters was done in two steps for this system. First, only the isopiestic measurements and the solubility measurements with the solid phase NaCl were used. Then, the ion activities for the solubility measurements with the solid phase $2NaCl{\cdot}CdCl_2{\cdot}3H_2O$ were calculated and the solubility constant for this compound was derived (log K = -0.64). In the same way, a solubility constant for $3NaCl{\cdot}4CdCl_2{\cdot}14H_2O$ was calculated. However, since already the measuring points for $2NaCl{\cdot}CdCl{\cdot}3H_2O_2$ were not correctly reproduced with increasing concentrations, the derived value for $3NaCl{\cdot}4CdCl_2{\cdot}14H_2O$ is not trustworthy.

Up to a cadmium concentration of about 2 mol/kg the agreement between calculated and measured solubilities and isoactivity curves is good to satisfactory (Fig. 7.12).

7.9 The system $CdCl_2$ – KCl – H_2O

The system was investigated with the help of solubility measurements by HERING (1936), DMITREVSKIJ et al. (1961) and FILIPPOV et al. (1971a). The measured values of DMITREVSKIJ et al. scatter strongly and are not considered further. According to consistent data, three potassium-cadmium double salts occur in the system in the temperature range from 19 to 54 °C: $CdCl_2 \cdot 4KCl$, $CdCl_2 \cdot KCl \cdot H_2O$ and $3CdCl \cdot KCl \cdot 4H_2O$ (SUDHAUS, 1914).

Additional isopiestic data were provided by FILIPPOV et al. (1971b). Potentiometric measurements were available from BRÜLL (1934c) and NÁRAY-SZABÓ and SZABÓ (1935). The data of the latter authors referred to measuring cells with transition potential and were not used in this study. The determination of the interaction parameters was carried out in two steps for this system. First, only the isopiestic measurements and the solubility measurements with the solid phase KCl were used. After that, the ion activities for the solubility measurements with the solid phases $CdCl_2 \cdot 4KCl$ and $CdCl_2 \cdot KCl \cdot H_2O$ were calculated and the solubility constant for this compound was derived. The following values were obtained:

$\log K (CdCl \cdot 4KCl_2) = -0.96$

$\log K (CdCl_2 \cdot KCl \cdot H_2O) = -3.04$

The derived values for $3CdCl_2 \cdot KCl \cdot 4H_2O$ scattered too strongly. In the area of existence of this compound, the parameter set for Cd^{2+} is not applicable.

As already indicated above, the modelling of the potassium-containing system presents difficulties. Up to a $CdCl_2$ concentration of about 1 mol/kg, the agreement between the calculated and the experimental data is quite good. After that, the deviations become stronger. Above $CdCl_2$ concentrations of about 1.5 mol/kg, the parameter set is no longer reliably applicable (Fig. 7.13).

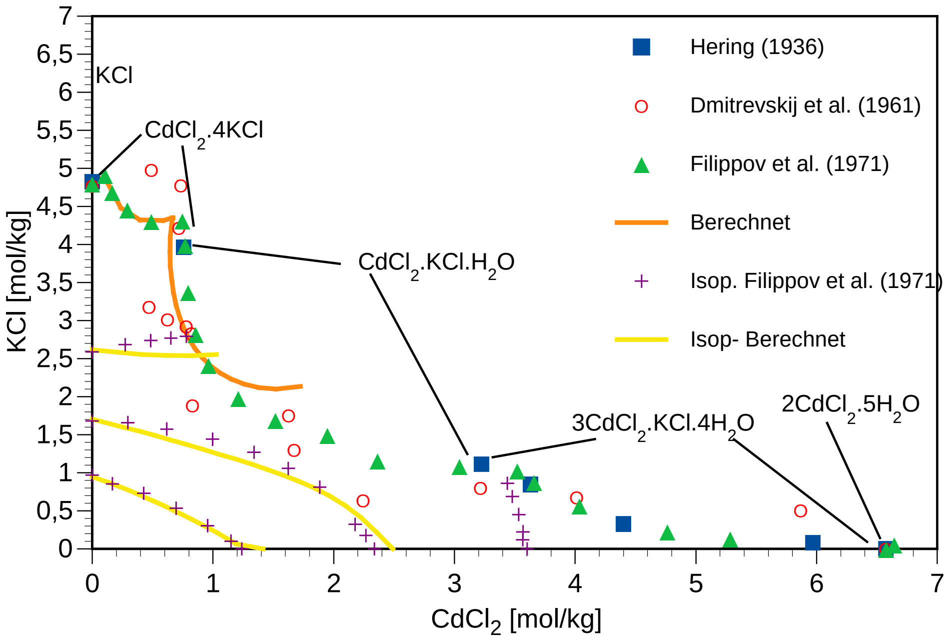

Fig. 7.13 Phase equilibria in the system $CdCl_2$-KCl-H_2O at 25°C

7.10 The system $CdCl_2$ – $MgCl_2$ – H_2O

Solubility studies are only available from BASSETT and STRAIN (1952). Two double salts, $CdCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ and $2CdCl_2 \cdot MgCl_2 \cdot 12H_2O$, occur in the system. Due to the very high solubilities of all salts occurring in the system, modelling of this system as well as of the Ca analogue was not possible so far. To extend the data basis to the area of medium and low concentrations, additional isopiestic measurements were carried out in this study. While the isopiestic data can be reproduced well up to very high $CdCl_2$ concentrations, the solubility curves of BASSETT and STRAIN (1952) are only reproduced sufficiently well up to the range 1.5 - 2 mol/kg (Fig. 7.14). After the interaction parameters had been derived from the isopiestic measurements, the solubility constant for $CdCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ was computed: log K = 5.4. For $2CdCl_2 \cdot MgCl_2 \cdot 12H_2O$, no constant values could be derived.

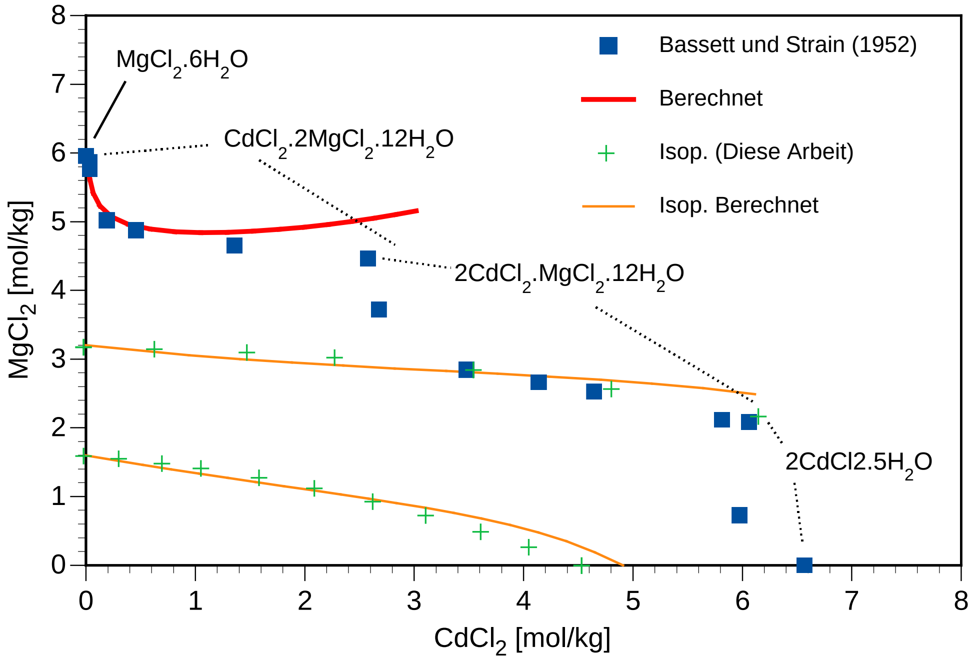

Fig. 7.14 Phase equilibria in the system $CdCl_2 - MgCl_2 - H_2O$ at 25°C

7.11 The system $CdCl_2$ – $CaCl_2$ – H_2O

Solubility studies are only available from BASSETT and STRAIN (1952). In addition to the double salt $CdCl_2 \cdot 2CaCl_2 \cdot 12H_2O$, a solid solution of the formula $(Cd,Ca)Cl_2 \cdot 4H_2O$ occurs in the system. Some potentiometric measurements at low concentrations were from BRÜLL (1934c). Further measurements of the same type were made by BEN`JAŠ and MASLAKOVA (1964), but they cannot be evaluated due to the lack of molal concentration data. To supplement the data gaps, isopiestic measurements were made in this study. As in the system with $MgCl_2$, the isopiestic data could be reproduced fairly well up to very high $CdCl_2$ concentrations. The calculated solubilities only agreed with the experimental data up to about 1 mol/kg (Fig. 7.15). It should be added that the modelling of concentrated $CaCl_2$ solutions is only successful up to $CaCl_2$ concentrations of about 4 mol/kg even with the data set of HARVIE et al. (1984). After the interaction parameters had been derived from the isopiestic measurements, a value of log K = 5.0 resulted for the solubility constant for $CdCl_2 \cdot 2CaCl_2 \cdot 12H_2O$.

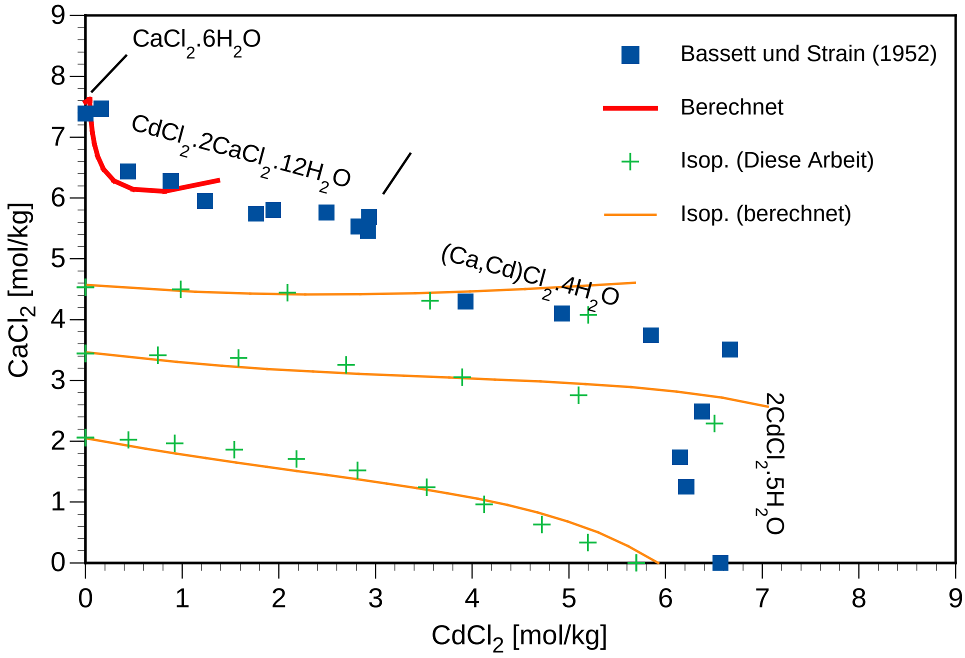

Fig. 7.15 Phase equilibria in the system $CdCl_2 - MgCl_2 - H_2O$ at 25 °C

7.12 The system $CdCl_2$ – LiCl – H_2O

The heterogeneous phase equilibria in the system $CdCl_2 - LiCl - H_2O$ at 25 °C was investigated for the first time by BLIDIN (1954). The results and especially the phase sequence could not be confirmed by FILIPPOV et al. (1975). According to their results, which was also based on the analytical examination of grown single crystals, the two double salts $3CdCl_2 \cdot 4LiCl \cdot 12H_2O$ and $2CdCl_2 \cdot LiCl \cdot 5H_2O$ occur in the system in addition to $LiCl \cdot H_2O$ and $2CdCl_2 \cdot 5H_2O$ (Fig. 7.16). The data of BLIDIN are therefore not considered. For the evaluation, the isopiestic investigations of FILIPPOV et al. (1975) were also taken into account. The early potentiometric measurements by BIRON AND AFANAS'EV (1908) could not be used.

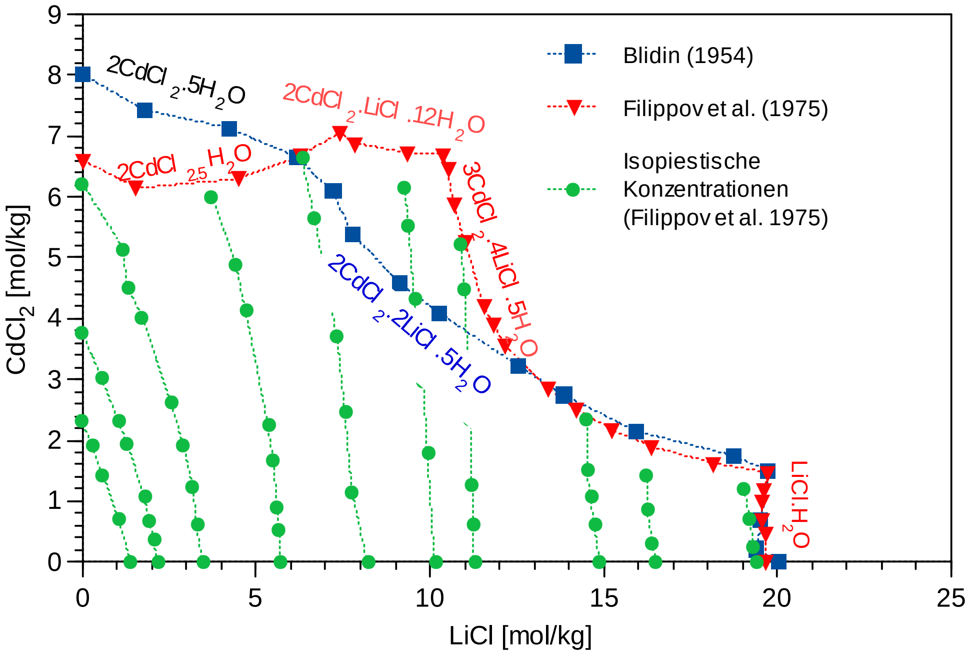

Fig. 7.16 Phase equilibrium in the LiCl – $CdCl_2$ – H_2O system at 25°C

7.13 The system $CdSO_4$ – Na_2SO_4 – H_2O

The phase equilibria in the system were studied by KOPPEL (1905), KARNAUCHOV et al. (1971), BALAREV and DOBREVA (1979) and FILIPPOV et al. (1985). The latter authors also made some isopiestic measurements. In addition to the binary salts $3CdSO_4\cdot8H_2O$ and $NaSO_4\cdot10H_2O$, the double salt $CdSO_4\cdot Na_2SO_4\cdot2H_2O$ was found. The report of KARNAUCHOV et al. (1971) about a compound $3CdSO4\cdot4Na_2SO_4\cdot3H_2O$ could not be confirmed, as well as the other solubility data of these authors. Only the isopiestic experiments and those solubility data, where $3CdSO_4\cdot8H_2O$ or $NaSO_4\cdot10H_2O$ were present as solid phases, were used for the parameter determination. Subsequently, the newly determined parameters were used to determine the ion activity coefficients and the water activities for the equilibrium solutions of the solubility branch $CdSO_4\cdot Na_2SO_4\cdot2H_2O$. The result was a constant ion activity product of

$$\log K = -3.39 \pm 0.01$$

The agreement of the calculated curve with the measured data is very good. Only the two-salt points $NaSO_4\cdot10H_2O$, $CdSO_4\cdot Na_2SO_4\cdot2H_2O$ and $CdSO_4\cdot Na_2SO_4\cdot2H_2O$/$3CdSO_4\cdot8H_2O$/saturated solution found by KOPPEL (1905) deviated strongly from the other measured data. They were not taken into account in the calculation of the solubility constants for $CdSO_4\cdot Na_2SO_4\cdot2H_2O$.

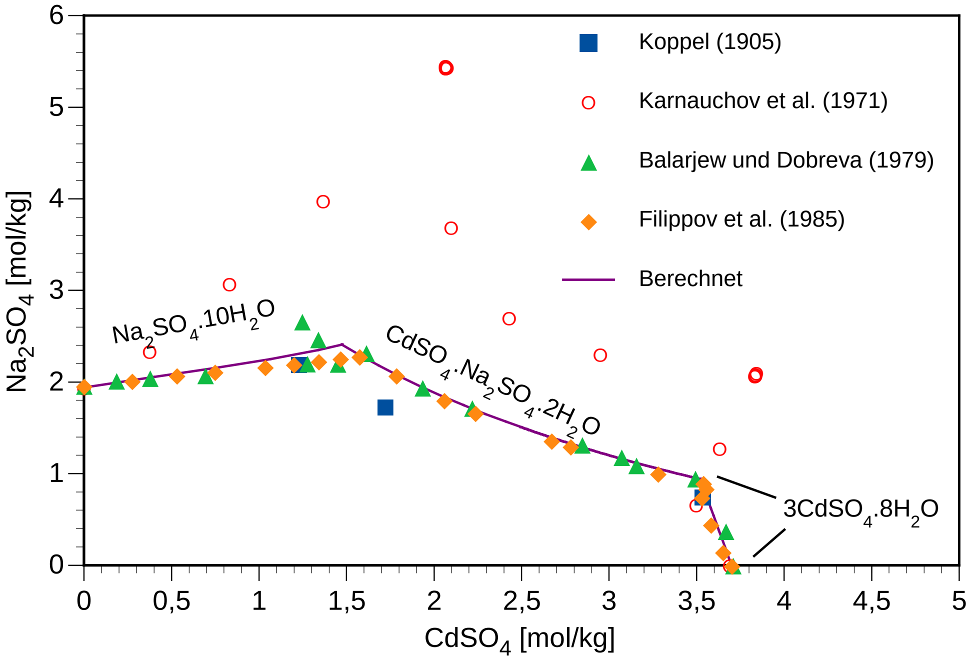

Fig. 7.17 Phase equilibria in the system $CdSO_4 - Na_2SO_4 - H_2O$ at 25°C

7.14 The system $CdSO_4 - K_2SO_4 - H_2O$

Solubility measurements for this system were available from MALHOTRA and SURI (1930), BENRATH and THÖNNESSEN (1932) and FILIPPOV et al. (1973). The latter also presented isopiestic measurements. The parameter evaluation was initially based only on the isopiestic measurements and the solubilities of the pure salts K_2SO_4 and $3CdSO_4 \cdot 8H_2O$. No consideration was given to the potentiometric measurements of STONEHILL (1938), who only dealt with very dilute solutions. They are irrelevant for the determination of ion interaction parameters.

According to BENRATH and THÖNNESSEN (1932) and FILIPPOV et al. (1973), the two double salts $2CdSO_4 \cdot 2K_2SO_4 \cdot 3H_2O$ (already described by VON HAUER, 1868) and $3CdSO_4 \cdot K_2SO_4 \cdot 5H_2O$ occur at 25 °C, while MALHOTRA and SURI (1930) found only one anhydrous compound $CdSO_4 \cdot K_2SO_4$. Especially in the stability range of the double salts, the experimental results differed considerably. While the solubility branch of $3CdSO_4 \cdot K_2SO_4 \cdot 5H_2O$ shows a consistent position in BENRATH and THÖNNESSEN as well as in FILIPPOV et al. (1973), FILIPPOV et al. found significantly higher solubilities for $2CdSO_4 \cdot 2K_2SO_4 \cdot 3H_2O$ (Fig. 7.18). This is also expressed in the solubility constants. For $3CdSO_4 \cdot K_2SO_4 \cdot 5H_2O$ the result was consistently:

$$\log K = -9.19 \pm 0.03$$

For $2CdSO_4 \cdot 2K_2SO_4 \cdot 3H_2O$, on the other hand:

log K = -9.29 (BENRATH and THÖNNESSEN)
log K = -9.06 (FILIPPOV et al.)

Due to the data situation, it is currently impossible to decide which solubility constant is closer to reality and we set as an average value:

log K = -9.18 ± 0.14

The agreement between calculated and experimental values is very good for all solubility ranges except for the branch of the double salt $2CdSO_4 \cdot 2K_2SO_4 \cdot 3H_2O$.

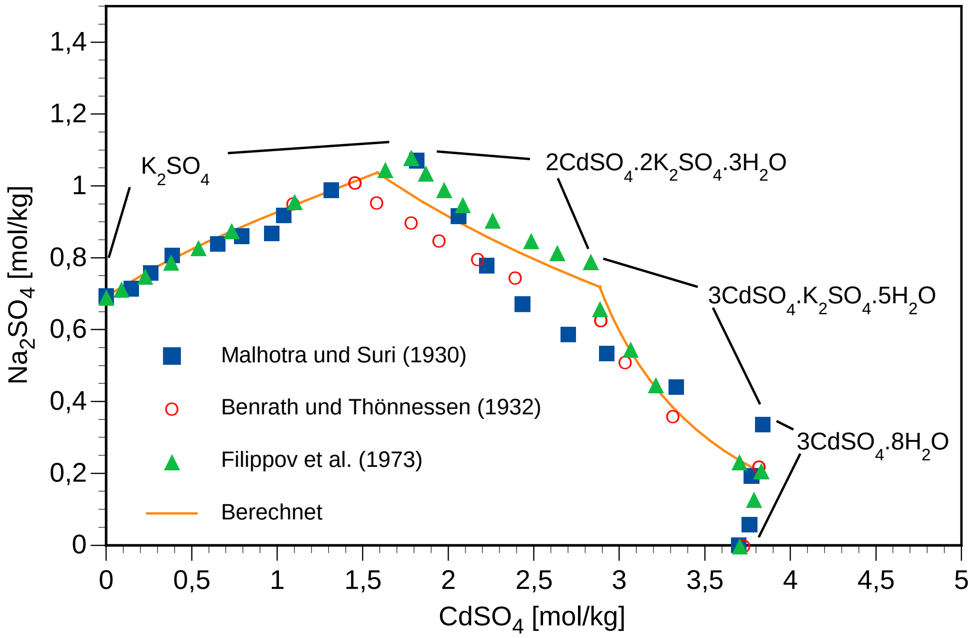

Fig. 7.18 Phase equilibria in the system $CdSO_4 - K_2SO4 - H_2O$ at 25°C

7.15 The system $CdSO_4 - MgSO_4 - H_2O$

This system has been studied in detail and with consistent results by VOSBURGH et al. (1940) and OJKOVA and BARKOV (1980). Neither a double salt nor a solid solution occurs in the system below 30.2 °C, but only the simple metal sulphates. The calculated solubility curve does not deviate significantly from the measured values (Fig. 7.19).

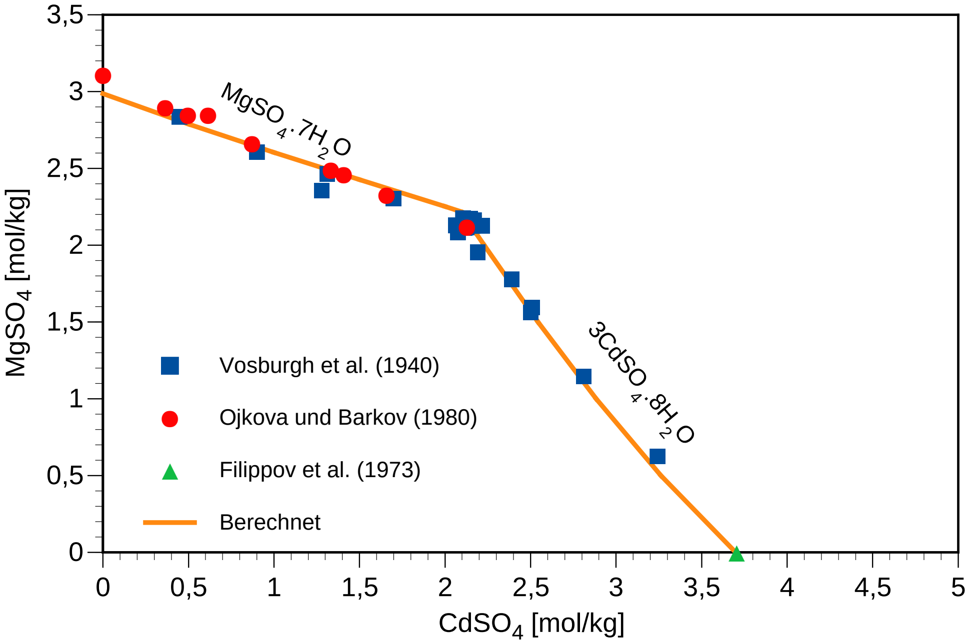

Fig. 7.19 Phase equilibria in the system $CdSO_4 - MgSO_4 - H_2O$ at 25°C

7.16 The system $CdSO_4 - CaSO_4 - H_2O$

Up to now, only a few individual points from KARNAUKHOV et al. (1974) were available. They were supplemented with some new solubility experiments (Tab. 7.13). The phase composition was determined radiographically and was gypsum in all cases. The shape of the solubility curve strongly resembles the results in the system $ZnSO_4$-$CaSO_4$-H_2O (see there). At small concentrations up to about 0.2 mol/kg $CdSO_4$, the calcium concentration passes through a minimum, then rises up to 1.5 mol/kg $CdSO_4$ and then continuously falls again. The solubility curve is well represented by the model calculation. However, the invariant point $CaSO_4 \cdot 2H_2O$/$3CdSO_4 \cdot 8H_2O$/saturated solution determined by KARNAUKHOV et al. (1974) is missed (Fig. 7.20).

Tab. 7.13 Experimental solubilities in the $CdSO_4$-$CaSO_4$-H_2O system.

$CdSO_4$ [mol/kg]	$CaSO_4$ [mol/kg]
0.094	0.0152
0.167	0.0139
0.388	0.0162
0.609	0.0174
0.830	0.0197
1.193	0.0208
1.370	0.0198
1.550	0.0210
2.098	0.0177
2.289	0.0173
2.489	0.0164
2.607	0.0168
2.741	0.0164
0.094	0.0152
0.167	0.0139

)* All solutions were in equilibrium with gypsum ($CaSO_4 \cdot 2H_2O$)

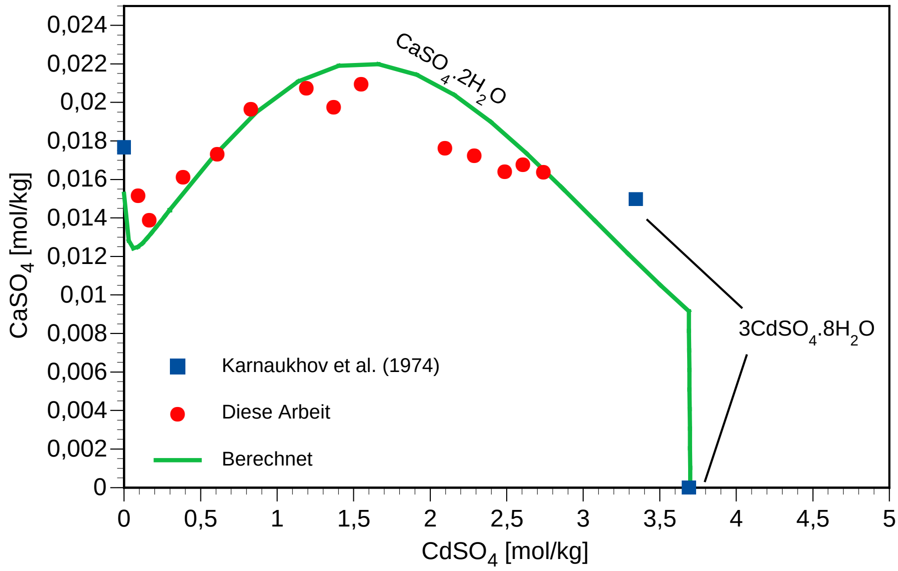

Fig. 7.20 Phase equilibria in the $CdSO_4 - CaSO_4 - H_2O$ system at 25°C

7.17 Quaternary systems with chloride and sulphate

There are only few published measurement data on quaternary systems. In the literature, only solubilities in system Cd, Na || Cl, $SO_4 – H_2O$ were described by the FILIPPOV working group (FILIPPOV et al. 1988; RUMYANTSEV and CHARYKOV 1989; FILIPPOV et al. 1991). The FILIPPOV working group also carried out isopiestic measurements in the analogue system Cd, K || Cl, $SO_4 – H_2O$, but did not publish the work (RUMYANTSEV, personal communication). The only known fact about the latter system was that, in contrast to zinc, cadmium kainite $KCdClSO_4$ cannot be synthesised (LUŠNAJA, 1949). No information was available for the systems Cd, Mg || Cl, $SO_4 – H_2O$ and Cd, Ca || Cl, $SO_4 – H_2O$.

The Pitzer model developed in this study allows to predict the isoactivity lines fairly well, especially in those case in which either the cadmium concentration or the concentration of the second salt is low. Significant deviations occur in situations where the cadmium concentration and the concentration of the second salt is above 1 mol/kg (Fig. 7.23 ff.).

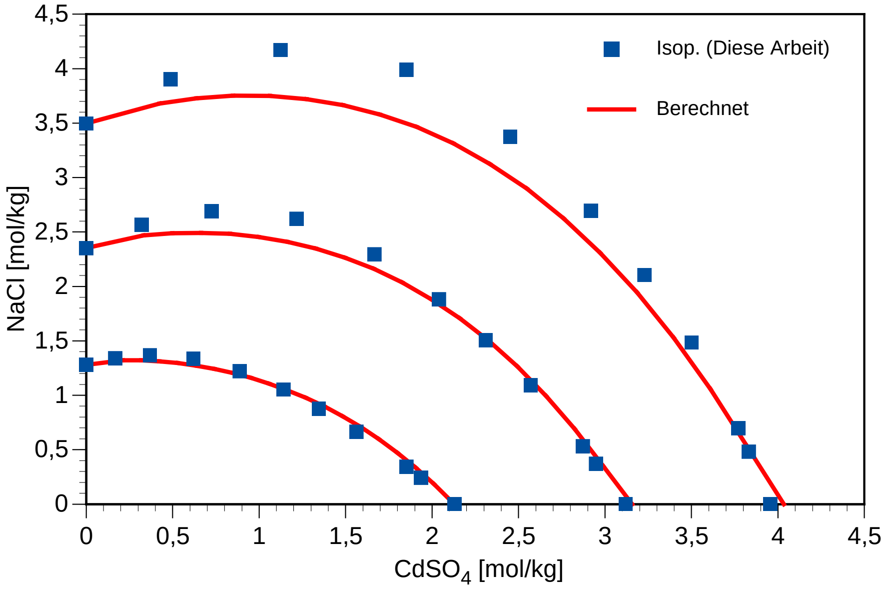

Fig. 7.21 Phase equilibria in the system $CdSO_4 – NaCl – H_2O$ at 25 °C

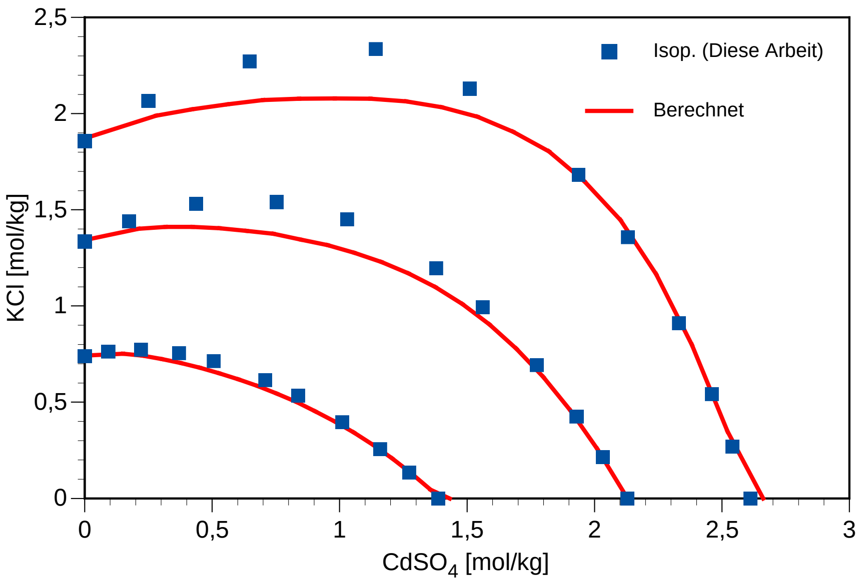

Fig. 7.22 Phase equilibria in the system $CdSO_4 - KCl - H_2O$ at 25 °C

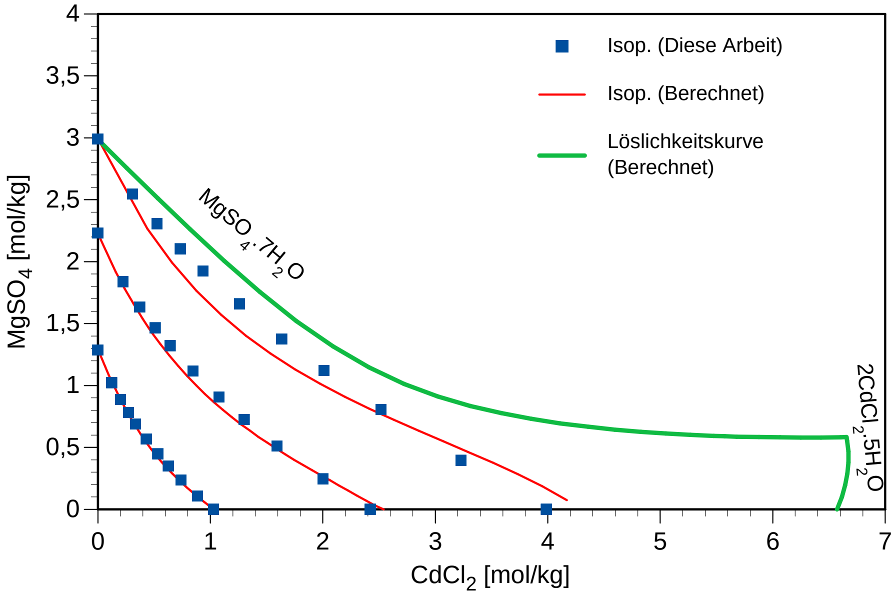

Fig. 7.23 Phase equilibria in the system $CdCl_2 - MgSO_4 - H_2O$ at 25 °C

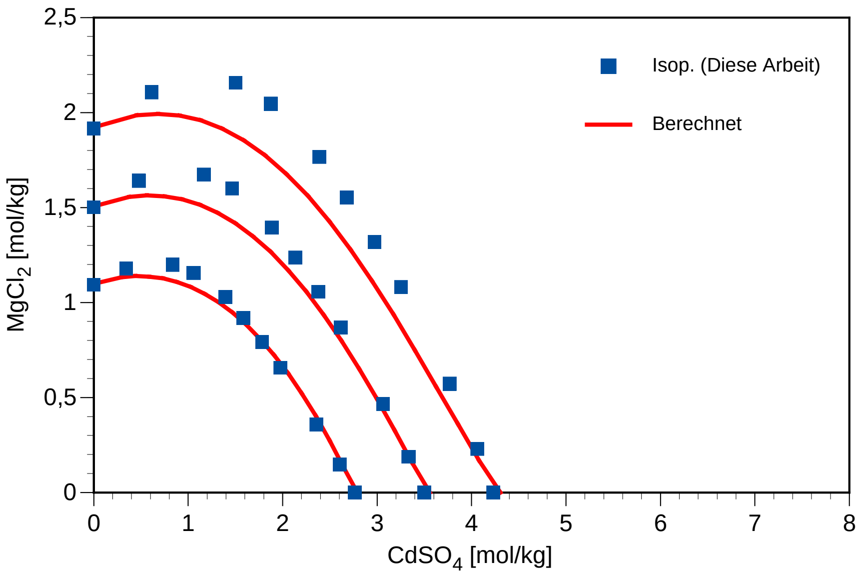

Fig. 7.24 Phase equilibria in the system $CdSO_4 - MgCl_2 - H_2O$ at 25 °C

7.18 The systems $NaClO_4 - H_2O$ and $LiClO_4 - H_2O$

Interaction coefficients for the ion pairs Na-ClO_4 and Li-ClO_4 may be found in KIM and FREDERICK (1988), but they are only based on the smoothed values from HAMER and WU (1972), not on the original data. Isopiestic measurement data were available from JONES (1947) in the concentration range 0.2 to 6.4 mol/kg ($NaClO_4$) and 0.2 to 4.2 mol/kg ($LiClO_4$). The isopiestic concentrations of the reference solutions (NaCl) were converted to water activities and osmotic coefficients using the regression function in CLARKE and GLEW (1985). To cover lower concentrations, correlation of the osmotic coefficients of equally concentrated sodium perchlorate and sodium chloride solutions was used. In the concentration range from 0 to 2 mol/kg, a linear correlation between the two quantities resulted in

$$\frac{\varphi_{NaCl}}{\varphi_{NaClO_4}} = 0{,}0241 c_{NaClO_4} + 1 \qquad R^2 = 0{,}9878 \tag{7.2}$$

which allowed a sufficiently accurate prediction of osmotic coefficients of low-concentration sodium perchlorate solutions from the calculated osmotic coefficient of equally concentrated sodium chloride solutions (Fig. 7.25). A similar relationship could also be established between low-concentration lithium perchlorate and sodium chloride solutions (Fig. 7.27). Here the relationship is

$$\frac{\varphi_{NaCl}}{\varphi_{LiClO_4}} = 0{,}0369\, c_{LiClO_4}^2 - 0{,}1701\, c_{LiClO_4} + 1 \qquad R^2 = 0{,}9962 \qquad (7.3)$$

In each case 20 equidistantly distributed values for solution concentrations between 0.01 and 0.2 mol/kg $NaClO_4$/$LiClO_4$ were determined in the determination of the ion interaction parameters (Tab. 7.14, S. 183) were taken into account. With their help, the experimental data can be reproduced very well (Fig. 7.26, Fig. 7.28).

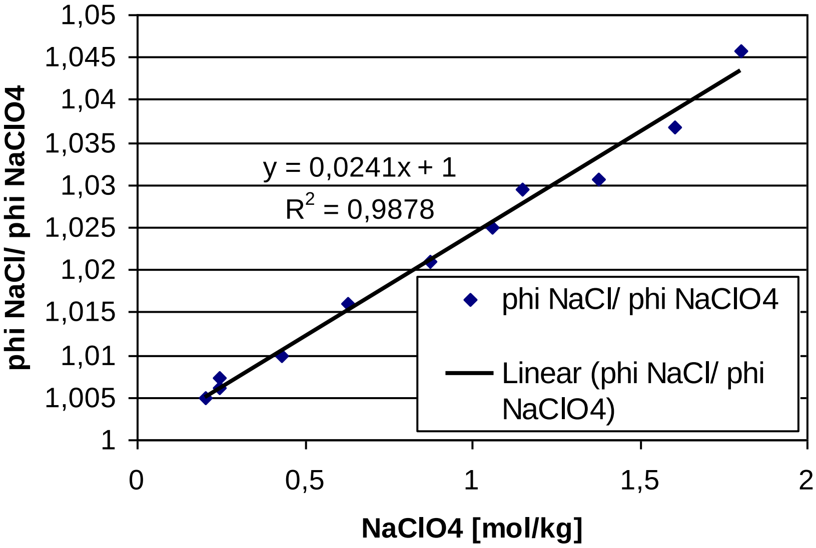

Fig. 7.25 Correlation between the osmotic coefficients of equally concentrated sodium chloride and sodium perchlorate solutions.

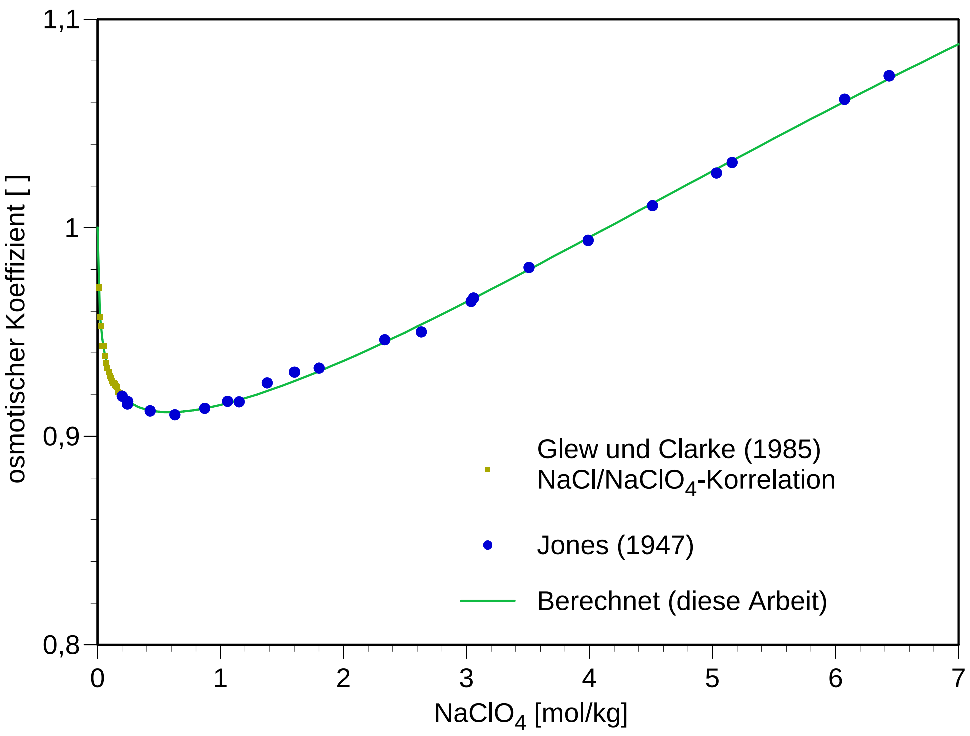

Fig. 7.26 Experimental and calculated osmotic coefficients in the $NaClO_4 - H_2O$ system at 25 °C

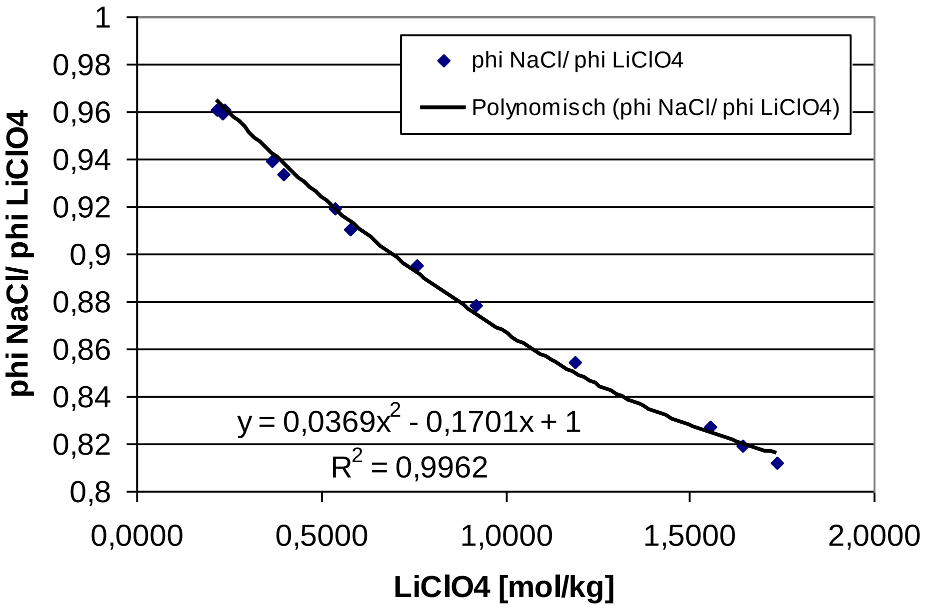

Fig. 7.27 Correlation between the osmotic coefficients of equally concentrated sodium chloride and sodium perchlorate solutions

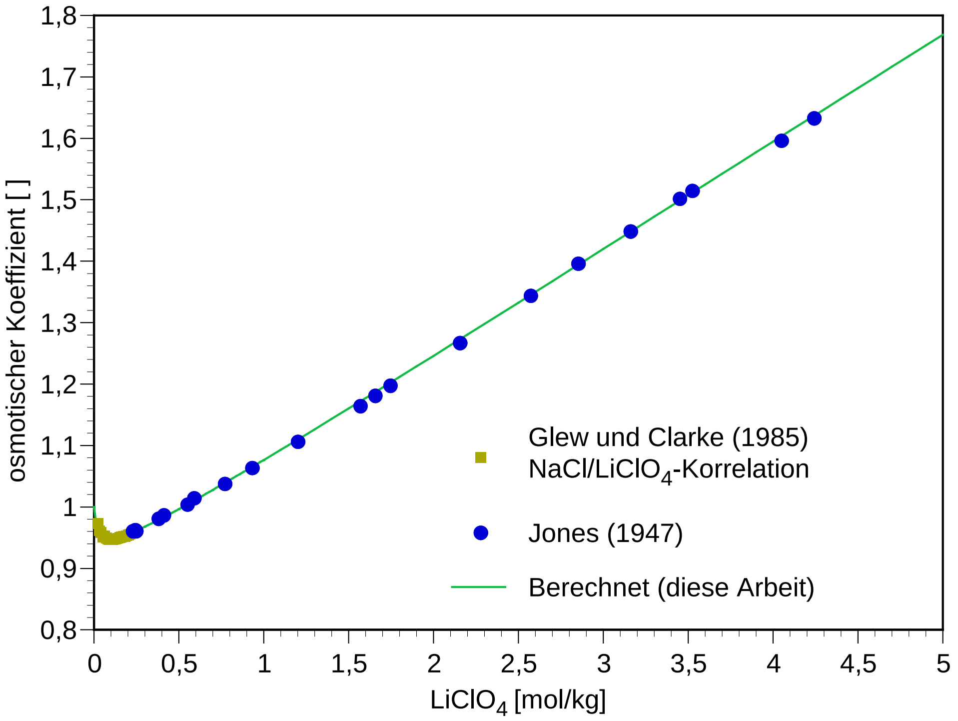

Fig. 7.28 Experimental and calculated osmotic coefficients in the system $LiClO_4 - H_2O$ at 25 °C

7.19 The system $NaCl - NaClO_4 - H_2O$

It was shown that with the binary interaction parameters the solubility system $NaCl - NaClO_4 - H_2O$ (Ševčuk 1959) could be described very well at least up to a perchlorate concentration of 9 mol/kg (Fig. 7.29). No ternary parameters were necessary as. This was also assumed to be the case in the analogous system with lithium, for which no measurement data were available in the relevant concentration range.

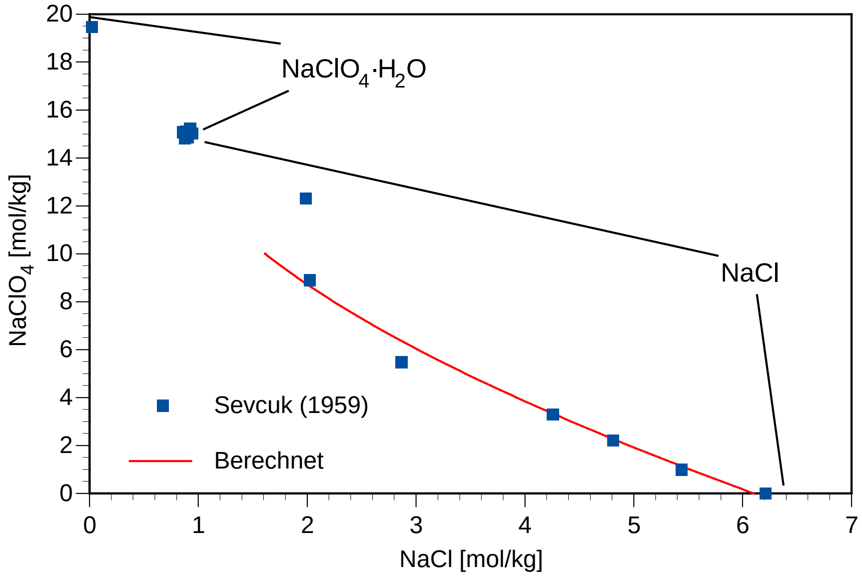

Fig. 7.29 Experimental and calculated phase solubilities in the $NaCl-NaClO_4-H_2O$ system at 25°C

7.20 Result overview

The following tables summarise the results of this chapter.

Tab. 7.14 Binary ion interaction coefficients for cadmium and some perchlorates

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	C^{γ}
$Cd^{2+} – Cl^-$	-0.04008	2.5	-3.1761	12	-44.9301	0.00188
$Cd^{2+} – SO_4^{2-}$	0.22487	1.4	2.3385	12	-59.824	0.001302
$Cd^{2+} – ClO_4^-$	0.38620	2	2.04634			0.008152
$Na^+ – ClO_4^-$	0.05796	2	0.27262			-0.00080
$Li^+ – ClO_4^-$	0.21091	2	0.34245			-0.00135

Tab. 7.15 Ternary ion interaction coefficients for cadmium and some perchlorate systems

Ion pair	**ψ**	**θ**
$Cd^{2+} – Na^+$		-0.06474
$Cd^{2+} – K^+$		-0.06308
$Cd^{2+} – Mg^{2+}$		-0.41211
$Cd^{2+} – Ca^{2+}$		-0.26274
$Cd^{2+} – Cl^- – SO_4^{2-}$	-0.00463	-
$Cd^{2+} – Na^+ – SO_4^{2-}$	0.01089	-
$Cd^{2+} – K^+ – SO_4^{2-}$	-0.03170	-
$Cd^{2+} – Mg^{2+} – SO_4^{2-}$	0.13094	-
$Cd^{2+} – Ca^{2+} – SO_4^{2-}$	0.11727	-
$Cd^{2+} – Na^+ – Cl^-$	-0.01935	-
$Cd^{2+} – K^+ – Cl^{--}$	-0.03826	-
$Cd^{2+} – Mg^{2+} – Cl^{--}$	-0.03701	-
$Cd^{2+} – Ca^{2+} – Cl^{--}$	-0.03212	-
$Na^+ – Cl^- – ClO_4^-$	0	0
$Li^+ – Cl^- – ClO_4^-$	0	0

Tab. 7.16 Solubility constants of cadmium-containing solid phases

Solid phase	**log K**
$2CdCl_2 \cdot 5H_2O$	-4.05
$CdCl_2 \cdot H_2O$	-1.736
$3CdSO_4 \cdot 8H_2O$	-5.858
$CdCl_2 \cdot 2NaCl\ 3H_2O$	-0.64
$CdCl_2 \cdot 4KCl$	-0.96
$CdCl_2 \cdot KCl \cdot H_2O$	-3.04
$CdCl_2 \cdot 2MgCl_2 \cdot 12H_2O$	5.4
$CdCl_2 \cdot 2CaCl_2 \cdot 12H_2O$	5.0
$CdSO_4 \cdot Na_2SO_4 \cdot 2H_2O$	-3.39
$3CdSO_4 \cdot K_2SO_4 \cdot 5H_2O$	-9.19
$2CdSO_4 \cdot 2K_2SO_4 \cdot 3H_2O$	-9.18

8 Thermodynamic model for zinc in saline solutions

8.1 The binary system $ZnCl_2 – H_2O$

8.1.1 Vapour pressure measurements

Vapour pressure and isopiestic measurements were available from a number of authors (Tab. 8.1). The vapour pressure measurements by ISHIKAWA and TAKAI (1937) deviated strongly from the results of the other authors and were not included in the parameter evaluation. In the work of DIESNIS (1935), the concentrations of the saturated solution investigated were not determined. The other measurement data agree well at high concentrations. At $ZnCl_2$ contents below 2.5 mol/kg, however, significant deviations are sometimes noticeable, which, according to RARD and MILLER (1989), can partly be attributed to non-stoichiometric zinc chloride solutions. Since concentrated zinc chloride solutions tend to hydrolyse, commercially available zinc chlorides are often contaminated by oxides and thus not exactly stoichiometric. It is not always possible to determine whether the solutions used by the various authors were stoichiometric. If not mentioned otherwise, all measured values given in the sources were included in the parameter determination.

Tab. 8.1 Previous isopiestic measurements on $ZnCl_2$ solutions at 25.0°C

Earlier work	Number of measuring points	Concentration range [mol/kg]
DIESNIS (1935)	1	saturated
ISHIKAWA and TAKAI (1937)*	5	0.52 - 3.15
ROBINSON and STOKES (1940)	28	0.11 - 3.19
STOKES (1948b)	19	3.35 - 23.19
PAN (1966)	19	0.16 - 2.42
RARD and MILLER (1989)	86	0.31 - 13.10
MILADINOVIC et al. (2003b)	15	0.49 - 2.38
This work	32	0.54 - 13.20

* Direct vapour pressure measurement

8.1.2 Potentiometric measurements

Potentiometric measurement data are available in large numbers (Tab. 8.2). The measured values mostly agree with each other. Differences arise mainly at smaller concentrations (Fig. 8.3). The following data were not taken into account:

- Some older measurements are referenced in GETMAN (1931b). They are of rather historical interest.
- From HARRIS and PARTON (1940) only smoothed data are available, but not the primary measured values.
- The potentials of the concentration cells of EGAN and PARTINGTON (1943) as well as AGNEW and PATERSON (1978) each referred to the non-experimentally determined potential of a zinc chloride solution of a certain concentration. Moreover, the solution concentrations were only given as molarities without densities. A conversion into molarity was only possible with a loss of quality.
- The measurements on a cell with transition potential (MASAKI, 1932) were also not evaluable.
- A comparison of the data showed that the results of GETMAN (1931b) and HORSCH (1919) deviated strongly from those of the other works. They were not taken into account in the parameter determination.

Tab. 8.2 Potentiometric measurements on zinc chloride solutions

Zinc electrode	**Counter electrode**	**Source**
Zn metal	AgCl | Ag	HORSCH (1919)
Zn(Hg, 2-phase)	AgCl | Ag	SCATCHARD and TEFFT (1930)
Zn metal	$HgCl_2$ | Hg	GETMAN (1931b)
Zn(Hg, 2-phase)	$HgCl_2$ | Hg	HOWLER (1934A)
Zn(Hg, 10%)	$HgCl_2$ | Hg	ISHIKAWA AND TAKAI (1937)
Zn(Hg x)	AgCl | Ag	HARRIS and PARTON (1940)
Zn(Hg, 2-phase)	AgCl | Ag	ROBINSON and STOKES (1940)
Zn(Hg, 2-phase)	AgCl | Ag	LUFULLAH et al. (1976)

8.1.3 Evaluation

As earlier investigations showed (HERBERT and MÖNIG, 1996), it is not possible to develop a single Pitzer parameter set without explicit consideration of complex formation, with which the entire concentration range of $ZnCl_2$ solutions (0 to over 30 mol/kg) can be satisfactorily described. Especially the highly concentrated solutions should rather be addressed as salt hydrate melts. Free water is hardly present there, so that even the basis of the Pitzer model, the Debye-Hückel theory for ionic interactions in aqueous media, can no longer be meaningfully applied. Nevertheless, there have been successful attempts with extended Pitzer approaches to describe the entire concentration space (ANSTISS and PITZER 1991), but the formalisms created in this way no longer have anything in common with physical reality.

The available measurement data were only evaluated up to a concentration of 6 mol/kg. This approximately corresponds to the highest chloride concentration usually found in the system of oceanic salts (saturated $MgCl_2$ solution). According to previous experience, the modelling of zinc chloride solutions can be improved considerably if the parameters $\alpha^{(1)}$ and $\alpha^{(2)}$ are also optimised. As optimal values we obtained $\alpha^{(1)} = 2$ and $\alpha^{(2)} = 2.5$ (Tab. 8.3).

Tab. 8.3 Ion interaction parameters for zinc chloride

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	C^{γ}
$Zn^{2+} - Cl^-$	0.06522	2	5.5187	2.5	-4.3578	0.00132

The agreement between the measured and modelled osmotic and activity coefficients (Fig. 8.1 - Fig. 8.3) is good to very good. Only at concentrations above 5 mol/kg and between 1 and 2 mol/kg $ZnCl_2$ (osmotic coefficients) smaller deviations are noticeable.

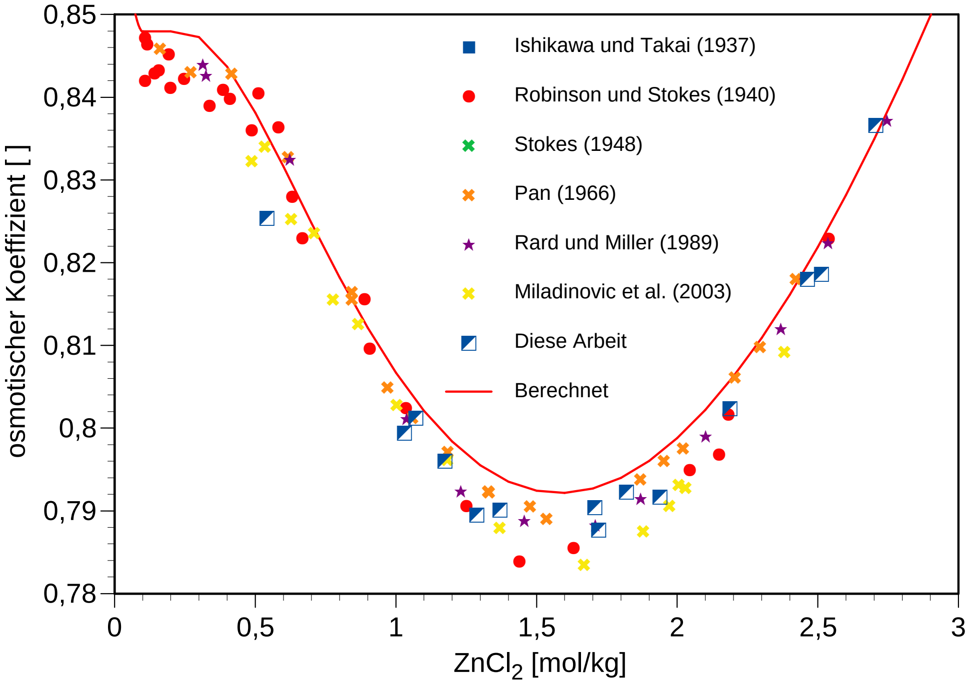

Fig. 8.1 Experimental and calculated osmotic coefficients in the system $ZnCl_2 - H_2O$ up to 3 mol/kg

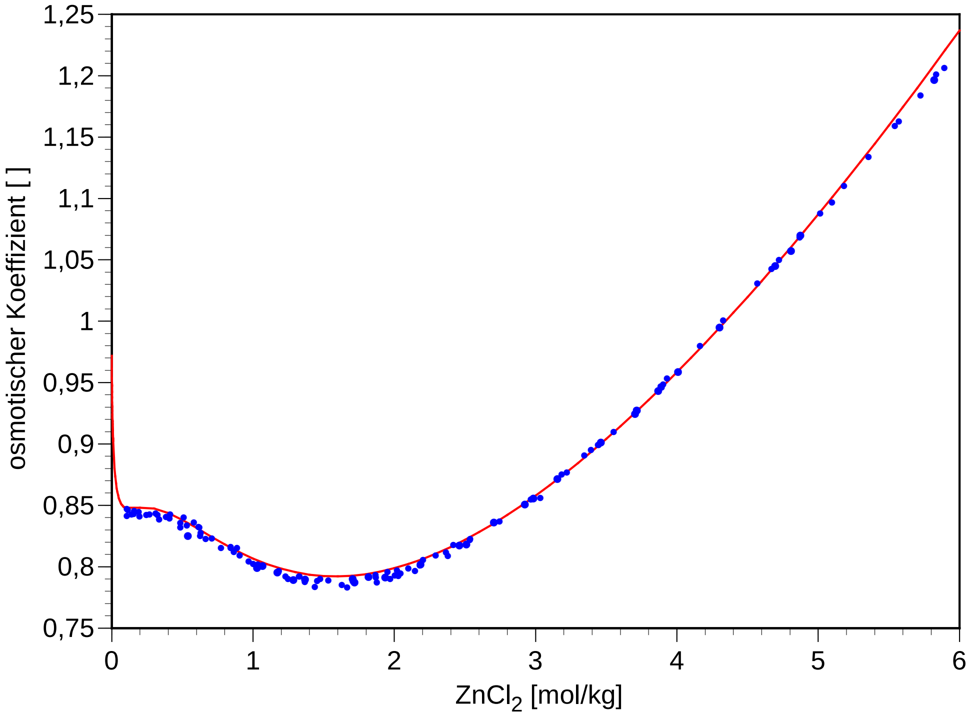

Fig. 8.2 Isopiestically determined (dots) and calculated (line) osmotic coefficients in the system $ZnCl_2 - H_2O$ up to 6 mol/kg

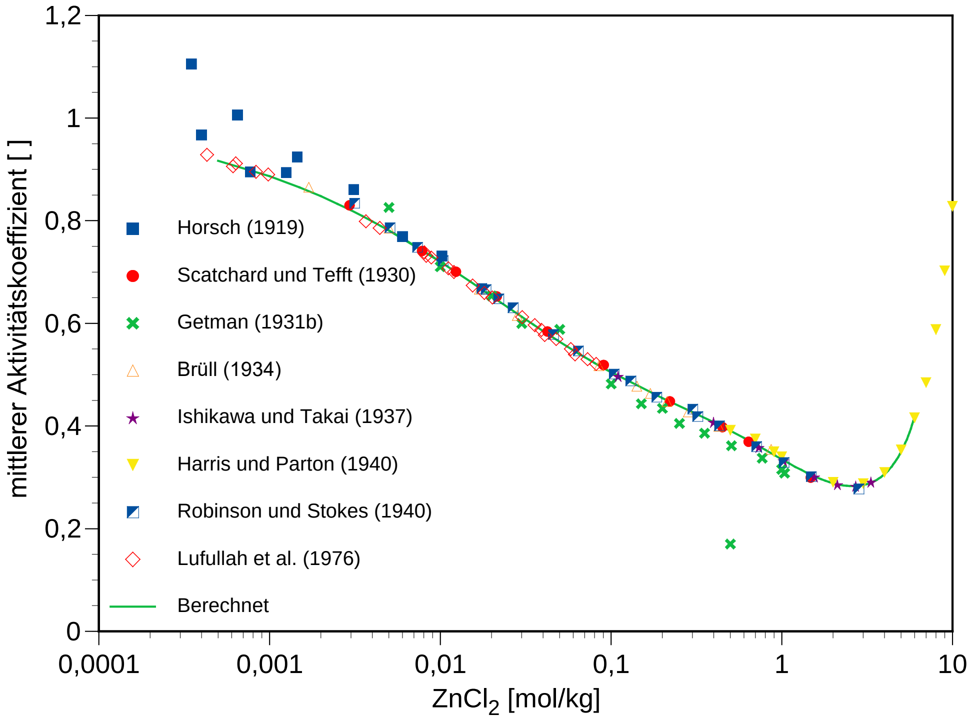

Fig. 8.3 Experimental and calculated mean activity coefficients in the $ZnCl_2 – H_2O$ system at 25°C

8.1.4 Solid phases

Zinc chloride is one of the most soluble inorganic salts. The zinc chloride content of the saturated highly viscous solution is of the order of about 80 – 81 wt.-% at 25 °C, corresponding to about 30 mol/kg, if such a mixture with a water/salt ratio of just over unity shall still be called ‘solution’. There is no agreement in the literature about the character of the solid occurring at 25 °C (cf. ZDANOVSKIJ et al., 1963). The solubility studies by DIETZ (1899), MYLIUS and DIETZ(1905) and ISHIKAWA et al. (1932) indicate that $ZnCl_2·1.5H_2O$ occurs up to 26 °C, from 26 to about 28 °C $ZnCl_2·H_2O$ and above that anhydrous $ZnCl_2$. Depending on the experimental procedure, one of these three forms is found at 25°C. Their solubility differs only slightly. We refrain from a more detailed evaluation at this point, since a thermodynamic modelling of saturated zinc chloride solutions with the developed parameter set was neither planned nor possible.

8.2 The binary system $ZnSO_4 – H_2O$

8.2.1 Vapour pressure measurements

A large number of isopiestic and direct vapour pressure measurements are available. They are summarised in Tab. 8.4. As already explained above, the agreement between the measured data is very good. The new data from the present study fitted in very well.

The following works were not considered in the parameter calculation: The measuring point of DIESNIS (1935) for the vapour pressure of a saturated solution was considerably higher than the other measured values after taking into account the solubility of $ZnSO_4$ derived below. The values of LIBUŚ et al. (1980) were systematically lower for all concentrations. They were not taken into account in the parameter determination. In the same way the strongly scattering values of OJKOVA et al. (1974) and the deviating vapour pressure measurements of TARTAR et al. (1941) were not included. ROBINSON and JONES (1936) did not publish the 62 isopiestic concentration pairs they determined experimentally, but only osmotic coefficients for smoothed interpolated zinc sulphate concentrations. These data were corrected again in ROBINSON and STOKES (1965). Since the raw data are still missing, an evaluation had to be omitted. APELBLAT (1992) investigated the vapour pressures of saturated zinc sulphate solutions, among others, also at 298.15 K, but did not provide a concentration. BALAREW and OJKOVA (1975) only gave the determined water activities, but not the isopiestic concentrations of the reference solution. Moreover, the values scattered strongly. Also, FILIPPOV et al. (1985) only published the calculated osmotic coefficients. No information could be found on the reference solutions and their equilibrium concentrations. GUENDOUZI et al. (2003) carried out hygrometric water activity measurements. Their water activities determined in this way were only given using interpolated concentrations. The measurements of AWAKURA et al. (1984) appeared only in graphical form and later in a private print (MAJIMA et al. 1988), which was only available after the parameter determination. The measured values of NINKOWIĆ et al. (2007) were also only available after the parameter development. However, they fit exactly into the values of earlier measurements and did not lead to significantly changed parameters.

Tab. 8.4 Previous vapour pressure determinations of $ZnSO_4$ solutions at 25.0°C

Earlier work	Number of measuring points	Method	Concentration range [mol/kg]
DIESNIS (1935)	1	direct	saturated
ROBINSON and JONES (1936)**	62	isopiestic	0.1 – 3.6)**
TARTAR et al. (1941)	4	direct	0.5 – 2
GROENEVELD (1956)*	6	direct	0.85 – 3.93
OJKOVA et al. (1974)	8	isopiestic	1.16 – 3.13
BALAREV and OJKOVA (1975)	4	isopiestic	1.14 – 2.42
LIBUŚ et al. (1980)	20	isopiestic	0.11 – 3.78
MAJIMA et al.(1988)**	8	isopiestic	0.25 – 2.50)**
FILIPPOV et al. (1985)	5	isopiestic	0.64 – 0.92
APELBLAT (1992)	1	Evaporimeter	saturated
ALBRIGHT et al. (2000)	76	isopiestic	0.10 – 4.31
PROSKURINA (2001)	1	isopiestic	3.13
MILADINOVIĆ et al. (2002)	20	isopiestic	1.35 – 3.02
MILADINOVIĆ et al. (2003a)	17	isopiestic	0.64 – 2.60
GUENDOUZI et al. (2003)**	16	Evaporimeter	0.2 – 3.0)**
NINKOWIĆ et al. (2007)	14	isopiestic	1.2 – 2.9
This work	16	isopiestic	1.39 – 4.19

* Direct vapour pressure measurement ** interpolated values

8.2.2 Potentiometric measurements

Tab. 8.5 summarises the potentiometric studies carried out earlier that were included in the parameter determination. The following measurements were not taken into account: The data of GÓMEZ HERRERA et al. (1944) were only available for molar concentrations. The measurements by ESPARZA et al. (1993) were carried out in a concentration cell without transition. The measured values refer to the activity of the zinc sulphate solution in the reference cell, which is not specified. The measurements of ARVIA (1955) deviated very strongly from the other measured values at low concentrations. Their data at $ZnSO_4$ < 0.02 mol/kg were therefore not considered. Like ARVIA, MASAKI and IKKATAI (1932) also worked with a $Hg_2SO_4|Hg$ reference electrode. Here, too, the measurement data for smaller zinc sulphate concentrations (here <0.06 mol/kg) deviated significantly. It is approximately the concentration above which, according to the authors, the inherent solubility of Hg_2SO_4 becomes noticeable. The measured cell voltages of STERNBERG and DRĂGĂNOIU (1984) were only available as a difference to an unnamed standard cell potential. The values were not used. The strongly scattering measured values of STERNBERG et al. (1980) were also excluded.

Tab. 8.5 Potentiometric measurements on zinc sulphate solutions

Source	**Zinc electrode**	**Counter electrode**
BRAY (1927)	Zn(Hg 2 phases)	$PbSO_4$ | Pb(Hg, 2 phases)
COWPERTHWAITE and LA MER (1931)	Zn(Hg 2 phases)	$PbSO_4$ | Pb(Hg, 2 phases)
MASAKI and IKKATAI (1932)	Zn(Hg 2 phases)	Hg_2SO_4 | Hg
KIELLAND (1936)	Zn(Hg 2 phases)	$PbSO_4$ | Pb(Hg, 2 phases)
ARVIA (1955)	Zn(Hg 2 phases)	Hg_2SO_4 | Hg
RASAIAH (1965)	Zn(Hg 2 phases)	$PbSO_4$ | Pb(Hg, 2 phases)
STERNBERG et al. (1980)	Zn	$PbSO_4$ | Pb
STERNBERG and DRĂGĂNOIU (1984)	Zn(Hg 2 phases)	Hg_2SO_4 | Hg

The following studies were also not included, as they were measurements with transition potential: HASS and JELLINEK (1932), WOLTEN and KING (1949), PURSER and STOKES (1951), LANG and KING (1954).

The measured values of MALATESTA and ZAMBONI (1997) also came from a concentration cell with transition potential, but they covered the otherwise little studied lowest concentration range well.

8.2.3 Evaluation

The thermodynamic properties of zinc sulphate solutions have also been studied in detail by ALBRIGHT et al. (2000). In their review article, parameters for an extended Pitzer equation were derived, which, however, are not compatible with the original formalism. The parameters were therefore re-determined (Tab. 8.9). It proved advantageous to increase the value for $\alpha^{(2)}$ slightly to 20 (instead of 14). This allowed a considerably better description of the lower concentration range. The agreement between experimental and calculated values is good to very good over the entire concentration range. Stronger deviations could only be observed with supersaturated zinc sulphate solutions (> 3.5 mol/kg) (Fig. 8.4, Fig. 8.5).

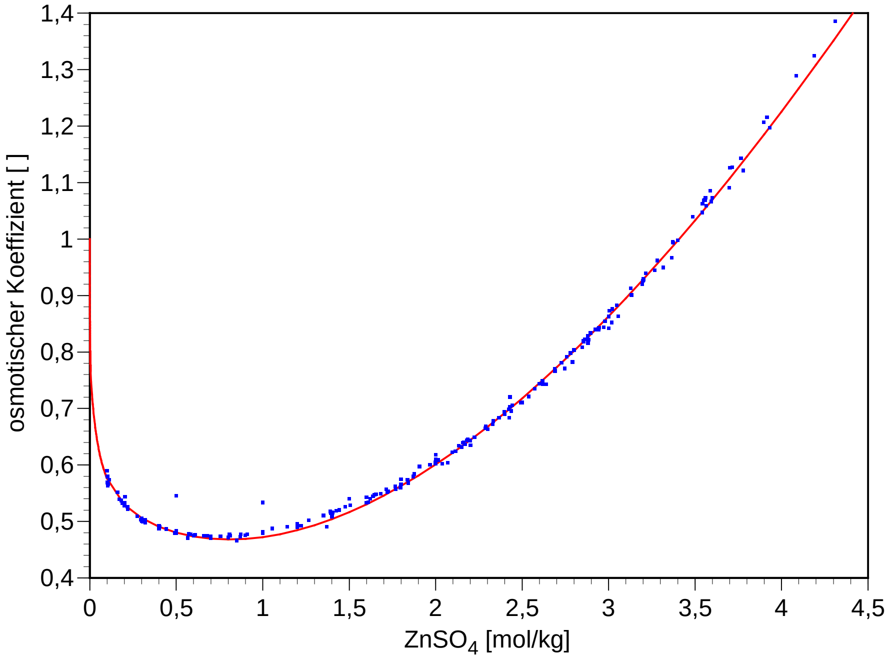

Fig. 8.4 Experimental (dots) and calculated (line) osmotic coefficients in the $ZnSO_4 - H_2O$ system at 25°C

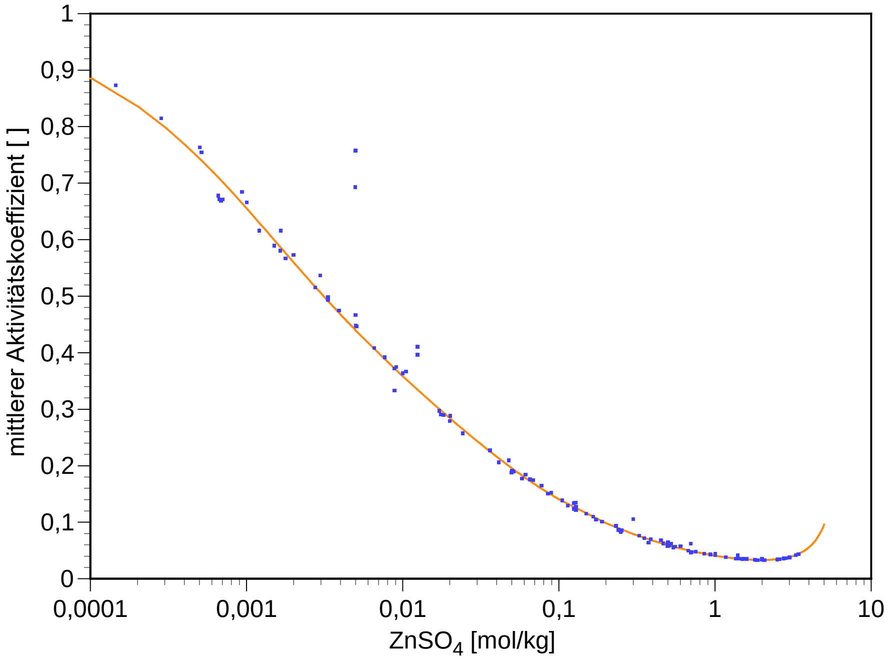

Fig. 8.5 Experimental (dots) and calculated (lines) mean activity coefficients in the system $ZnSO_4 - H_2O$ at 25°C

8.2.4 Solid phases

At 25 °C, a saturated zinc sulphate solution is in equilibrium with the thermodynamically stable solid phase goslarite ($ZnSO_4\cdot 7H_2O$). At about 38-39 °C, the compound loses one molecule of water and changes into bianchite ($ZnSO_4\cdot 6H_2O$). The latter can also appear as a metastable phase at 25 °C. When the transition to gunningite ($ZnSO_4\cdot H_2O$) occurs is disputed in the literature. The measured values range from 48 to about 70 °C. In a critical compilation, ZDANOVSKIJ et al. (1963) derived a value of 51.5 °C. Further, metastable phases are $ZnSO_4\cdot 4H_2O$ (known as a solid solution with Mg^{2+} as the mineral boyleite, WALENTA 1978) and $ZnSO_4\cdot 2H_2O$. The anhydrous zinc sulphate $ZnSO_4$, known as the mineral phase zincosite, does not occur under normal conditions.

For the solubility of $ZnSO_4\cdot 7H_2O$ at 25.0 °C the values listed in Tab. 8.7 were found. The mean value is 3.573 ± 0.007 mol/kg. At this concentration, an average activity coefficient $\gamma_\pm$ of 0.0465 and a water activity a_W of 0.8725 are calculated with the above parameters, resulting in the solubility constant of goslarite:

$$\log K\ (ZnSO_4\cdot 7H_2O) = -1.9744$$

Bianchite, $ZnSO_4\cdot 6H_2O$, which is only metastable at 25 °C, has a solubility of 3.94 ± 0.01 mol/kg (Tab. 8.6). With an average activity coefficient of 0.0536 and a water activity of 0.8442, the solubility constant is

$$\log K\ (ZnSO_4\cdot 6H_2O) = -1.859$$

Tab. 8.6 Solubility of bianchite, $ZnSO_4\cdot 6H_2O$ in water at 25°C

$ZnSO_4$ [wt. -%]	$ZnSO_4$ [mol/kg]	Source
38.93	3.948	COHEN and SINNIGE (1909)
38.80	3.927	BURY (1924) 24.90 °C
38.86	3.937	BURY (1924) 25.18 °C
39.9 ± 0.1	**3.94 ± 0.01**	**Mean value**

Tab. 8.7 Solubility of goslarite, $ZnSO_4 \cdot 7H_2O$ in water at 25 °C

$ZnSO_4$ [wt. -%]	**$ZnSO_4$ [mol/kg]**	**Source**
35.30	3.379	Tobler (1855)
36.67	3.586	Cohen (1900)
36.12	3.502	Cohen and Sinnige (1909)
37.00	3.638	Lipscomb and Hulett (1916)
36.49	3.559	Cohen and Hetterschij (1925)
36.22	3.517	Caven and Johnston (1928)
36.70	3.591	Palitzsch (1928)
36.60	3.576	Caven and Gardner (1933)
36.67	3.586	Schröder (1936)
36.72	3.594	Hill and Taylor (1938)
36.80	3.606	Copeland and Short (1940)
36.40	3.545	D'Ans and Kaufmann (1957)
36.63	3.580	Shevchuk and Kost' (1967)
36.49	3.559	Shevchuk and Moshinski (1969)
36.37	3.540	Balarev et al. (1973)
36.69	3.590	Ojkova et al. (1976)
36.74	3.597	Bursa and Stanisz-Lewicka (1981)
36.60	3.576	Filippov et al. (1982)
36.63	3.580	Filippov et al. (1985)
36.52	3.563	Proskurina et al. (2001)
36.58 ± 0.05	**3.573 ± 0.007**	**Mean value**

8.3 The binary system $Zn(ClO_4)_2 - H_2O$

Kim and Frederick (1988) also published ion interaction coefficients for this system based on smoothed data from Goldberg (1981). Primary measurement data were first published by Stokes and Levien (1946). From this work we used only the isopiestic data, while discarding the potentiometric measurements obtained in cells with transition potential. Stokes and Levien used potassium chloride and sulphuric acid as reference solutions, whose concentrations we converted into water activities using the regression functions of Archer (1999) and Rard et al. (1976) and Rard (1983), respectively. Further measurement data came from Libus and Sadowska (1970), but they only gave the already calculated water activities, not isopiestic concentrations of the reference solutions. We therefore refrained from evaluating their measured values.

The agreement between the measured osmotic coefficients of STOKES and LEVIEN (1946) and the calculated values are very good if the following ionic interaction parameters are used:

$\beta^{(0)} = 0.51678$

$\beta^{(1)} = 1.6891$

$C^{\gamma} = 0.00303$

Above 2 mol/kg $Zn(ClO_4)_2$ the results of LIBUS and SADOWSKA (1970) deviate significantly (Fig. 8.6).

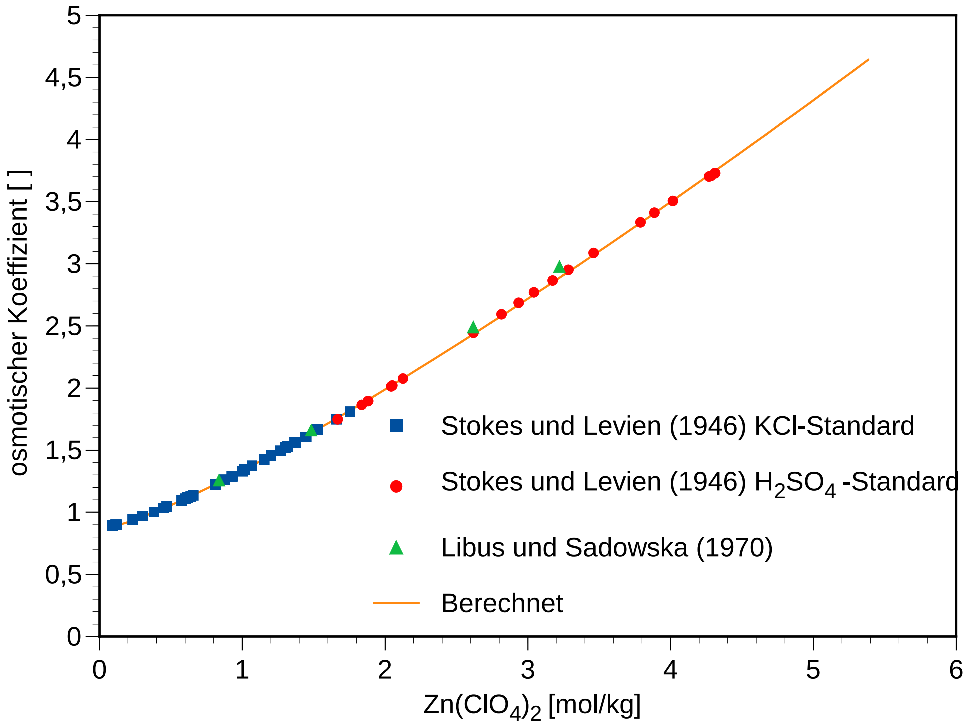

Fig. 8.6 Experimental and calculated osmotic coefficients of $Zn(ClO_4)_2$ solutions at 25.0 °C

8.4 The binary system $Zn(NO_3)_2 – H_2O$

The parameters calculated by KIM and FREDERICK (1988) were based on smoothed data from Goldberg (1981). Our evaluation, on the other hand, used the existing experimental basic data at 25 °C: the isopiestic measurements of STOKES and LEVIEN (1946) and MOTORNAJA et al. (1969) and additionally the direct vapour pressure measurements of JAKIMOV and GUŽAVINA (1971). The data sets agree well with each other, whereby the measured values of JAKIMOV and GUŽAVINA (1971) are somewhat lower. Nevertheless, they were used to obtain the following Pitzer coefficients:

$\beta^{(0)} = 0.32427$

$\beta^{(1)} = 2.02334$

$C^{\gamma} = -0.00296$

The agreement between the measured values and the osmotic coefficients calculated with the newly determined ion interaction parameters is very good (Fig. 8.7).

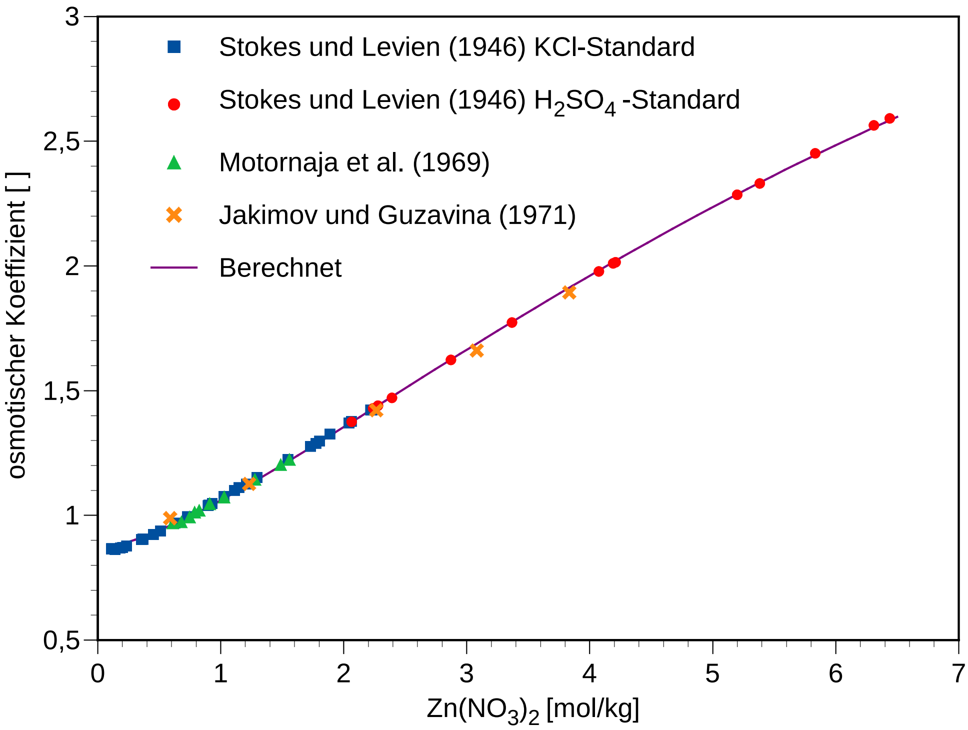

Fig. 8.7 Experimental and calculated osmotic coefficients of $Zn(NO_3)_2$ solutions at 25.0 °C

8.5 The system $ZnCl_2 – ZnSO_4 – H_2O$

The solubility equilibria in the $ZnCl_2 – ZnSO_4 – H_2O$ system were investigated by D'ANS and KAUFMANN (1957), SHEVCHUK and MOSHINSKI (1969), MOSHINSKII (1975), BURSA and STANISZ-LEWICKA (1981) and BOUCHACOURT et al. (1977b) at 27 °C. According to the authors' unanimous statements, only binary compounds occur in the system. Besides $2ZnCl_2·3H_2O$, these are the three zinc sulphate hydrates $ZnSO_4·7H_2O$, $ZnSO_4·6H_2O$ and $ZnSO_4·H_2O$. The stability field of $ZnSO_4·6H_2O$ is somewhat unclear. BURSA and STANISZ-

LEWICKA (1981) could only locate it between 5.6 and 5.9 mol/kg ZnCl, while both D'ANS and KAUFMANN and BOUCHACOURT et al. assume a range between about 5 and 7.5 mol/kg. Furthermore, $ZnSO_4 \cdot 4H_2O$ is observed as a metastable phase at about 6 mol/kg $ZnCl_2$. SHEVCHUK and MOSHINSKI, on the other hand, did not find any other phases besides $2ZnCl_2 \cdot 3H_2O$ and $ZnSO_4 \cdot 7H_2O$, but did not investigate the range of lower hydrate zinc sulphates in more detail. In a later paper, MOSHINSKII (1975) announced that a new investigation of the system had now also revealed the occurrence of $ZnSO_4 \cdot 6H_2O$, but contradictions occur in the article with regard to the concrete figures, so that it is not clear at which $ZnCl_2$ concentration the transition between the hydrate phases takes place. The potentiometric measurements of ESPARZA et al. (1993) for four equimolar $ZnCl_2$-$ZnSO_4$ solutions could not be reproduced.

Only measuring points with a $ZnCl_2$ concentration of less than 6 mol/kg were included in the data evaluation. The optimised interaction parameter $\psi_{Zn,Cl,SO4}$ is 0.0272. After the completion of our measurements and model development, isopiestic measurements were also published by NINKOVIĆ et al. (2007). They were not included in the data evaluation.

The solubility data could be followed well up to a $ZnCl_2$ concentration$_2$ of 5 mol/kg. The transition point between $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$ was obtained at 2.67 mol/kg $ZnCl_2$. The solubility curves of the two hydrates lie very flat on top of each other, so that the slightest changes in the parameters lead to considerable shifts. The isoactivity curves from our study are also well reproduced (Fig. 8.8).

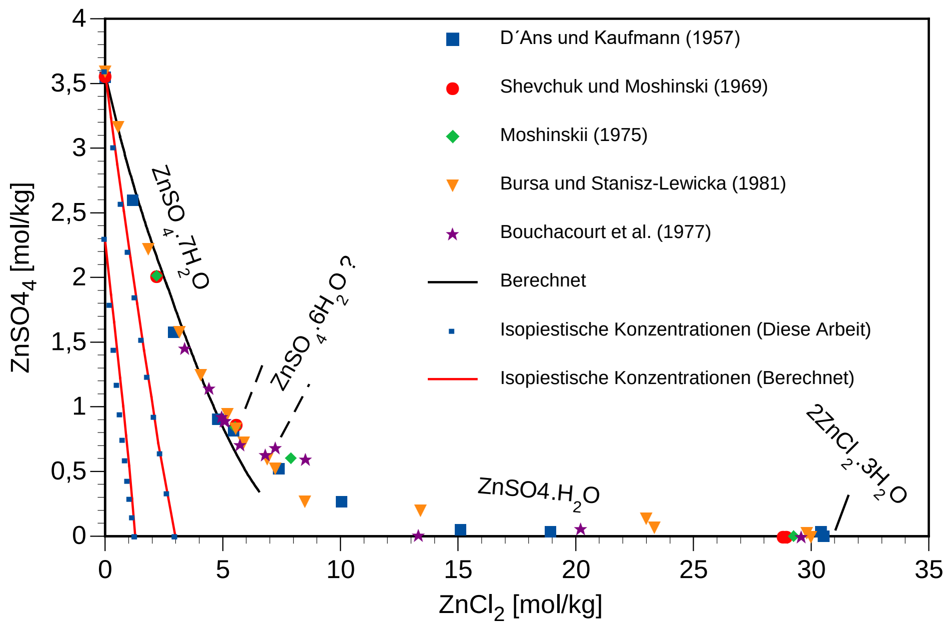

Fig. 8.8 Experimental and calculated phase equilibria in the $ZnCl_2 - ZnSO_4 - H_2O$ system at 25 °C

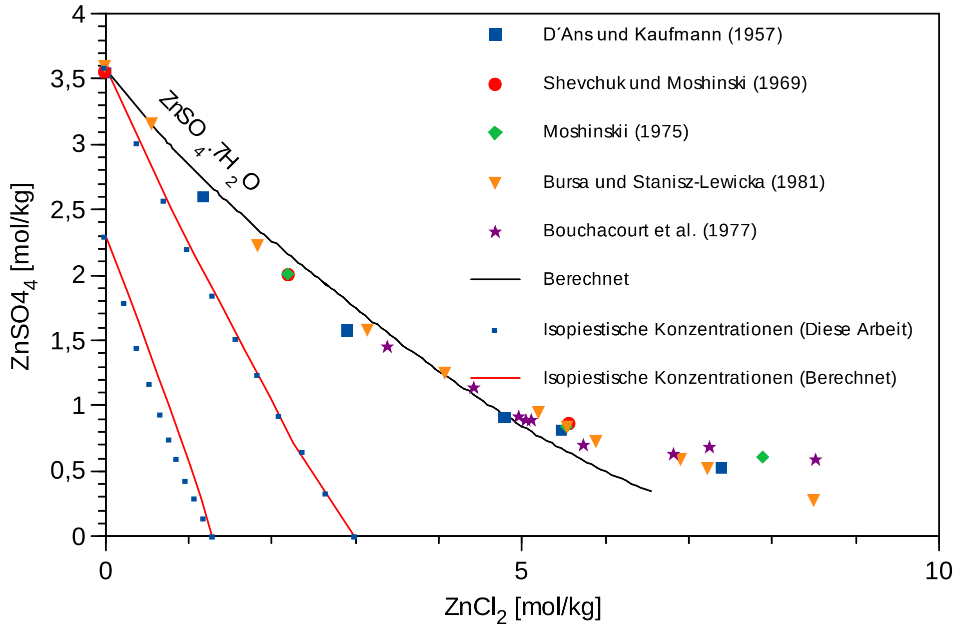

Fig. 8.9 Experimental and calculated phase equilibria in the system $ZnCl_2 - ZnSO_4 - H_2O$ at 25 °C (detail)

8.6 The system $ZnCl_2$ – NaCl – H_2O

According to the findings of SHEVCHUK and MOSHINSKII (1969), the double salt $Na_2ZnCl_4 \cdot 3H_2O$ forms in this system in addition to NaCl and $ZnCl_2 \cdot 1.5H_2O$. Already

Ephraim (1908) could not obtain a compound $NaZnCl_3$ analogous to the potassium containing system. The results were confirmed by Bouchacourt et al. (1977a) at a slightly different temperature (27°C). Filippov et al.[10] also investigated the solubilities in this system. Their data were mentioned and used as personal communication in Anstiss and Pitzer (1991), but later never published. Thanks to a personal communication from Rumyantsev, these data from the original investigator (Popov 1989) were made available to us[11]. Because of Rumyantsev's doubts about the quality, we do not use the data for parameter determination for the time being. Nevertheless, it remains to be noted that Popov (1989) found the same phase sequence as Shevchuk and Moshinskii (1969), and no systematic deviation between the two data sets could be detected. More recent studies, published after the parameter set was developed, were undertaken by Belova et al. (2016), Zhang et al. (2020) and Demirci et al. (2021). Some isopiestic measurements were made by Stokes (1948a). The isopiestic concentrations of their reference solutions and the calculated vapour pressure reductions were not published. A smaller number of potentiometric measurement data was provided by Brüll (1934b), whose results, however, could not be reproduced and therefore remained unconsidered. In addition, isopiestic data from the present study were considered (see above).

The two systems $ZnCl_2$-NaCl-H_2O and $ZnSO_4$-Na_2SO_4-H_2O are described by the parameter group $\theta_{Zn,Na}$, $\psi_{Zn,Na,Cl}$, and $\psi_{Zn,Na,SO4}$. It was shown that no ternary parameter would be necessary to reproduce the solubility curve in the system $ZnSO_4$-Na_2SO_4-H_2O. The agreement between measured and experimental curve was very good. However, for the second system, $ZnCl_2$-NaCl-H_2O, the introduction of and $\theta_{Zn,Na}$ and $\psi_{Zn,Na,Cl}$ was necessary. Neither with $\theta_{Zn,Na}$ nor with $\psi_{Zn,Na,Cl}$ alone could our isopiestic measurement curves be reproduced in a closed manner. It was not possible to calculate a continuous isoactivity line for the water activity 0.7542, the calculated curve broke out to infinite concentrations. The consideration of one parameter $\theta_{Zn,Na}$ leads to a significant improvement of the modelling of the system $ZnCl_2$-NaCl-H_2O (Fig. 8.10), but to a clear deterioration of the modelling quality of the system $ZnSO_4$-Na_2SO_4-H_2O. In the end, all three ternary interaction parameters had to be optimized, as otherwise modelling of zinc-rich and NaCl-rich solutions would not have been possible at all. For the double salt $Na_2ZnCl_4\cdot 3H_2O$, there were no consistent values for the solubility constant.

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[10] Filippov V. K., Rumjancev A. V. and Popov, A. S., unpublished data. According to information from Rumjancev (personal communication), the isopiestic experiments carried out in the same work by Popov had systematic errors and were therefore never published.

[11] The data are listed in the appendix (Tab. 13.15, S. 490)

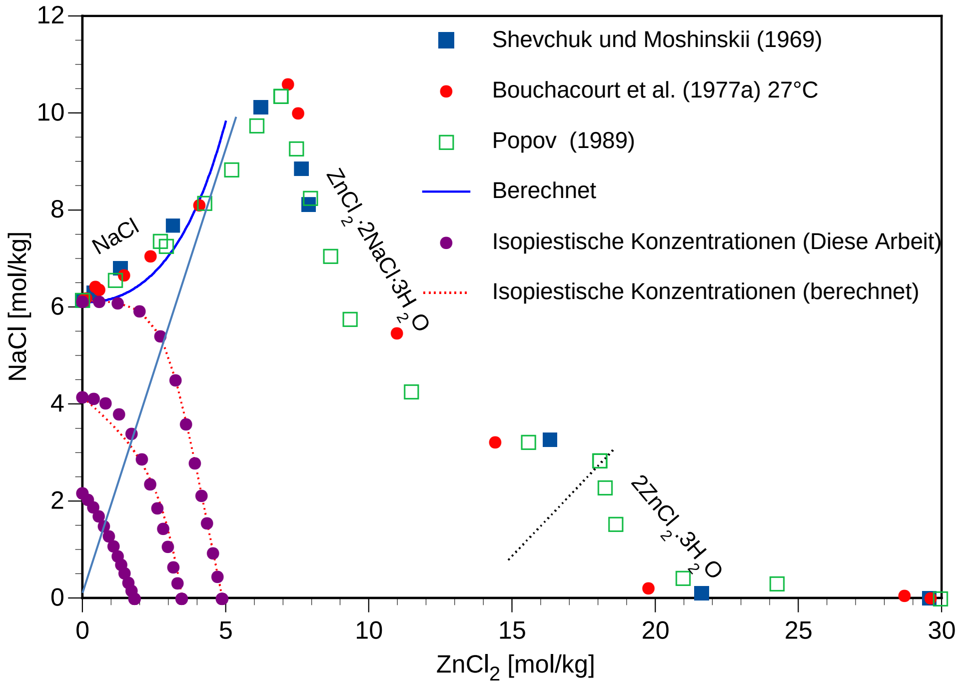

Fig. 8.10 Experimental and calculated phase equilibria in the system $ZnCl_2$-NaCl-H_2O at 25°C

8.7 The system $ZnCl_2 – KCl – H_2O$

The phase equilibria in this system were investigated by LIPSCOMB and HULLET (1916) and by D'ANS and KAUFMANN (1957). Up to a $ZnCl_2$ concentration of about 7 mol/kg, the results agree very well. Sylvite (KCl) occurs as the solid phase. At concentrations above 7 mol/kg $ZnCl_2$, LIPSCOMB and HULLET (1916) found a double salt. However, it is not clear from their article whether they meant $ZnCl_2·2KCl$ or $ZnCl_2·2KCl·6H_2O$. Contrary to these findings, the KCl branch found by D'ANS and KAUFMANN (1957) continues for some time and reaches a new equilibrium with anhydrous $ZnCl_2·2KCl$ (also known as flinteite) at just under 11 mol/kg $ZnCl_2$. This salt occupies only a narrow area in the solution system and reaches the stability limit of the compound $ZnCl_2·KCl·2H_2O$, also known as the mineral cryobostryxite, at 12 mol/kg (PEKOV et al. 2015). $ZnCl_2·2KCl_2$ is metastable up to at least 15 mol/kg. $ZnCl_2·KCl·2H_2O$ changes to $ZnCl_2·KCl·H_2O$ above 24 mol/kg $ZnCl_2$. From 33 mol/kg, D'ANS and KAUFMANN found three more phases: the solid solution $(Zn,K_2)Cl_2$ and the zinc chloride hydrates $ZnCl_2·H_2O$ and $2ZnCl_2·3H_2O$.

In addition to these solubility measurements, potentiometric measurements by BRÜLL (1934b) were available. Furthermore, some vapour pressure determinations were also carried out: Potassium chloride - zinc chloride mixed solutions were investigated by

SARNOWSKI and ŚCIEŃSKA (1960) and later also by MAZGAJ et al. (1965) using the isopiestic method. In their publication, however, there is only a graphical representation of the results.

Some isopiestic measurements were made by STOKES (1948a). Unfortunately, the publication only contains the calculated vapour pressure reductions, not the isopiestic concentrations of the reference solutions used. Nevertheless, the data were used. The new isopiestic measurements from the present study complemented the existing data very well.

The isoactivity lines are strongly curved in the $ZnCl_2-KCl-H_2O$ system - an indication of the strongly pronounced complex formation. The development of a suitable parameter set caused extraordinary problems. In order not to endanger the modelling of the simultaneously evaluated system $ZnSO_4-K_2SO_4-H_2O$, the measurement data used for parameter determination were limited to solutions with a maximum of 6 mol/kg $ZnCl_2$.

With the determined interaction parameters, the isopiestic data and the solubilities could be reconstructed up to a $ZnCl_2$ concentration of about 4 mol/kg. Already the isoactivity curve at $a_W = 0.7933$, ($c_{ZnCl2} = 4.3$ mol/kg) can no longer be calculated consistently because a numerical divergence occurs. Up to this concentration, the agreement between experimental and calculated data is good (Fig. 8.11). For the Zn-K double salts a determination of the solubility constants was not possible.

Compounds occurring in the system were also found in similar form as minerals:

- Mellizinkalite, $K_3Zn_2Cl_7$: (PEKOV et al. 2015c)
- Flinteite, K_2ZnCl_4 (PEKOV et al. 2015b)
- Cryobostryxite, $KZnCl_3{\cdot}2H_2O$ (PEKOV et al. 2015a)

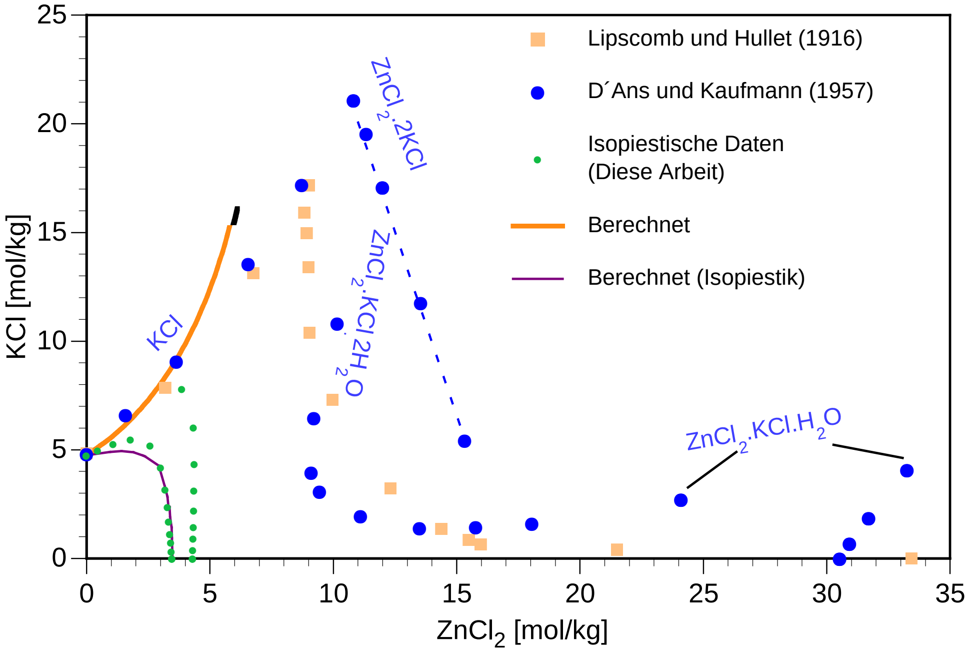

Fig. 8.11 Experimental and calculated phase equilibria in the system $ZnCl_2$ – KCl – H_2O at 25°C

8.8 The system $ZnCl_2$ – $MgCl_2$ – H_2O

The solubilities in this system have been studied so far by BALAREV and SPASOV (1980) and later by ZHANG et al. (2020)[12]. Besides magnesium chloride and zinc chloride, the double salt $ZnCl_2 \cdot MgCl_2 \cdot 5H_2O$ occurs. The data scattered strongly. The solubility of magnesium chloride determined by BALAREV and SPASOV is about 5% higher than other tabulated data (D'ANS, 1933).

Some isopiestic measurements were made by STOKES (1948a). Supplementary isopiestic measurements were produced in the present study (see above).

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[12] Published after the end of the original evaluations and therefore not considered further

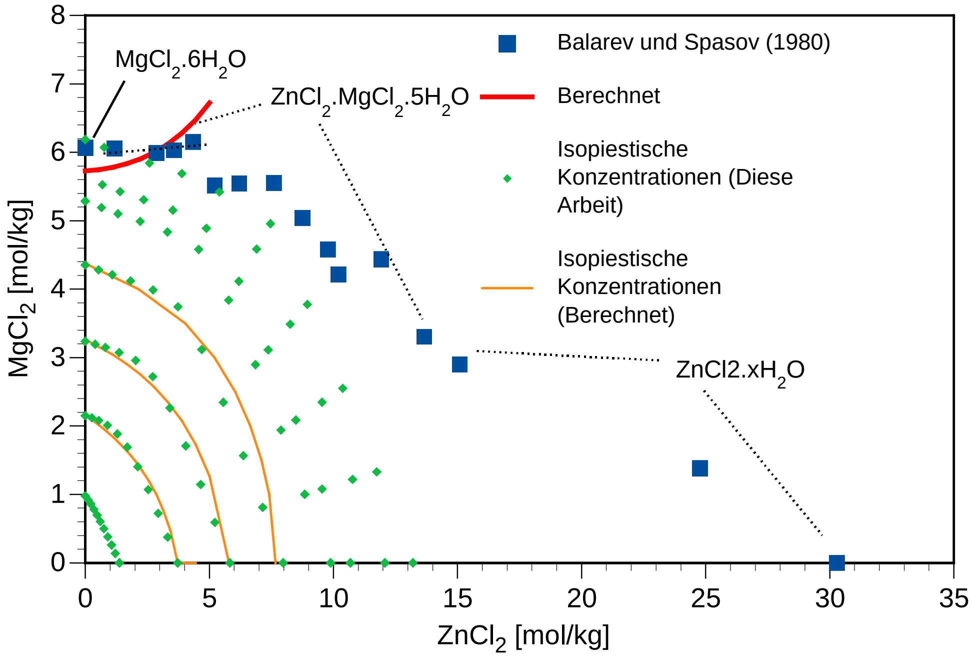

Fig. 8.12 Experimental and calculated phase equilibria in the system $ZnCl_2 – MgCl_2 – H_2O$ at 25°C

The curves of the isoactive concentrations could be reproduced well up to a water activity of 0.52 (Fig. 8.12). This corresponds to solutions with a maximum of 8 mol/kg $ZnCl_2$. For the Zn-Mg double salt a determination of the solubility constants was not possible.

8.9 The system $ZnCl_2 – CaCl_2 – H_2O$

Mineral formations in this system were first observed by Ephraim and Model (1910), who reported two double salts: $CaCl_2·ZnCl_2·5.5H_2O$ (according to them probably with a lower real water content because the compound was very hygroscopic) and $2CaCl_2·ZnCl_2·6H_2O$. Both compounds form when concentrated $CaCl_2/ZnCl_2$ solutions are concentrated above H_2SO_4 and only after larger amounts of $CaCl_2$ have already been precipitated.

Systematic solubility studies were carried out by Čižikov and Šachov (1936) and Hudgins (1964). Hudgins observed two calcium chloride hydrates ($CaCl_2·6H_2O$ and $CaCl_2·4H_2O$), an unspecified zinc chloride and a double salt $CaCl_2·ZnCl_2·5H_2O$ in the system. In contrast, Čižikov and Šachov found only calcium chloride over the entire concentration range. Moreover, the solubilities listed by them were regularly higher than those of Hudgins. Probably the chosen reaction time of only 2-3 hours was not sufficient to allow the formation of a double salt. The solubility curve found by Čižikov and Šachov must therefore be regarded as metastable. There are also some potentiometric measurements for mixed solutions of $CaCl_2$/$ZnCl_2$ by Robinson and Farrelly (1947). However, since they only indicated molarities and not densities, an evaluation must be omitted. New isopiestic data were added in the present study (see above). The calculated solubility curve up to about 6 mol/kg $ZnCl_2$ lies in the range of the strongly scattering experimental data of Čižikov and Šachov (1936). Since the parameter set of Harvie et al. (1984) is only conditionally applicable at the high $CaCl_2$ concentrations, a better result was not to be expected. The isoactivity lines are satisfactorily reproduced up to a water activity of 0.68 (c_{ZnCl2} max 6 mol/kg). At higher concentrations considerable deviations become noticeable. For the Zn-Ca double salt, a determination of the solubility constants was not possible.

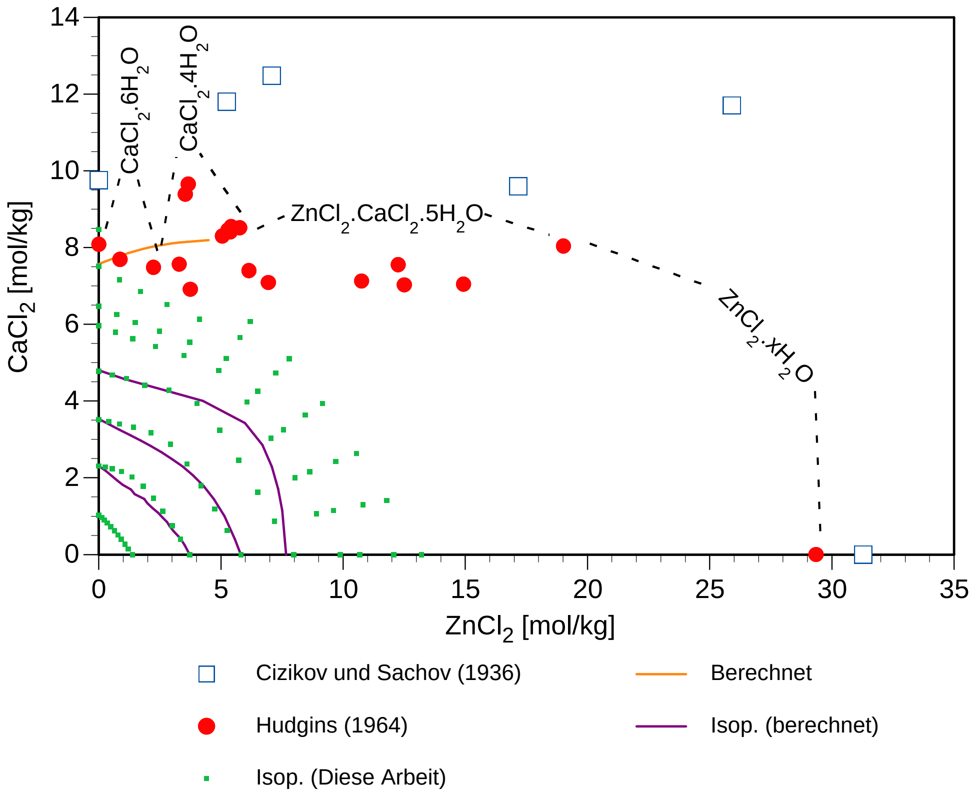

Fig. 8.13 Experimental and calculated phase equilibria in the system $ZnCl_2$ – $CaCl_2$ – H_2O at 25 °C

8.10 The system $ZnSO_4 – Na_2SO_4 – H_2O$

Solubility studies of this system at 25 °C were available from KOPPEL (1905), CAVEN and JOHNSTON (1928,1929), SHEVCHUK and MOSHINSKI (1970), VEVERCA and KUČOVÁ (1979) and FILIPPOV et al. (1985). In Fig. 8.14 the study by BOUCHACOURT et al. (1977a, 1977b) at 27 °C is also entered. The double salt $ZnSO_4·Na_2SO_4·4H_2O$ occurring in the system was described as zinc bloedite (SABELLI and TROSTI-FERRONI, 1985), but was later described as the mineral changoite (SCHLÜTER et al. 1999).

The measured values of the authors agreed very well, but the results of VEVERCA and KOČOVÁ (1979) scattered quite strongly. The two points provided by SHEVCHUK and MOSHINSKI (1970) deviated very strongly and were not taken into account. The strongly increased sodium sulphate solubilities of BOUCHACOURT et al. (1977a, 1977b) can be attributed to the large temperature dependence of the solubility of mirabilite, $Na_2SO_4·10H_2O$

FILIPPOV et al. (1985) also provided isopiestic measurements. No isopiestic concentrations of the NaCl reference solutions were given, only the calculated osmotic coefficients. Further measurements were available from MARJANOVIĆ et al. (2005). The measured cell voltages of STERNBERG and DRĂGĂNOIU (1984) were only available as a difference to an unnamed standard cell potential.

For the parameter determination, only the isopiestic data and solubility data with binary salts as equilibrium phases were considered. For the double salt $ZnSO_4·Na_2SO_4·4H_2O$ the following solubility constant was obtained:

$$\log K (ZnSO_4·Na_2SO_4·4H_2O) = -3.41$$

The agreement between experimental and calculated data (Fig. 8.14) is good to very good.

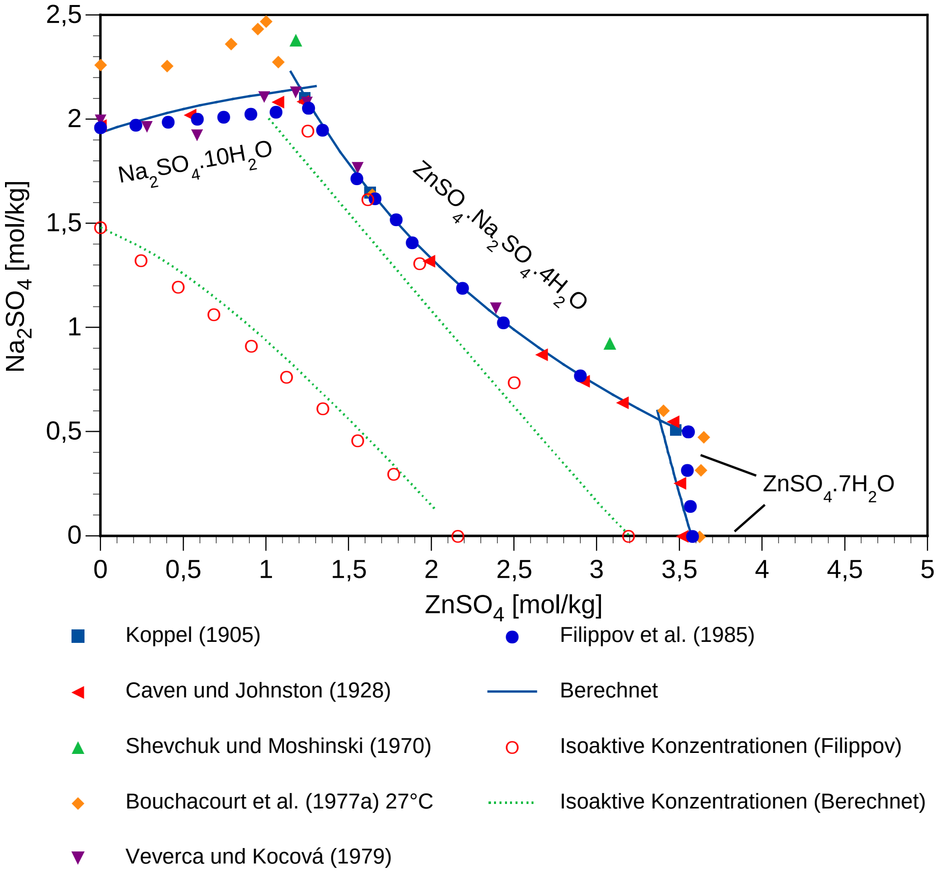

Fig. 8.14 Experimental and calculated phase equilibria in the $ZnSO_4$-Na_2SO_4-H_2O system at 25 °C

8.11 The system $ZnSO_4 – K_2SO_4 – H_2O$

The phase equilibria were investigated by LIPSCOMB and HULETT (1916), CAVEN and JOHNSTON (1926a, 1926b), D'ANS and KAUFMANN (1957), SHEVCHUK and PILIPCHENKO (1970), TUCHTAJEV et al. (1978) and FILIPPOV et al. (1982). These were supplemented by solubility experiments on the double salt $ZnSO_4·K_2SO_4·6H_2O$ by LOCKE (1902) and HILL et al. (1940). However, the data of LOCKE (1902) were only available in molarity units.

As with other systems, the measured values of SHEVCHUK and PILIPCHENKO (1970) deviated significantly from the rest and are therefore discarded. Below 1.5 mol/kg $ZnSO_4$, the measured solubilities agreed very well. Near the invariant point $ZnSO_4·7H_2O$/ $ZnSO_4·K_2SO_4·6H_2O$ /saturated solution, the data divided into two clearly distinguishable groups. While LIPSCOMB and HULETT (1916) as well as FILIPPOV et al. (1982) found a K_2SO_4 solution concentration of about 0.13 mol/kg for the point, CAVEN and JOHNSTON

(1926a, 1926b), D'ANS and KAUFMANN (1957) and TUCHTAJEV et al. (1978) consistently reported 0.17 mol/kg. These latter authors have in common that they provided only few solubility data for the branch of the double salt. It is therefore not clear at what concentration their solubility curves separate from those of LIPSCOMB and HULETT as well as FILIPPOV. The double salt $ZnSO_4 \cdot K_2SO_4 \cdot 6H_2O$ occurring in this system has a schoenite structure (EGLI, 1948), and can therefore be called zinc schoenite.

Supplementary potentiometric measurements by BRÜLL (1934b) and STERNBERG and DRĂGĂNOIU (1984) were available. In the publications, not the measured cell potentials are given, but only their differences to an unnamed standard cell potential. The data fluctuated strongly and could not be brought into agreement with isopiestic measurements. They were discarded.

Because of these uncertainties, the parameter determination was initially based exclusively on the isopiestic measurements of FILIPPOV et al. (1982). Subsequently, the activity product was determined for those solutions that are in equilibrium with the double salt $ZnSO_4 \cdot K_2SO_4 \cdot 6H_2O$. This did not result in constant values. Instead, the products followed a trend (Fig. 8.15), from which the following average solubility constant results:

log K ($ZnSO_4 \cdot K_2SO_4 \cdot 6H_2O$) = -5.95 ± 1[13]

The complex formation of zinc with sulphate or the formation of a ternary ion pair/ complex may be the reason for this behaviour.

The calculated solubility curves follow the experimental values very well (Fig. 8.16). It is clear that the measured potassium sulphate concentrations (at c_{ZnSO4}around 3.5 mol/kg) were too high in CAVEN and JOHNSTON (1926a, 1926b), D'ANS and KAUFMANN (1957) and TUCHTAJEV et al. (1978).

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[13] In the original version of this report the ln K was given instead of the log K value

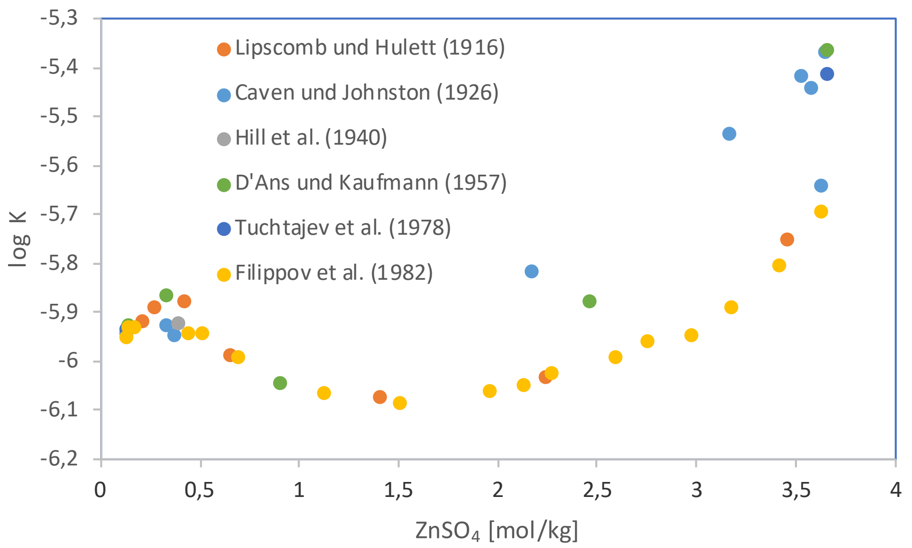

Fig. 8.15 Calculated solubility constant for $ZnSO_4 \cdot K_2SO_4 \cdot 6H_2O$

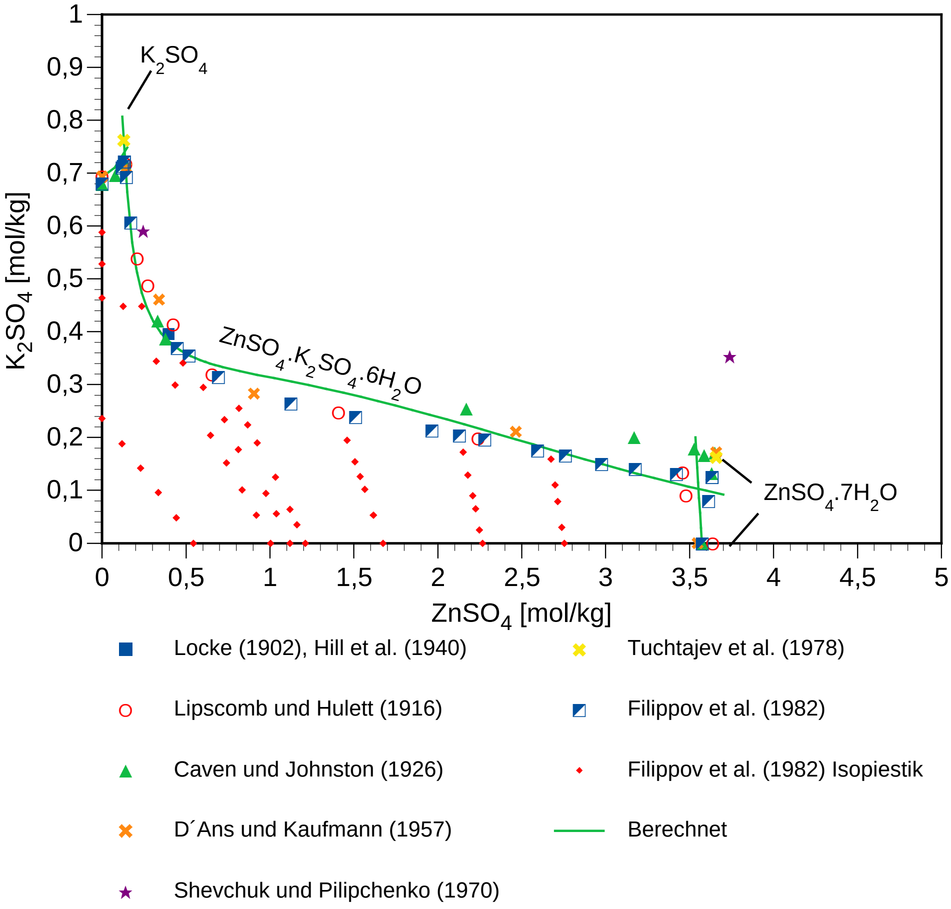

Fig. 8.16 Experimental and calculated phase equilibria in the system $ZnSO_4 – K_2SO_4 – H_2O$ at 25 °C

8.12 The system $ZnSO_4 - MgSO_4 - H_2O$

At 25 °C, the system $ZnSO_4 - MgSO_4 - H_2O$ forms a homogeneous series of solid solutions of the composition $(Zn,Mg)SO_4 \cdot 7H_2O$. SHEVCHUK and KOST' (1967), BALAREV et al. (1973), OIKOVA ET AL. (1976), OJKOVA (1979) and PROSKURINA et al. (2001) provided largely consistent studies on this. The work of GIRIČ et al. (1976, cited in TUCHTAEV and KUCHAROV, 1983) on the same subject was not obtainable. The solid solutions were observed up to 45 °C.

Lower hydrated forms are also found in nature such as the boyleite, $(Zn,Mg)SO_4 \cdot 4H_2O$ (WALENTA, 1978, SABELLI and TROSTI-FERRONI, 1985). However, little is known about their conditions of existence and formation. The compound loses water rapidly in dry air and changes into the monohydrate.

The solubility data cannot be used to determine ion interaction parameters as long as the solid activities of the components in the solid solution are unknown. However, isopiestic data on this system are available from PROSKURINA et al. (2001). Mixed zinc sulphate-magnesium sulphate solutions have also already been investigated by OIKOVA et al. (1976). However, the publication only contains the calculated activity coefficients for both components, not their concentrations.

Supplementary potentiometric measurements by STERNBERG and DRĂGĂNOIU (1984) are available. In the publication, not the measured cell potentials are given, but only their differences to an unnamed standard cell potential. The measured values scattered strongly and were not used. The experimental isoactivity curve was very well reproduced by the calculation. Assuming that goslarite ($ZnSO_4 \cdot 7H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$) form an ideal solid solution, the solubility curve is very close to the experimental values (Fig. 8.17).

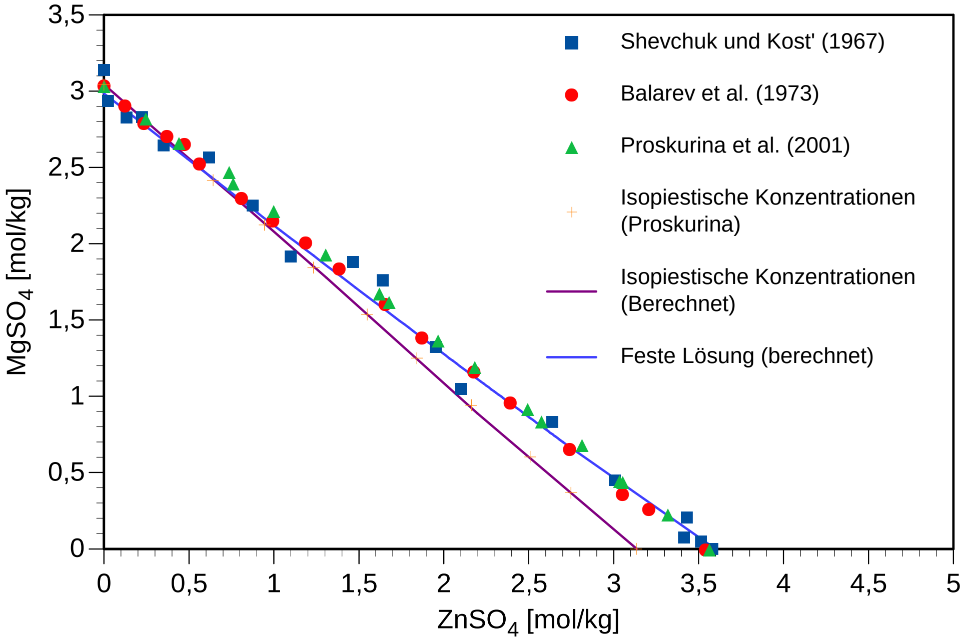

Fig. 8.17 Experimental and calculated phase equilibria in the $ZnSO_4 - MgSO_4 - H_2O$ system at 25 °C

8.13 The system $ZnSO_4 - CaSO_4 - H_2O$

The solubility of calcium sulphate in zinc sulphate solutions at 25 °C has so far been investigated by MUTALA et al. (1988) in the concentration range up to 0.6 mol/kg and by UMETSU et al. (1989) with two data points. From the measured values of KRUPKOWA and SOSNOWSKI (1994) at 20 and 30 °C, solubilities for 25 °C can be interpolated. Both series of measurements are only available in molarities. They were converted into molalities by taking into account the density data in equation (12.5) (p. 361) for $CaSO_4$-saturated $ZnSO_4$ solutions. In each case, gypsum occurred as the solid phase ($CaSO_4 \cdot 2H_2O$). Due to the weak data situation, some supplementary solubility experiments were conducted (Tab. 8.8). The solubility curve passes through an early minimum at about 0.1 mol/kg $ZnSO_4$, rises again to values around 0.16 mol/kg Ca and drops again slightly at higher zinc sulphate concentrations (> 2 mol/kg). The $CaSO_4$ solubilities of KRUPKOWA and SOSNOWSKI (1994) are up to 30% higher than our values and the results of UMETSU et al. (1989) over the entire measuring range. We could not find an explanation for this. Their values were not taken into account in the evaluation. After the end of the parameter determination, we received the measurement results of WOLLMANN and VOIGT (2008). They largely agreed with our measurement results, although their measurement scatter is smaller. Although these data were not included in the parameter determination, the agreement between calculated and measured solubilities is good (Fig. 8.18).

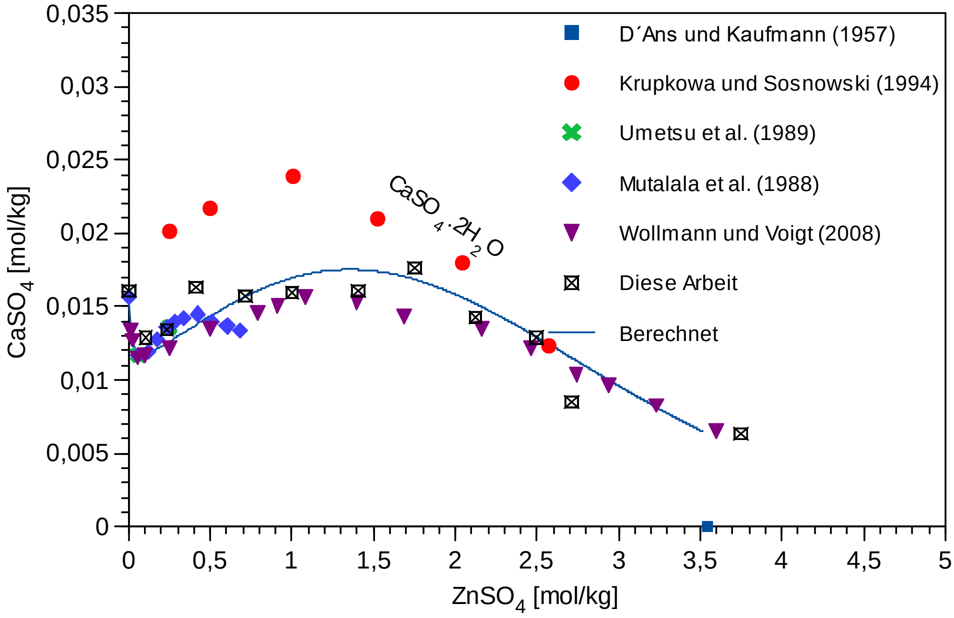

Fig. 8.18 Experimental and calculated phase equilibria in the $ZnSO_4$-$CaSO_4$-H_2O system at 25°C

Tab. 8.8 Experimental solubilities in the system $ZnSO_4$-$CaSO_4$-H_2O

$ZnSO_4$ [mol/kg]	$CaSO_4$ [mol/kg]	Density [kg/l])*
0	0.0161	0.9995
0.105	0.0129	1.0153
0.234	0.0134	1.035
0.413	0.0163	1.0612
0.716	0.0157	1.1064
1.002	0.0160	1.1466
1.405	0.0161	1.2096
1.751	0.0176	1.2598
2.122	0.0143	1.3061
2.497	0.0129	1.3447
2.715	0.00850	1.4294
3.749	0.00635	1.486

)* All solutions were in equilibrium with gypsum ($CaSO_4 \cdot 2H_2O$)

8.14 Further solid phases

The compound $3NaCl \cdot 9Na_2SO_4 \cdot ZnSO_4$ known as d'ansite is known from the literature. Lange and Burzlaff (1995) described its crystal structure. More detailed information on its stability is not available. According to IG Farbenindustrie and Kircher (1940, cited in Eiermann and Gedschold 1956, p. 1007), the non-deliquescent salt $NaCl \cdot Na_2SO_4 \cdot ZnCl_2$ can be obtained from a mixed solution of NaCl, $NaSO_4$ and $ZnCl_2$. No further information was available. A compound $ZnNaClSO_4$ comparable to kainite ($KMgClSO_4 \cdot 2.75\ H_2O$) does not exist, but an anhydrous zinc kainite $KZnClSO_4$ can be synthesised (Lužnaja 1949, later described as mineral belousovite, Siidra et al. 2018b). Another recently found mineral is majzlanite, $K_2Na(ZnNa)Ca(SO_4)_4$ (Siidra et al. 2020). Thermodynamically usable information is also lacking for these compounds.

8.15 Result overview

The following tables summarise all thermodynamic parameters and constants obtained in the course of this work.

Tab. 8.9 Binary ion interaction coefficients for zinc

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	C^{γ}
$Zn^{2+} - Cl^-$	0.06522	2	5.5187	2.5	-4.3578	0.00132
$Zn^{2+} - SO_4^{2-}$	0.18207	1.4	2.9430	20	-197.89	0.00836
$Zn^{2+} - ClO_4^-$	0.51678	2	1.6891			0.00303
$Zn^{2+} - NO_3^-$	0.32427	2	2.0233			-0.00296

Tab. 8.10 Ternary ion interaction coefficients for zinc

Ion pair	**ψ**	**θ**
$Zn^{2+} - Na^{+}$		-0.12816
$Zn^{2+} - K^{+}$		-0.31819
$Zn^{2+} - Mg^{2+}$		-0.69247
$Zn^{2+} - Ca^{2+}$		-0.16835
$Zn^{2+} - Cl^{-} - SO_4^{2-}$	0.02720	0.02
$Zn^{2+} - Na^{+} - SO_4^{2-}$	0.05260	
$Zn^{2+} - K^{+} - SO_4^{2-}$	0.08863	
$Zn^{2+} - Mg^{2+} - SO_4^{2-}$	0.22435	
$Zn^{2+} - Ca^{2+} - SO_4^{2-}$	0.07290	
$Zn^{2+} - Na^{+} - Cl^{-}$	-0.02583	
$Zn^{2+} - K^{+} - Cl^{--}$	-0.00568	
$Zn^{2+} - Mg^{2+} - Cl^{--}$	-0.02458	
$Zn^{2+} - Ca^{2+} - Cl^{--}$	-0.04623	

Tab. 8.11 Solubility constants of neutral compounds containing zinc chloride and zinc sulphate

Connection	**Reaction**	**log K**	**Mineral name**
$ZnSO_4 \cdot 7H_2O$	$ZnSO_4 \cdot 7H_2O \rightleftharpoons Zn^{2+} + SO_4^{2-} + 7H_2O$	-1.9744	Goslarite
$ZnSO_4 \cdot 6H_2O$	$ZnSO_4 \cdot 6H_2O \rightleftharpoons Zn^{2+} + SO_4^{2-} + 6H_2O$	-1.859	Bianchite
$ZnSO_4 \cdot Na_2SO_4 \cdot 4H_2O$	$ZnSO_4 \cdot Na_2SO_4 \cdot 4H_2O \rightleftharpoons$ $Zn^{2+} + 2Na^{+} + 2SO_4^{2-} + 4H_2O$	-3.41	Changoite
$ZnSO_4 \cdot K_2SO_4 \cdot 6H_2O$	$ZnSO_4 \cdot K_2SO_4 \cdot 6H_2O \rightleftharpoons$ $Zn^{2+} + 2K^{+} + 2SO_4^{2-} + 6H_2O$	-5.95	

9 Thermodynamic properties of hydroxide and carbonate compounds of cadmium

9.1 Formation of hydroxo complexes

9.1.1 Overview and procedure

Cadmium forms mononuclear and polynuclear complexes with hydroxide. The mononuclear complexes $[CdOH]^+$, $[Cd(OH)_2]^0$ and $[Cd(OH)_4]^{2-}$ have been clearly demonstrated. The complex $[Cd(OH)_3]^-$ was postulated several times (e.g., Dyrssen and Lumme 1962, Spivakovskii and Moisa 1964), but never actually found. Especially in the solubility experiments of $Cd(OH)_2$ in NaOH, one can easily do without $[Cd(OH)_3]^-$ when interpreting the results. If this species actually exists, it only occurs in non-significant amounts. Higher complexes such as $[Cd(OH)_5]^{3-}$ and $[Cd(OH)_6]^{4-}$ were postulated by Spivakovskii and Moisa (1964). They may exist in concentrated hydroxide solutions as the existence of the solid phases $Na_3[Cd(OH)_5(H_2O)]\cdot H_2O$, $Sr_2[Cd(OH)_6]$, and $Ba_2[Cd(OH)_6]$ suggests (Scholder and Staufenbiel 1941).

Multinuclear complexes such as $[CdOH_2]^{3+}$ and $[Cd_4(OH)_4]^{4+}$ were found by Biedermann and Ciavatta (1962) during the hydrolysis of concentrated cadmium solutions (>0.1 mol/kg). Baes and Mesmer (1976) also confirmed in their review that these two species are very likely to exist. They are not needed for the evaluation of thermodynamic measurements at lower cadmium concentrations. Since cadmium concentrations above 0.1 mol/kg have not been found so far even in waste leaching tests, no further treatment is given.

First, the complex formation constant for $[CdOH]^+$ was derived from potentiometric measurements. Then the solubility constant of the hydroxide modification β-$Cd(OH)_2$, which is stable at 25 °C, was estimated from solubility experiments. From this, the complex formation constant for $[Cd(OH)_2]^0$ and the dependence of its activity coefficient on the sodium perchlorate concentration could then be derived. In the last step, the simultaneous determination of the formation constants for $[Cd(OH)_4]^{2-}$ and their interaction coefficients with Na^+ and K^+ was carried out on the basis of solubility experiments.

9.1.2 The formation of the hydroxo complex $[CdOH]^+$

Complex formation with hydroxide only starts from -log c_H around 9. The first hydroxo complex, $[CdOH]^+$ is not very stable and is soon replaced by the formation of the second complex $[Cd(OH)_2]^0$ according to consistent literature data. RAI et al. (1991a) even managed to describe the behaviour of Cd^{2+} without this complex when describing their pH-dependent solubilities of $Cd(OH)_2$ in 1M $NaClO_4$. However, in the range where $[CdOH]^+$ is expected to play a significant role, their measurement curves showed only a few measurement points and also scattered strongly. The other solubility investigations are also of little help. Although the data of GÜBELI and TAILLON (1971) in particular indicates the occurrence of a complex between Cd^{2+} and $[Cd(OH)_2]^0$ in the range of -log c_H= 9 to 11, the evaluation of the measurement data is difficult because of data scattering and the calibration method of the pH electrode used, which is unclear to the authors.

For a detailed description, we relied on a broader basis. The results determined potentiometrically proved to be the most consistent. The liquid-liquid extraction or solubility measurements by DYRSSEN and LUMME (1962) as well as by GÜBELI and TAILLON (1971) did not give consistent results. As a reason, it can be stated that the measurement data in these methods fluctuate strongly in relation to potentiometric experiments. The values contributed by MIZETSKAYA et al. (1983) originated from spectrophotometric measurements on solutions containing a very large organic molecule as a competing ligand. Since no information is available on the activity coefficients of this ligand in the potassium nitrate solutions used, the evaluation of the experiments was not possible.

Due to the lack of detailed information on pH calibration and background salt concentration, the work of SANTILLAN-MEDRANO and JURINAK (1975) and ANTONETTI et al. (1976) had to be disregarded. GAYER and WOONTNER (1957) as well as RYAN et al. (1965) carried out solubility measurements with cadmium hydroxide and derived complex formation constants. Since their solubility data differed greatly from other literature values, their complex formation constants should also be regarded with great caution. The solubility experiments of SPIVAKOVSKII and MOISA (1964) were carried out in solutions containing bromide, in which complex formation with bromide may have occurred.

MARCUS (1957) determined the pH value at the beginning of the precipitation of cadmium hydroxide. He himself reported a clear measurement scatter and possible contamination of the initial preparations. According to his evaluation, complex formation already takes place at pH values around 6, which contradicts the observations of the other authors and is also reflected in the considerably higher complex formation constant derived by him. The three other potentiometric measurements from Tab. 9.1 are in better agreement with each other.

The complex formation products given in the papers were extrapolated[14] to zero ionic strength using the SIT approach. The evaluation led to a complex formation constant of

$\log \beta_1$ (SIT) = 4.16 ± 0.11

The evaluation using the Pitzer approach, which was carried out for test purposes only, resulted in highly scattered values for the complex formation constant:

$\log \beta_1$ (Pitzer) = 3.9 ± 0.6

The reason could be the frequently missing Pitzer coefficients for Cd^{2+}. The following interaction coefficients were not available at the time of reporting: $\psi_{Cd2+,\ Na+,\ ClO4-}$ as well as $\psi_{Cd2+,\ Li+,\ ClO4-}$. Their contribution to the activity coefficient of Cd^{2+} must not be underestimated, since the associated parameters $\theta_{Cd2+,Na+}$ and $\theta_{Cd2+,\ Li+}$ have a rather high value due to the modelling of chloride-containing systems with strong complex formation and must be counter -"compensated". It is also problematic that, in contrast to the SIT approach, there is currently no possibility to estimate ion interaction coefficients for complex ions. We therefore assume that the derivation with SIT is currently more reliable. The complex formation constant derived with SIT is consistent with the value obtained via the Pitzer evaluation and can also be used together with Pitzer parameters.

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[14] Chapter 12.1 explains the SIT approach and lists the SIT parameters used in this report.

Tab. 9.1 Experimentally determined complex formation constants for $[CdOH]^+$

Source	**Medium**	**Method**	**log K_{c1} (molar)**	**log β_1*****	
				Pitzer	**SIT**
Goward (1954)	1 M KNO_3	voltam.	6.38		7.09
Marcus (1957)	3 M $NaClO_4$	potentiom.	5.22	5.80	5.60
Biedermann (1962), Biedermann and Ciavatta (1962)	3 M $LiClO_4$	potentiom.	3.67	**3.72**	**4.19**
Dyrssen and Lumme (1962)	3 M $NaClO_4$	l-l distribution benzene	4.3	4.79	4.68
Ste-Marie et al. (1964)	1 M $NaClO_4$	solubility	17.76*		
Gübeli and Taillon (1971)**	1 M $NaClO_4$	solubility	4.7	5.65	5.34
Matsui and Ohktaki (1977)	3 M $LiClO_4$	potentiom.	3.57	**3.62**	**4.09**
Mizetskaya et al. (1983)	1 M KNO_3	spectroph.	6.96		7.67
Kanekiyo et al. (2000)	0.1 M $NaClO_4$	potentiom.	3.78	**4.32**	**4.20**
Mean value				**3.9 ± 0.6**	**4.16 ±0.11**

* probably misprint

** re-evaluated

*** Derived from literature values using the respective approach for the determination of the ion activity coefficients

9.1.3 The hydroxides and oxides of cadmium

Cadmium forms four hydroxides and oxides, of which only one is stable in aqueous solution according to investigations by Feitknecht and Reinmann (1951) and Schindler (1959): β-$Cd(OH)_2$ (Tab. 9.2). It forms when a cadmium-containing solution is mixed with an excess of alkali. The measured values for freshly precipitated, "active" preparations of β-$Cd(OH)_2$ scatter strongly, while those for aged samples (after about one week, "inactive") are relatively constant. Freshly precipitated and aged samples do not differ in their XRD image, i.e., they do not undergo any structural transformation, but rather particle enlargement (Schindler, 1959). Feitknecht and Reinmann (1951), however, could not perceive such a particle size change. Instead, they assumed a repair of imperfect lattice districts.

Tab. 9.2 Modifications of cadmium hydroxide and cadmium oxide

Modifications
γ-$Cd(OH)_2$ (metastable)
β-$Cd(OH)_2$ (active) metastable
β-$Cd(OH)_2$ (inactive) stable
α-$Cd(OH)_2$ (metastable)
CdO (metastable) (monteponite)

For the preparation of the metastable compounds α-$Cd(OH)_2$ and γ-$Cd(OH)_2$, special reaction conditions have to be observed (FEITKNECHT 1938, 1940a, 1940b; GLEMSER et al. 1957). According to LECERF et al. (1988), γ-$Cd(OH)_2$ can be obtained by agitation of CdO in 8M NaOH at 50 °C. According to RIOU ET AL. (1990), γ-$Cd(OH)_2$ is better understood as $Cd_2O(OH)_2(H_2O)$, since at least one molecule of water is not bound as hydroxide on the basis of X-ray spectroscopic investigations.

Both α-$Cd(OH)_2$ and γ-$Cd(OH)_2$ transform into β-$Cd(OH)_2$ after some time. Cadmium oxide (monteponite) also converts to β-$Cd(OH)_2$ in the presence of water (FEITKNECHT and SCHINDLER, 1963). The latter reaction seems to be very slow, because TOMANEK (1967) could not observe any hydroxide formation after one month of storage of CdO in carbonate-free water. This seems to occur only in the presence of excess alkali.

9.1.4 Solubility constant for aged cadmium hydroxide, β-$Cd(OH)_2$ (inactive)

After reviewing the available data material, the evaluation of the solubility experiments by SCHINDLER (1959) appears to be a suitable starting point. The experiments were carried out at constant ionic strength in a pH range in which only the free Cd^{2+} occurred as a species. Aged, inactive β-$Cd(OH)_2$ was used. Solubility data was obtained from both supersaturation and dissolution experiments. Temperature control as well as the exclusion of CO_2 were ensured. The measured value scatter is very small.

For other authors, at least one of the criteria above did not apply. In most cases, fresh $Cd(OH)_2$ preparations or CdO, were used. According to SCHINDLER (1959), the value of DE WIJS (1925) frequently mentioned in earlier compilations was measured in a system that was considerably distant from equilibrium. The remaining studies are listed in Tab. 9.3.

Tab. 9.3 Solubility constants (I = 0) for β-$Cd(OH)_2$ (inactive, aged samples)

log K_S^0	Method	Source
-13.81	Solubility at constant ionic strength	GÜBELI and TAILLON (1971) converted to activities with SIT, pH calibration unclear
-13.93	potentiometric activity measurement in saturated solution	ISHIKAWA and Shibata (19329
-14.09	potentiometric activity measurement, bromide-containing solution	SPIVAKOVSKII and MOISA (1964)
-14.14 ± 0.21	Solubility	RAI et al. (1991)
-14.2	I = 0 (calculated from I= 0.0025 to 0.04)	REINMANN (1950), FEITKNECHT and REIMANN (1951). Derivation unclear. These values must still be corrected with regard to the hydrolysis of Cd (SCHINDLER, 1959). This is difficult to do retrospectively, as we lack the primary data.
-14.22	Solubility	PIATER (1928)
-14.25	Solubility at constant ionic strength	GÜBELI and TAILLON (1971), but assumption. $-\log c_H$= pH(mess) + 0.37 (Rai et al., 1991), converted to activities with SIT
-14.4 ± 0.3	corrected for $CdOH^+$	FEITKNECHT and REIMANN (1951) and PIATER (1928), hydrolysis-corrected by SCHINDLER (1959), back-calculated from Δ_rG = 113.4 ± 0.4 kcal/mol
-14.46	Solubility at constant ionic strength	SCHINDLER (1959). Molar solubility constant at 3 M $NaClO_4$ (-14.41) converted with SIT to I = 0
-14.3 ± 0.05	Solubility at constant ionic strength corrected for $CdOH^+$	SCHINDLER (1959). Calculated back from Δ_rG = 113.36 ± 0.07 kcal/mol
-14.7	Solubility	SANTILLAN-MEDRANO and JURINAK (1975)

For the molar solubility product K_S, SCHINDLER (1959) gave a value of

$\log K_{sp}$ (molar) = -14.41 ± 0.05 (3 mol/l $NaClO_4$)

Assuming a density of 1.2256 for a 3-molar $NaClO_4$ solution (calculated with the data from Tab. 12.7) results in a molar solubility product of

$\log K_{sp}$ (molal) = -14.21 ± 0.05 (3 mol/l $NaClO_4$)

If the contribution of complex formation, i.e., the formation of $[CdOH]^+$, is also taken into account, this value changes only slightly to

$\log K_{sp}$ (molal) = -14.22 ± 0.05 (3 mol/l $NaClO_4$)

When converting to activities, we are faced with the same problem as above. While the evaluation with Pitzer leads to an average activity coefficient of the completely dissociated $Cd(OH)_2$ of 0.390 and thus to

log K (Pitzer) = -15.44 ± 0.05

leads to a mean activity coefficient of 0.827 with SIT, and thus arrives at

log K (SIT) = -14.46 ± 0.05

It is not unusual that different equilibrium constants are obtained when applying different activity models. However, a value of -15.44 deviates strongly from all other values. There are also determinations of the solubility constant at very low ionic strengths, these values are mainly around -14.2. This means that also for the determination of the solubility constant of $Cd(OH)_2$ the current Pitzer data base is insufficient.

Schindler calculated the free molar enthalpy of formation of β-$Cd(OH)_2$ by applying a circular process and adding further potentiometric data. He obtained:

$\Delta_f G$ = -113.6 kcal/mol = -474.31 kJ/mol

Together with

$\Delta_f G$ (Cd^{2+}) = -77.733 kJ/mol and

$\Delta_f G$ (OH^-) = -157.22 kJ/mol (GRENTHE et al. , 1992) one obtains via

$$\Delta_\rho G^0 = \Sigma \nu_\iota \Delta_f G^0_\iota = -RT \ln K \qquad (9.1)$$

the solubility constant

log K = -14.39

This is only slightly different from the value of -14.35 given by BAES and MESMER (1976) in a re-evaluation of Schindler's data and adding the complex formation data of BIEDERMANN and CIAVATTA (1962). Schindler's value is adopted in the database.

9.1.5 The complex $[Cd(OH)_2]^0$

In the -log c_H range from 11 to about 13, the solubility of β-$Cd(OH)_2$ remains at a constant level (Fig. 9.1). It can be assumed that in this range only the complex $[Cd(OH)_2]^0$ occurs in substantial amounts. In that case the complex formation equilibrium

$$a_{[Cd(OH)_2]^0} = \beta_2 a_{Cd^{2+}} \cdot a_{OH^-} \tag{9.2}$$

and the solubility equilibrium

$$K(Cd(OH)_2) = a_{Cd^{2+}} \cdot a_{OH^-} \tag{9.3}$$

summarise to

$$a_{[Cd(OH)_2]^0} = m_{[Cd(OH)_2]^0} \cdot \gamma_{[Cd(OH)_2]^0} = \beta_2 K \tag{9.4}$$

or

$$m_{[Cd(OH)_2]^0} = \frac{\beta_2 K}{\gamma_{[Cd(OH)_2]^0}} \tag{9.5}$$

or

$$\ln m_{Cd,tot} = +\ln \beta_2 + \ln K - \ln \gamma_{Cd(OH)2} \tag{9.6}$$

At constant ionic strength, the expression contains only constants. If one assumes (according to HARVIE et al. 1984) that the activity coefficient of the neutral species $[Cd(OH)_2]^0$ in $NaClO_4$ solutions is given by the formula

$$\ln \gamma_{Cd(OH)_2} = 2\lambda_{Na,Cd(OH)_2} m_{Na} + 2\lambda_{ClO_4,Cd(OH)_2} m_{Na} \tag{9.7}$$

and $\lambda_{ClO4,Cd(OH)2}$ is set to zero because the two interaction parameters in the formula above cannot be determined independently of each other, the following expression is obtained

$$\ln \gamma_{Cd(OH)_2} = 2\lambda_{Na,Cd(OH)_2} m_{Na} \tag{9.8}$$

If suitable measurement data are available, the following relationship can be established and evaluated:

$$\ln m_{Cd,tot} - \ln K = \ln \beta_2 - 2\lambda_{Na,Cd(OH)_2} m_{Na} \tag{9.9}$$

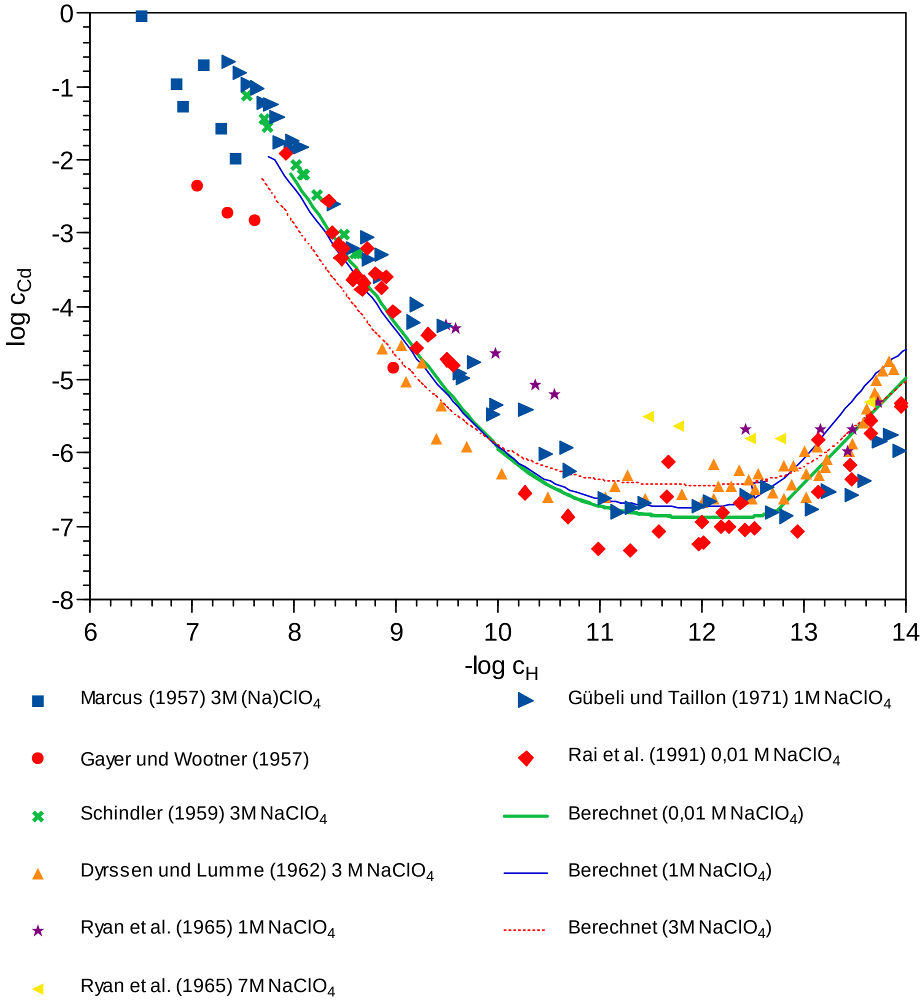

Fig. 9.1 Solubility of β-$Cd(OH)_2$ (inactive) in basic solutions of $NaClO_4$

For sodium perchlorate solutions, three series of measurements are available from which the minimum concentrations log $m_{Cd,tot}$ can be taken. The measurements of RYAN et al.

(1965) at 7 M $NaClO_4$ did not show a range with constant Cd concentration (Tab. 9.4, Fig. 9.2).

Tab. 9.4 Minimum solubility of -$Cd(OH)_2$ in $NaClO_4$ solutions

Source	**Medium**	**log $c_{Cd,tot}$ minimal**	**m $NaClO_4$**	**log $c_{Cd,tot}$ minimal**
Dyrssen and Lumme (1962)	3 M $NaClO_4$	-6.53	3.50	-6.46
Gübeli and Taillon (1971)	1 M $NaClO_4$	-6.72	1.05	-6.70
Rai et al. (1991)	0.01M $NaClO_4$	-6.95	0.01	-6.95

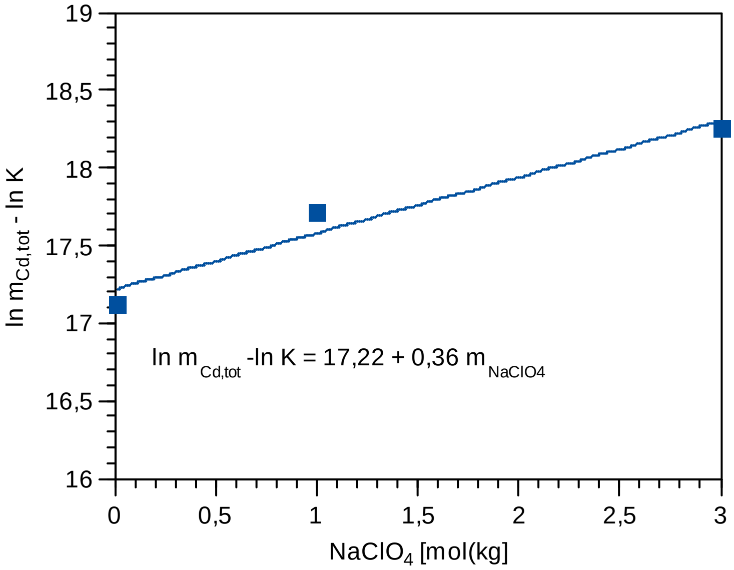

Fig. 9.2 Minimum solubility of $Cd(OH)_2$ in $NaClO_4$ solutions: Determination of the complex formation constants by linear regression.

We get as a result

$\ln \beta_2 = 17.22$ or $\log \beta_2 = 7.49$

and

$\lambda_{Na,Cd(OH)2} = -0.15$

9.1.6 The complex $[Cd(OH)_4]^{2-}$ and the system $NaOH-Cd(OH)_2-H_2O$

Above an OH concentration of about 0.1 mol/kg, the logarithm of the cadmium solubility increases linearly. This type of concentration change and the height of the slope of the solubility curve can only be interpreted by assuming the formation of a predominant complex. In principle, this can be $[Cd(OH)_3]^-$ or $[Cd(OH)_4]^{2-}$. ICHIKAWA and SATO (1973), on the other hand, deduced from their ion exchange and centrifugation experiments that only one complex $HCdO_2^-$ occurs at least up to 3 M NaOH. It is not clear from the sparse information in their article how the composition of this compound was derived. Both possibilities were therefore tested.

For the evaluation, the solubility measurements from the references listed in Tab. 9.5 were used for the evaluation. It should be noted that SOLOVEVA et al. (1973b) dealt with the solubility of CdO in NaOH. The differences to their measurement data on the solubility of $Cd(OH)_2$ published in SOLOVEVA et al. (1973a) are not significant, however, so that we assume that the conversion of CdO into $Cd(OH)_2$ takes place sufficiently quickly at the high NaOH concentrations used. SCHOLDER and STAUFENBIEL (1941) and SCHOLDER and SCHWOCHOW (1966) reported on the formation of a sodium cadmate $NaCd_2(OH)_4$ by boiling a $Cd(OH)_2$suspension in concentrated NaOH. It does not seem to be stable below 14 N NaOH. Corresponding results were also documented by CUDENNEC et al. (1999) at 25 °C.

The comparatively too high solubilities of GAYER and WOONTNER (1957) were not used. The publication by ROZENCVEJG et al. (1953) does not contain any information on temperature (probably room temperature). The measurements of GÜBELI and TAILLON (1971) as well as RAI et al. (1991a) did not reach far enough into the range of high NaOH concentrations to completely exclude the influence of the complex $[Cd(OH)_2]^0$.

Only data from solutions with more than 1 mol/kg NaOH were used to determine the thermodynamic quantities sought.

Tab. 9.5 Suitable solubility experiments for the determination of the complex formation constants for $[Cd(OH)_4]^{2-}$

Source	**Medium**	**Temperature [°C]**
Piater (1928)	NaOH (var)	25.0
Ryan et al. (1965)	7 M $NaClO_4$	24.5
Soloveva et al. (1973a)	NaOH (var)	20
Soloveva et al. (1973b)	NaOH (var)	20
Cudennec et al. (1999)	NaOH (var)	25

From the measurements of Ryan et al (1965) at 7M NaClO4 , it was found that the ratio of the logarithmic concentrations of OH and Cd above 1.5 mol/kg is about 2. Since the solutions are in equilibrium with $Cd(OH)_2$, the reaction equation must contain 2 molecules of hydroxide and thus leads to $[Cd(OH)_4]^{2-}$:

$$Cd(OH)_2 + 2\ OH^- \rightarrow [Cd(OH)_4]^{2-}$$

In solutions with more than 7 mol/kg, the cadmium concentrations increase even stronger. The increase between 7 and 15 mol/kg is almost twice as high as between 1 and 7 mol/kg. A clear explanation is difficult. Higher hydroxo complexes such as $Cd(OH)_5^{3-}$ or $Cd(OH)_6^{4-}$ are a possibility. At least in solids, such compositions have already been found, e.g., as $Na_3[Cd(OH)_5(H_2O)]$-H_2O and $Ba_2[Cd(OH)_6]$ (Scholder and Staufenbiel 1941). Whether they are really based on the corresponding complex anions has not yet been clarified. Ternary complexes of the type $M_xCd(OH)_{4+y}^{-2-x-y}$ can also not be ruled out.

Due to the variable high background salt concentrations, the measurement results can only be evaluated if the specific interactions of the ion $[Cd(OH)_4]^{2-}$ with Na^+ are taken into account. The following mathematical relationships were assumed:

Due to the complexation of cadmium with OH^-, its total solution concentration is composed of

$$m_{Cd,tot} = m_{Cd^{2+}} + m_{Cd(OH)^+} + m_{Cd(OH)_2^0} + m_{Cd(OH)_4^{2-}} \tag{9.10}$$

In the range of high OH concentrations (>1 mol/kg), practically only the complex $[Cd(OH)_4]^{2-}$ occurs. Then it may be assumed:

$$m_{\mathrm{Cd,tot}} \approx m_{\mathrm{Cd(OH)_4^{2-}}} \qquad (9.11)$$

The stability of $[Cd(OH)_4]^{2-}$ is defined by

$$a_{\mathrm{Cd(OH)_4^{2-}}} = \beta_4 a_{\mathrm{Cd^{2+}}} a_{\mathrm{OH^-}}^4 \qquad (9.12)$$

The solubility of cadmium hydroxide is determined by its solubility constant

$$K = a_{\mathrm{Cd^{2+}}} a_{\mathrm{OH^-}}^2 \qquad (9.13)$$

Both equations can be merged into

$$a_{\mathrm{Cd(OH)_4^{2-}}} = \beta_4 K a_{\mathrm{OH^-}}^2 \qquad (9.14)$$

and thus

$$\gamma_{\mathrm{Cd(OH)_4^{2-}}}\, m_{\mathrm{Cd(OH)_4^{2-}}} = \beta_4 K \gamma_{\mathrm{OH^-}}^2\, m_{\mathrm{OH^-}}^2 \qquad (9.15)$$

and

$$m_{\mathrm{Cd(OH)_4^{2-}}} = \frac{\beta_4 K \gamma_{\mathrm{OH^-}}^2\, m_{\mathrm{OH^-}}^2}{\gamma_{\mathrm{Cd(OH)_4^{2-}}}} \qquad (9.16)$$

The solubility $c_{\mathrm{Cd,tot}}$ in hydroxide-containing solutions can be represented as

$$m_{\mathrm{Cd,tot}} \approx m_{\mathrm{Cd(OH)_4^{2-}}} = \frac{\beta_4 K_S\, \gamma_{\mathrm{OH^-}}^2\, m_{\mathrm{OH^-}}^2}{\gamma_{\mathrm{Cd(OH)_4^{2-}}}} \qquad (9.17)$$

Or in logarithmic form

$$\ln m_{\mathrm{Cd,tot}} \approx \ln\beta_4 + \ln K_S + 2\ln\lambda_{\mathrm{OH^-}} + 2\ln m_{\mathrm{OH^-}} - \ln\gamma_{\mathrm{Cd(OH)_4^{2-}}} \qquad (9.18)$$

In this equation, the total concentrations of cadmium and hydroxide and the solubility constant of cadmium hydroxide are known or measurable. Using the Pitzer formalism, the expressions for the activity coefficients consist of aggregated terms for specific and non-specific interactions. For $[Cd(OH)_4]^{2-}$in a NaOH solution, the expression has the following structure:

$$\begin{aligned}\ln\gamma_{Cd(OH)_4^{2-}} &= DH(I) + P(I) + z^2_{Cd(OH)_4^{2-}} B'_{Na+,Cd(OH)_4^{2-}} m_{Na^+} m_{Cd(OH)_4^{2-}} \\ &+ z^2_{Cd(OH)_4^{2-}} \Phi'_{OH^-,Cd(OH)_4^{2-}} m_{OH^-} m_{Cd(OH)_4^{2-}} + 2B_{Na+,Cd(OH)_4^{2-}} m_{Na+} \\ &+ \Psi_{Na^+,Cd(OH)_4^{2-},OH^-} m_{Na+} m_{OH^-} \\ &+ ZC_{Na+,Cd(OH)_4^{2-}} m_{Na+} + \left|z_{Cd(OH)_4^{2-}}\right| C_{Na+,Cd(OH)_4^{2-}} m_{Na+} m_{Cd(OH)_4^{2-}}\end{aligned} \tag{9.19}$$

Here DH(I) stands for the unspecific interactions, which are represented by a Debye-Hückel expression dependent only on ionic strength, and P(I) for Pitzer terms, which are not specific for $[Cd(OH)_4]^{2-}$. The expressions B and B' contain terms for the Pitzer coefficients $\beta^{(0)}$, $\beta^{(1)}$ and $\beta^{(2)}$.

Some of the terms appearing in this equation also appear in the expression for the activity coefficient for OH^-. If the expressions for all measurements are combined, a linear system of equations results which can be easily solved by a multilinear regression. The regression coefficients correspond to the logarithm of the complex formation constant $\ln \beta_4$ and the Pitzer coefficients for $[Cd(OH)_4]^{2-}$. Depending on the quality of the data material, it makes sense to use only a limited set of coefficients. In the case of the system $Cd(OH)_2$-NaOH-H_2O these were the complex formation constant β_4 and the interaction parameters $\beta^{(0)}$ and $\beta^{(1)}$ (Tab. 9.14). The measurements were evaluated together with those for the K-Cd-OH system. Only those data were taken into account where the hydroxide concentration was between 1 and 6.5 mol/kg. At lower concentrations, other hydroxo complexes also occur. At higher concentrations, as described above, another unidentified species appears.

As complex formation constant we obtained

$\log \beta_4 = 9.51$

and for the interaction $Na/^+[Cd(OH)_4]^2$

$\beta^{(0)} = 0.254$

$\beta^{(1)} = 4.286$

It can be seen that the solubility data are well reproduced (Fig. 9.3). A general overview of the pH-dependent speciation to be expected in 1 mol/kg $NaClO_4$ solutions is given in Fig. 9.4.

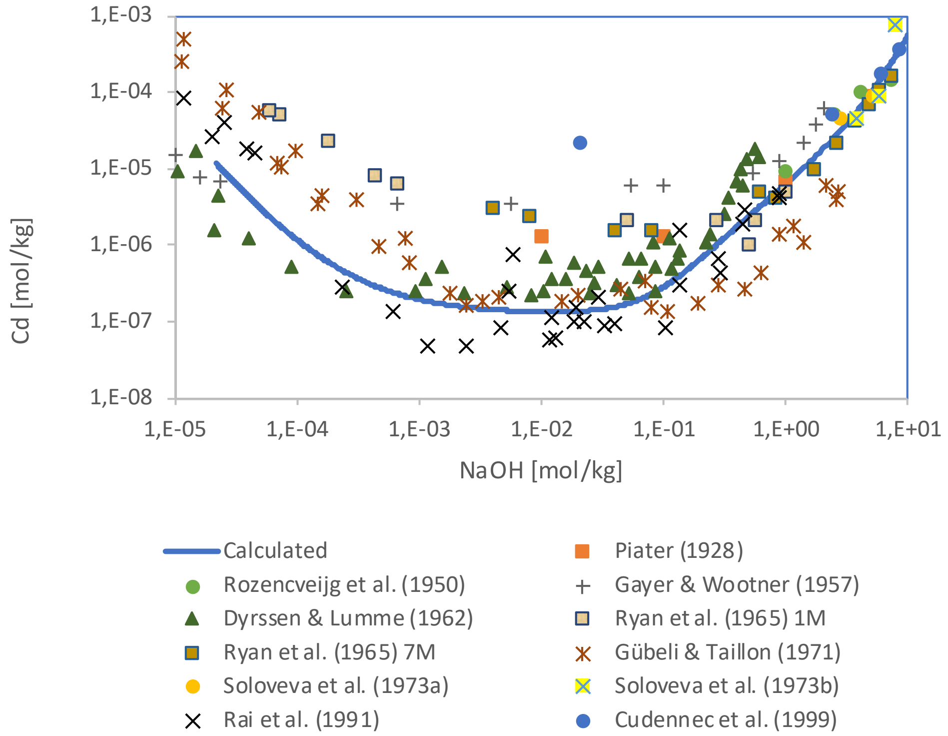

Fig. 9.3 Solubility of β-$Cd(OH)_2$ NaOH solutions

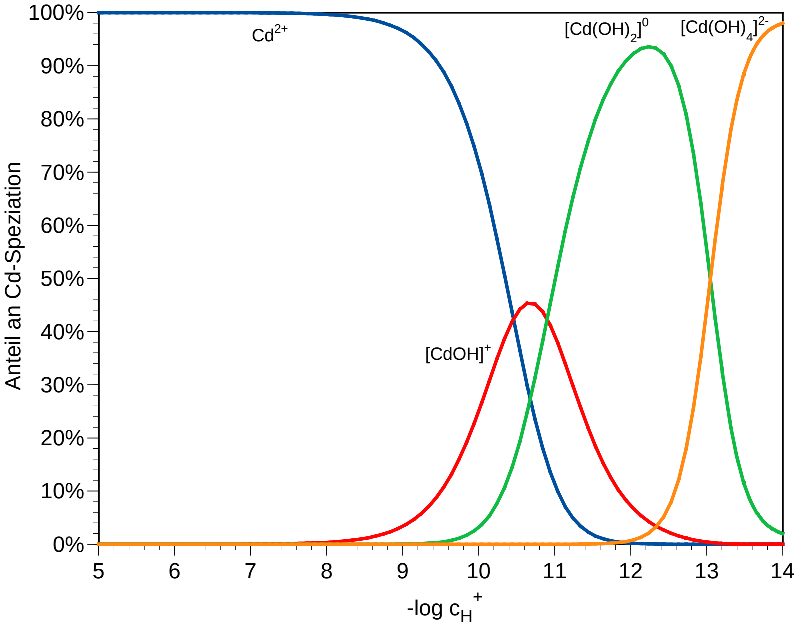

Fig. 9.4 Calculated speciation of cadmium (II) in 1 mol/kg $NaClO_4$

9.1.7 The system KOH – $Cd(OH)_2$ – H_2O

Only a few data are available for the cadmium hydroxide solubility in KOH. They come on the one hand from ROZENCVEJG et al. (1953) at a temperature not mentioned in the article (probably room temperature) and on the other hand from LAKE and GOODINGS (1958). The latter authors only published the KOH concentrations of the equilibrium solutions, the cadmium concentrations are only shown in a diagram. From there we recovered them by scanning and digitising. In the KOH-$Cd(OH)_2$-H_2O system, no potassium cadmate $K_2Cd(OH)_4$ has been found so far. It is possible that it only occurs above the highest KOH concentrations investigated (8.5 mol/kg).

The data of ROZENCVEJG showed, as with the corresponding system NaOH-$Cd(OH)_2$-H_2O, a bend in solubility towards higher NaOH concentrations. This behaviour was not found by LAKE and GOODINGS (1958). The data of ROZENCVEJG were therefore also discarded because of the missing temperature information. LAKE and GOODINGS (1958) presented either CdO or $Cd(OH)_2$ in their experiments. A continuous difference in solubility is not apparent in their measurement data, but $Cd(OH)_2$ shows lower solubilities at lower concentrations. This contradicts the experience from the experiments with NaOH and also the observations of LAKE and GOODINGS (1958) themselves, who report that the brown colour of the CdO slowly disappears, i.e., $Cd(OH)_2$ is formed. Both series of measurements (with CdO and $Cd(OH)_2$ as the starting material) were treated simply as $Cd(OH)_2$.

The evaluation was carried out together with the data for NaOH solutions. The interaction coefficients $\beta^{(0)}_{K+,[Cd(OH)4]2-}$ and $\beta^{(1)}_{K+,[Cd(OH)4]2-}$ were determined this way (Tab. 9.14). Suing these parameters, the solubility data of LAKE and GOODINGS (1958) can be reproduced well in part (Fig. 9.5). There are deviations in the medium concentration range (4 - 6 mol/kg KOH). The question arises whether in some experiments a potassium hydroxo cadmate was formed and the other solubility points correspond to metastable equilibria. Since neither ROZENCVEJG et al. (1953) nor LAKE and GOODINGS (1958) examined the solid phases of the equilibrium solutions, this question cannot be answered.

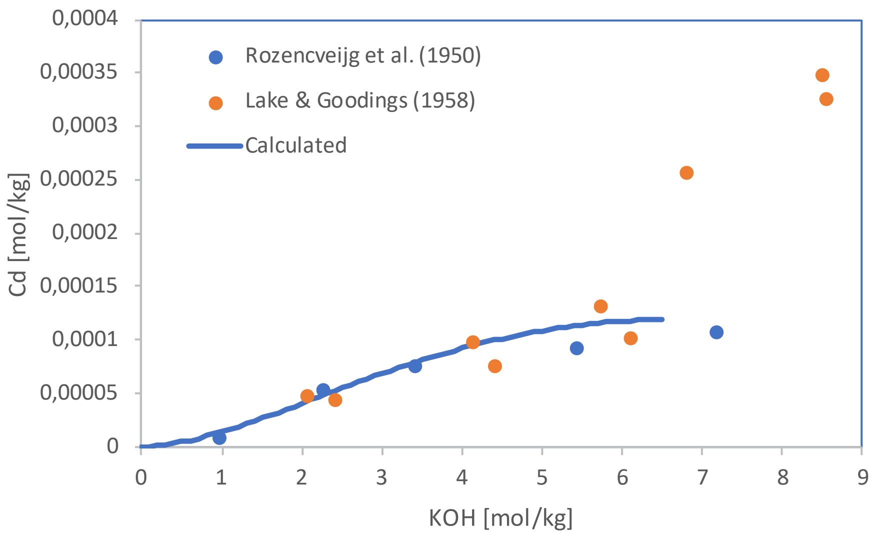

Fig. 9.5 Solubility of $Cd(OH)_2$ in KOH solutions

9.1.8 The system $Cd(OH)_2 – Ca(OH)_2 – H_2O$

Cadmium hydroxide forms a continuous series of solid solutions with calcium hydroxide. If calcium silicate hydrate (CSH) phases are present, Cd^{2+} can replace Ca^{2+} in these compounds (HERRERA et al., 1992; POMIÈS et al., 2001a, b). The maximum cadmium content of portlandite corresponds to a molecular formula of $Cd_{0.5}Ca_{0.5}(OH)_2$ or $Ca[Cd(OH)_4]$, a calcium tetrahydroxo cadmate. More detailed information on the stability of these phases is not available.

9.2 Compounds with carbonate

9.2.1 Cadmium carbonate (otavite)

The thermodynamic properties of cadmium carbonate (otavite) were last discussed in detail by STIPP et al. (1993). It is thanks to their almost detective-like efforts that the "reference values" for the solubility constant of otavite appearing so far in many data compilations were unmasked as end points of a long chain of derivations, which were ultimately not based on thermodynamic equilibrium measurements but on thermochemical estimates of the 19th and early 20th century. Until then, the most important basis was an investigation of the enthalpy of formation of otavite by THOMSEN (1883) and an estimate of the entropy of formation based on a dissociation pressure measurement by

ANDRUSSOV (1925). For a long time, the only experimental solubility determination came from GAMSJÄGER et al. (1965).

A total of eight direct experimental studies on the solubility of cadmium carbonate are available. In addition, there are two measurements on soil samples containing cadmium (Tab. 9.6). With the exception of the results of DAVIS et al. (1987) and HOLM et al. (1996), all results are close to each other. According to a personal communication by DAVIS listed in STIPP et al. (1993), the higher solubility in his study was probably due to poorly crystallised starting material. These experiments involved the dissolution of $CdCO_3$ samples in distilled water. No statements are made on the exclusion of air CO_2, nor on the question of the extent to which the pH electrode used still provides meaningful values in this weakly buffered solution system even after several weeks of experimentation. HOLM et al. (1996) also have no information on the characterisation of the $CdCO_3$ preparation. Experimental basic data are missing, so that a re-evaluation of the data is not possible.

Overlooked by STIPP et al (1993) was the potentiometric determination of the solubility constant by SAEGUSA (1950). He used a measuring cell of the type Cd(Hg, 10 %)|$CdCO_3$ (s), K_2CO_3(0.1 M), $KHCO_3$(0.1 M), Ag_2CO_3|Ag for direct determination of the activity product $a_{Cd2+}a_{CO32-}$ in solution. The experiments were carried out for a total of nine days. In all three cells used, the cell potential still dropped significantly between the sixth and ninth day, so that the cell voltage ultimately used by Saegusa cannot yet be regarded as the equilibrium voltage.

The most recent series of measurements was contributed by GAMSJÄGER et al. (1999). They repeated the measurements they had carried out some years earlier at different $NaClO_4$ concentrations and included an overall evaluation of all data with the help of a simultaneous determination of Pitzer coefficients for the interactions between cadmium, sodium and perchlorate. Not adjusted and obviously not taken into account were the equally important interactions between Na^+, H^+ and ClO_4^-. It also seems doubtful whether the cadmium carbonate solubility is a suitable parameter to determine the parameters $\theta_{Cd,Na}$ and $\psi_{Cd,Na,ClO4}$. In particular, since c_{Na+} and c_{ClO4-} are no independent variables, $\theta_{Cd,Na}$ and $\psi_{Cd,Na,ClO4}$ were likely strongly correlated. We therefore do not use the quantity derived by the authors for the solubility constant of otavite. Their solubility constant determined for ionic strength one turns out to be too high after correction to zero ionic strength and is also not taken into account. For this as well as for other ionic strengths, it is noticeable that the measurement scatter is considerable.

Instead, we adopt the mean value of the four remaining papers (GAMSJÄGER et al. .1965; KÖNIGSBERGER et al., 1991; RAI ET AL., 1991b; STIPP et al., 1993) and obtain for the reaction (Tab. 9.6):

$$CdCO_{3(s)} + H^+ \rightleftharpoons Cd^{2+} + HCO_3^- \qquad (9.20)$$

the value

$$\log{}^*K\,(\text{otavite}) = -1.8 \pm 0.1$$

or for the reaction

$$CdCO_{3(s)} \rightleftharpoons Cd^{2+} + CO_3^{2-} \qquad (9.21)$$

$$\log K\,(\text{otavite}) = -12.13 \pm 0.1.$$

Tab. 9.6 Experimental determinations of the solubility constant of cadmium carbonate (otavite) $CdCO_{3(s)} + H+ \rightleftharpoons Cd^{2+} + HCO_3^-$

Medium	log Kc	log K	log *K	Source/ Remarks
Experiments with synthetic otavite				
I = 0		-11.6	-1.27	SAEGUSA (1950), potentiometric measurements
3 M $NaClO_4$	-10.90	**-12.08 ± 0.15**	**-1.73**	GAMSJÄGER et al. (1965), converted with the carbonic acid equation data of GAMSJÄGER et al. (1973), activities with SIT
		-11.3	-0.97	DAVIS et al. (1987), insufficient experimental details
3 m $NaClO_4$	-10.96	**-12.14**	**-1.78**	KÖNIGSBERGER et al. (1991), converted with the carbonic acid equation data of GAMSJÄGER et al. (1973), activities with SIT
		-12.24 ± 0.1	**-1.91 ± 0.1**	RAI et al. (1991b), 21 °C, probably room temperature
variable I < 0.03		**-12.1 ± 0.1**	**-1.77 ± 0.1**	STIPP et al. (1993)
0.022 M NaHCO3		-12.8		HOLM et al. (1996)
1 mol/kg $NaClO_4$	-10.79		-2.16	GAMSJÄGER et al. (1999)
		-12.13 ± 0.1	-1.80 ± 0.1	Mean value (only values in bold are taken into account)
Experiments with soil samples containing cadmium				
		-11.6	-1.27	SANTILLAN-MEDRANO and JURINAK (1975)
		-12.14	-1.78	MILLER et al. (1984)

9.2.2 Cadmium carbonato complexes: overview

In the literature, three carbonato complexes are considered to be proven so far, the hydrogen carbonato complex $[CdHCO_3]^+$ and the two carbonato complexes $[CdCO_3]^0$ and $[Cd(CO_3)_2]^{2-}$. LAKE and GOODINGS (1958) concluded from their solubility measurements of $CdCO_3$ in concentrated K_2CO_3 solutions that a complex $[Cd(CO_3)_3]^{4-}$ exist. However, their proof is weak because they did not carry out their investigations in a constant medium and therefore the complex formation is also superimposed by a change in the activity coefficients of the ions involved. For mixed hydroxo carbonato complexes, RAI et al. (1991b) could not find any evidence based on their solubility measurements.

Tab. 9.7 Previously determined formation constants of cadmium carbonato and hydrogen carbonato complexes

Medium	$[CdCO_3]^0$ log $K_{1.1}$	$[CdCO_3]^0$ log $\beta_{1.1}$	$[Cd(CO_3)_2]^{2-}$ log $K_{1.2}$	$[Cd(CO_3)_2]^{2-}$ log $\beta_{1.2}$	$[CdHCO_3]^+$ log $K_{1.1.1}$	$[CdHCO_3]^+$ log $\beta_{1.1.1}$	Method*	Source
0.001 M KNO_3	4.02 ± 0.04	4.14					pot. 2°C0	Gardiner (1974), Activities with SIT
0.1 M KNO_3	3.5	4.37					pol.	Bilinski et al. (1976), Activities with SIT
		3.48		6.25		0.26	unknown, probably pol.	Sipos et al. (1980)
0.05 M KNO_3	3.49 ± 0.04	4.17	6.37 ± 0.1	6.70	2.02 ± 0.01	2.36 ± 0.01	pot. 20 °C	Stella et al. (1984) 20 °C)
variable		4.7 ± 0.1		6.4 ± 0.1			sol.	Rai et al. (1991b), probably 21 °C or room temperature
3 M $NaClO_4$					0.77 ± 0.1	1.22	pot.	Néher-Neumann (1992)
Estimated values								
I = 0		5.4				2.1	estim.	Zirino and Yamamoto (1972)
						2.00	estim.	Foulliac and Criaud (1984)

* pot. =potentiometric, pol. = polarographic, estim. = estimate, sol. = solubility

9.2.3 The cadmium hydrogen carbonato complex $[CdHCO_3]^+$

Néher-Neumann (1992) investigated the complex formation with hydrogen carbonate in the medium 3 M $NaClO_4$. The high cadmium concentrations used (up to 0.7 M) led to non-quantifiable, concentration-dependent diffusion potentials with the reference electrode used. Furthermore, it is not clear from the article how the calibration of the glass electrode used was carried out. Sipos et al. (1980) refer to their own measurement data, the publication of which was announced but apparently never took place. Further details on the experimental conditions and measurement procedure are not known. Therefore, preference is given to the potentiometric measurements of Stella et al. (1984, log β = 2.36 at 20 °C), whose other two derived complex formation constants agree well with the values found elsewhere in the literature. The values estimated earlier by Zirino and

YAMAMOTO (1972) and FOULLIAC and CRIAUD (1984) around log = 2 - 2.1 are also very close to this value. Nevertheless, doubts remain as to whether there is really a complex formation or rather an influence of the relatively high cadmium concentrations in the measuring solutions on the activity coefficient of the hydrogen carbonate (see also the discussion of the hydrogen carbonate complexes of lead).

9.2.4 The cadmium carbonato complexes $[CdCO_3]^0$ and $[Cd(CO_3)_2]^{2-}$

Three direct polarographic and potentiometric measurements were available for the complexation of the complex $[CdCO_3]^0$ (Tab. 9.7), the results of which agree well with each other. The value of SIPOS et al. (1980) was not used. Their source is an announced but apparently never publication of probably voltammetric measurements. Further details on experimental conditions and measurement methods are not known.

After correction to zero ionic strength using the SIT approach, the mean value for the first complex formation constant was

$$\log \beta_1 = 4.23 \pm 0.1$$

On the basis of solubility measurements, RAI et al. (1991b) derived a value of 4.71. However, it is not clear from their article to which temperature this value refers and from which measurements this value was determined. The determination of the complex formation constant for $[Cd(CO_3)_2]^{2-}$ was based on the solubility experiments of LAKE and GOODINGS (1958) in K_2CO_3 solutions and of RAI et al. (1991b) in Na_2CO_3 solutions. In all cases, $CdCO_3$ was encountered as a solid phase. Since in both cases a print of the numerical measurement data was missing, the measured values had to be digitised from the printed graphs. Estimates showed that at carbonate concentrations above 0.1 mol/kg, at least ten times more dicarbonato complexes than monocarbonato complexes must be present. The increase in solubility cannot be attributed to hydroxo complexes either, since the pH of more concentrated carbonate solutions is stable at about 11.5. In this case, the solubility of cadmium can be simplified as:

$$m_{Cd(CO_3)_2^{2-}} = \frac{\beta_2 K_S\, \gamma_{CO_3^{2-}}\, m_{CO_3^{2-}}}{\gamma_{Cd(CO_3)_2^{2-}}} \tag{9.22}$$

The derivation of this equation was analogous to the case of the solubility of $Cd(OH)_2$ in NaOH solutions explained above. From this, the following determination equations can then be derived

$$\ln m_{Cd,tot} \approx \ln\beta_2 + \ln K_S + 2\ln\gamma_{CO_3^{2-}} + \ln m_{CO_3^{2-}} - \ln\gamma_{Cd(CO_3)_4^{2-}} \tag{9.23}$$

with

$$\begin{aligned} \ln\gamma_{Cd(CO_3)_4^{2-}} &= DH(I) + P(I) + z^2_{Cd(CO_3)_4^{2-}} B'_{Na+,Cd(CO_3)_4^{2-}} m_{Na^+} m_{Cd(CO_3)_4^{2-}} \\ &+ z^2_{Cd(CO_3)_4^{2-}} \Phi'_{CO_3^{2-},Cd(CO_3)_4^{2-}} m_{CO_3^{2-}} m_{Cd(CO_3)_4^{2-}} + 2B_{Na+,Cd(CO_3)_4^{2-}} m_{Na+} \\ &+ \Psi_{Na^+,Cd(CO_3)_4^{2-},CO_3^{2-}} m_{Na+} m_{CO_3^{2-}} \\ &+ ZC_{Na+,Cd(CO_3)_4^{2-}} m_{Na+} + \left| z_{Cd(CO_3)_4^{2-}} \right| C_{Na+,Cd(CO_3)_4^{2-}} m_{Na+} m_{Cd(CO_3)_4^{2-}} \end{aligned} \tag{9.24}$$

Not all parameter terms are really needed. Our evaluation is limited to the complex formation constant β_2 and the interaction coefficients $\beta^{(0)}$ and $\beta^{(1)}$ which are contained in the terms B and B'. As a result of the joint optimisation, the parameters given in Tab. 9.8 and Tab. 9.9 were determined. For the evaluation of the measurement data in the system K_2CO_3-$CdCO_3$-H_2O (Lake and GOODINGS, 1958), the ion interaction coefficients for K_2CO_3 by ROY et al. (1984) were used. In contrast to the parameters in HARVIE et al. (1984), these are based on experimental measurements corrected for the hydrolysis of the carbonate. With the help of these parameters, the measured data can be reproduced much better.

The agreement between measured data and calculated solubilities is very good in potassium and sodium carbonate solutions (Fig. 9.6).

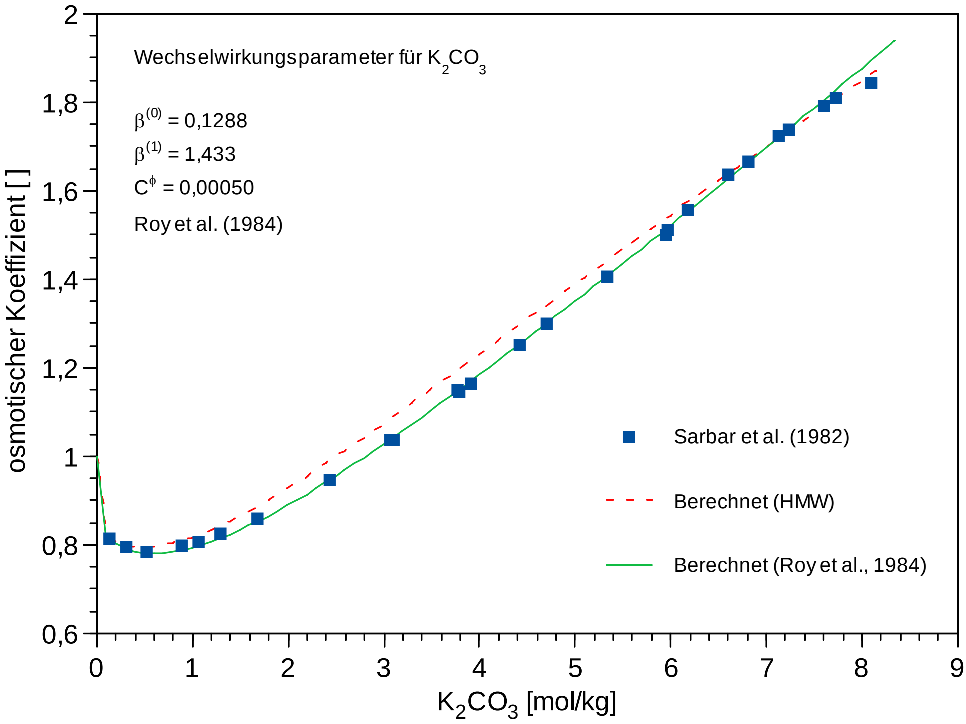

Fig. 9.6 Experimental and calculated osmotic coefficients in the system $K_2CO_3 - H_2O$ at 25 °C

Tab. 9.8 Equilibrium constants determined in this work in the system $Cd^{2+} - HCO_3^- - CO_3^{2-} - H_2O$

Reaction	**value (log K)**	**Source**
$CdCO_{3(s)}$ + H+ ⇌ Cd^{2+} + HCO_3^-	-1.80 ± 0.10	This work, based on solubility studies by Gamsjäger et al. (1965), Königsberger et al. (1991), Rai et al. (1991b), Stipp et al. (1993).
Cd^{2+} + CO_3^- ⇌ $[CdCO_3]^0$	4.23 ± 0.1	This work based on Gardiner (1974), Bilinski et al. (1976), Stella et al. (1984)
Cd^{2+} + $2CO_3^-$ ⇌ $[Cd(CO_3)_2]^{2-}$	6.38 ± 0.1	This work based on the solubility experiments of Lake and Goodings (1958) and of Rai et al. (1991b)
Cd^{2+} + HCO_3^- ⇌ $[CdHCO_3]^+$	2.36 ± 0.1	Stella et al. (1984)

Tab. 9.9 Binary ion interaction coefficients for cadmium carbonato species

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	C^{γ}	Source
$[Cd(CO_3)_2]^{2-} – Na^+$	-0.14171	-	-	-	this work
$[Cd(CO_3)_2]^{2-} – K^+$	-0.09614	-	-	-	this work

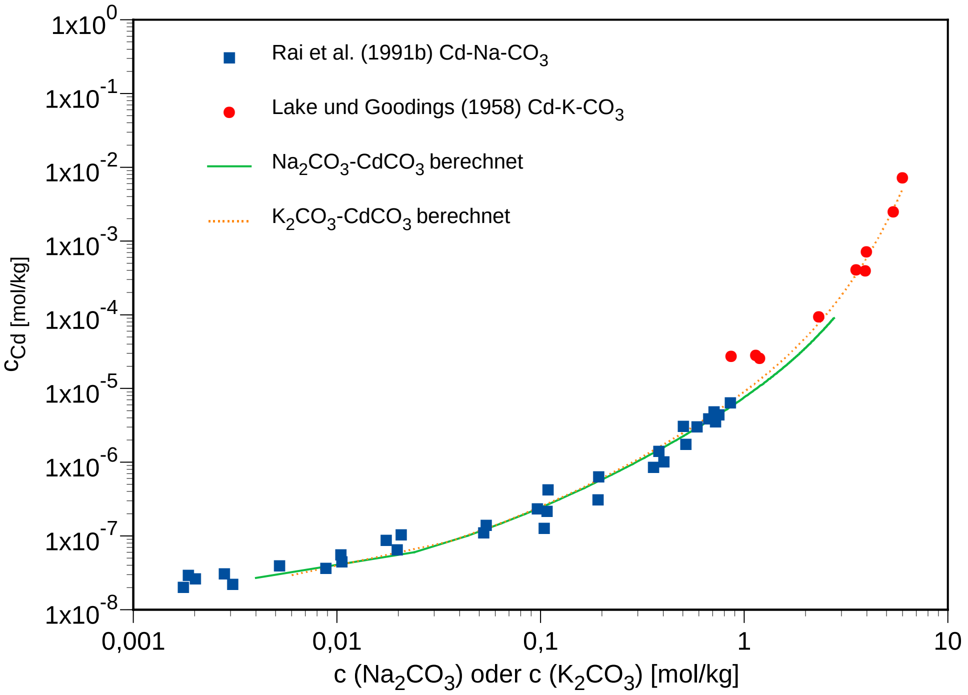

Fig. 9.7 Solubility of otavite ($CdCO_3$) in sodium and potassium carbonate solutions at 25°C

The modelling is not yet satisfactory in the $NaCl – CdCO_3 – CO_{2(g)}$ system. It was investigated by SHLYAPNIKOV and SHTERN (1979) at CO_2 pressures of 1 to 50 atm. The calculated solubility curves are about 40 % lower than the experimental data series. However, it should be noted that already the $CdCO_3$ solubility measured by SHLYAPNIKOV and SHTERN in the absence of NaCl is about a factor of 3 higher than the calculated one (their value at 1 atm CO_2: 0.0036 mol/l ; calculated: 0.0011). The deviations at other NaCl concentrations could therefore have the same cause, e.g., a poorly crystallised preparate or insufficient filtration of the samples.

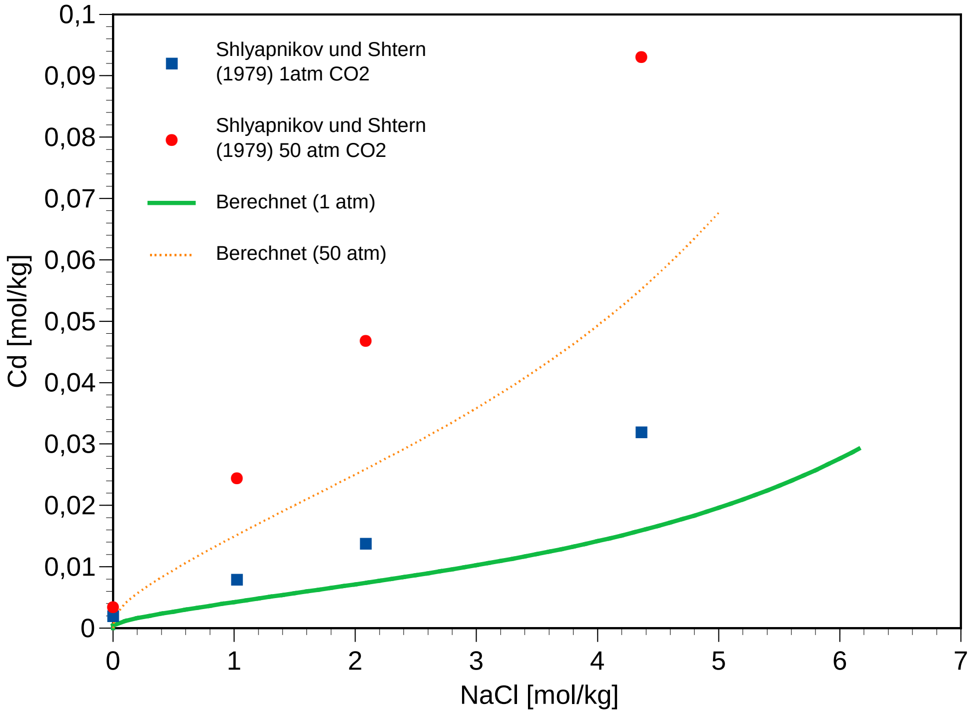

Fig. 9.8 Solubility of otavite in NaCl solutions at constant CO_2 pressure

9.2.5 Hydroxocarbonato complexes

Both zinc and lead have been reported to form hydroxocarbonato complexes (FERRI et al., 1987a,b). It is possible that cadmium also forms such compounds. However, it should be noted that hydroxide formation is much weaker for cadmium than for zinc and lead. Therefore, the stability of mixed complexes should also be lower. RAI et al. (1991b) concluded from their experiments at different pH conditions and carbonate concentration ranges that the measured data can also be explained without a hydroxocarbonato complex.

9.2.6 Other neutral cadmium carbonates

Cadmium carbonate forms solid solutions with various metal carbonates. Well-known examples are otavite-calcite (DAVIS et al., 1987; KÖNIGSBERGER ET AL., 1991; STIPP ET AL., 1992; ROCK et al., 1994; TESEORIERO and PANKOW, 1996[15]) or otavite-magnesite (GOLDSMITH, 1972; BURTON, 1987; CAPOBIANCO ET al., 1987; TAREEN et al., 1995), which

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[15] as well as numerous other sources, see the listed references for a more detailed list

also includes a cadmium dolomite $CdMg(CO_3)_2$. For two defined compounds ($CdMg(CO_3)_2$ and $CdZn(CO_3)_2$), TAREEN et al. (1995) determined free enthalpies of formation. A more detailed evaluation must be omitted for the time being within the narrow framework of this work.

9.2.7 Basic cadmium carbonates

FEITKNECHT and WYLER (1951) found a finely fibrous hydroxide carbonate during the corrosion of cadmium in dilute CO_2-containing solutions. The composition could not be determined because the compound is always interspersed with β-$Cd(OH)_2$. According to BIESTEK and NIEMIEC (1967), during the corrosion of cadmium-plated steel in a natural atmosphere, a hydroxide carbonate of the composition $Cd_5(OH)_6(CO_3)_2$ was formed in addition to cadmium carbonate, i.e., the cadmium analogue of hydrozincite. GRAUER (1980) assumed that it could possibly be a basic chloride, since $CdCl_2$ was also found in the same samples. The reaction of CdO or $Cd(OH)_2$ with water containing carbonate directly produces $CdCO_3$ (NICOL, 1947; TOMANEK, 1967), not a basic carbonate.

Based on the available information, we assume that basic cadmium carbonate has only a small stability range, if any. It obviously does not show the same dominance as the zinc hydroxycarbonate hydrozincite (see there). Since no thermodynamically usable information is currently available, we refrain from further consideration.

9.3 Compounds with chloride

9.3.1 Hydroxo chloro complexes

The formation of the mixed complex $[CdClOH]^0$ was determined by GAYER and HAAS (1960) based on the hydrolysis of dilute $CdCl_2$ solutions. As equilibrium constant K for the reaction

$$[CdCl]^+ + H_2O \rightleftharpoons [CdClOH]^0 + H^+ \qquad (9.25)$$

they obtained the value log K = -10.15. Assuming a complex formation constant of log $\beta_1 = 1.96$ for the reaction

$$Cd^{2+} + Cl^{-} \rightleftharpoons [CdCl]^{+} \qquad (9.26)$$

from (Tab. 7.4) and taking into account the autoprotolysis equilibrium of the water $pK_W = 13.9969$ the equilibrium constant log $ß_{11} = 5.8$ is obtained for the formation of the hydroxochloro complex

$$Cd^{2+} + Cl^{-} + OH^{-} \rightleftharpoons [CdClOH]^{0} \qquad (9.27)$$

Complex formation is relatively weak and plays no role even in seawater (0.7 M NaCl) up to pH 9 (BARIĆ and BRANICA, 1967).

9.3.2 Basic chlorides

The formation of basic cadmium chlorides has been intensively studied by Feitknecht's working group (e.g., FEITKNECHT and GERBER 1937; GERBER, 1938; FEITKNECHT and REINMANN, 1951; FEITKNECHT 1953). They found a total of six main types of basic chlorides $CdCl_{2-x}OH_x$ with x = .1…1.94 and also a number of subtypes. More recent work also confirmed the phase sequence found by FEITKNECHT et al. (WALTER-LÉVY and GROULT, 1970). Basic cadmium chlorides form during the reaction of cadmium chloride-containing solutions with sodium hydroxide or ammonia, depending on the cadmium to hydroxide ratio (Tab. 9.11). Only $CdCl_2 \cdot Cd(OH)_2$ and $CdCl_2 \cdot 3Cd(OH)_2$ have been shown to be thermodynamically stable phases. In particular, the more hydroxide-rich phases are often more or less disordered cadmium hydroxides whose hydroxide ions are partially replaced by chloride. The rates of transformation appear to be very low under certain environmental conditions.

The transition from $CdCl_2 \cdot 3Cd(OH)_2$ to $Cd(OH)_2$ is very slow, even with NaOH excess, from which it can be concluded that the compound is at least kinetically stable (TIKHONOV et al., 1957). According to CUDENNEC et al. (1997), for example, γ-$Cd(OH)_2$ converts in $CdCl_2$ solutions to Cd(OH)Cl at 323 K, but to α-$CdCl_2 \cdot 3Cd(OH)_2$. at 343 K. If this preparate is heated to above 343 K, the phase converts to a non-stoichiometric product $Cd(OH)_{2-x}Cl_x$ and few crystals of β-$CdCl_2 \cdot 3Cd(OH)_2$.

The solubility of the compound $CdCl_2 \cdot Cd(OH)_2$ was investigated by GERBER (1938) and later by REINMAN (1950) and FEITKNECHT and REINMANN (1951,1952). GERBER (1938) provided only incomplete information on the composition of the equilibrium solutions. With the help of some assumptions, a solubility constant can be calculated from them (log K = -23.2). However, we give preference to the more recent investigations by REINMANN (1950) and FEITKNECHT and REINMANN (1952), who obtained a solubility constant of log K = -21.0

Solubility constants for other phases synthesised and investigated by REINMAN (1950) and FEITKNECHT and REINMANN (1951,1952) is included in Tab. 9.10. Not shown are results for the mixed phases $CdCl_{0.30}(OH)_{1.70}$ to $CdCl_{0.03}(OH)_{1.97}$, whose solubility comes closer cadmium hydroxide with decreasing chloride content.

Tab. 9.10 Solubility constants of basic cadmium chlorides determined by REINMANN (1948) and FEITKNECHT and REINMANN (1952).

Reaction	**value (log K)**
$CdCl_2 \cdot Cd(OH)_2 \rightleftharpoons 2Cd^{2+} + 2Cl^- + 2OH^-$	-21
$3CdCl_2 \cdot 5Cd(OH)_2 \rightleftharpoons 8Cd^{2+} + 6Cl^- + 10OH^-$	-46.8
$CdCl_2 \cdot 2Cd(OH)_2$ (active) $\rightleftharpoons 3Cd^{2+} + 2Cl^- + 4OH^-$	-34.8
$CdCl_2 \cdot 2Cd(OH)_2$ (inactive) $\rightleftharpoons 3Cd^{2+} + 2Cl^- + 4OH^-$	-36.0
$CdCl_2 \cdot 3Cd(OH)_2 \rightleftharpoons 4Cd^{2+} + 2Cl^- + 6OH^-$	-50.55

Tab. 9.11 Systematics of the basic cadmium chlorides according to FEITKNECHT and REINMANN (1951)

Formula	**Method**	**Source**
$CdCl_2 \cdot Cd(OH)_2$ (I)	Most stable phase at m $CdCl_2$ 0.01 to saturation	REINMANN (1948), structure HOARD and GRENKO (1934) FEITKNECHT (1952), ASTLER (1962)
$3CdCl_2 \cdot 5Cd(OH)_2$ (II)	Converts to I after a few days. Stable at about 0.0001 to 0.01 and pH7-8 .5 (Possibly conversion rate too small (comment), Also observed in the corrosion of Cd).	REINMANN (1950), FEITKNECHT AND REINMANN (1952), ASTLER (1962)
Approx. $CdCl_2 \cdot 2Cd(OH)_2$ active form (IIIa), line-poor	always metastable. When diluted cadmium chloride solutions (0.1 m) are mixed with lye. Converts to II in a few hours under the mother liquor (0.06 m). Structure like $Cd(OH)_2$	FEITKNECHT (1945)
$CdCl_2 \cdot 2Cd(OH)_2$ inactive form (IIIb)	always metastable. When diluted cadmium chloride solutions (0.05 m) are mixed with alkali	ASTLER (1962)
$CdCl_2 \cdot 2Cd(OH)_2$ (IIIc)		
$CdCl_2 \cdot 3Cd(OH)_2$ (IV)	When mixing 0.1 m $CdCl_2$ solution with 100% NaOH. Slight excess of NaOH leads to the formation of the hydroxide.	FEITKNECHT (1937); FEITKNECHT (1953), REINMANN (1948)
β-$CdCl_2 \cdot 3Cd(OH)_2$	Atacamite structure	CUDENNEC et al. (1997)
$CdCl_2 \cdot 4Cd(OH)_2$ (IV)	Stable at pH 8.5 - 9.5	TANNER (1938)
Mixed hydroxide (V) $CdCl_{0.30}(OH)_{1.70}$ to $CdCl_{0.03}(OH)_{1.97}$	Is isomorphous with hydroxide but cannot be produced by mixing Cd hydroxide and Cd chloride. Stable at pH 9.5 - 12	GERBER (1938), REINMANN (1948)
$Cd(OH)_{1.94}Cl_{0.06}$ (VI)	Forms only in the presence of small amounts of aluminium chloride. Can be considered as a second modification of cadmium hydroxide.	FEITKNECHT and AMMAN (1951)

9.4 Compounds with sulphate

9.4.1 Sulphato complexes

The formation of an ion pair of cadmium and sulphate was demonstrated by RUDOLPH and IRMER (1994) and RUDOLPH (1998) by Raman spectroscopy. It is a very weak outer sphere complex at room temperature, which can be characterised by a complex formation constant of about 0.14. There is no spectroscopic evidence for other anionic complexes $[Cd(SO_4)_n]^{2-2n}$ (FEDOROV et al. 1971,1973 postulated compounds up to n = 5!). The exceptionally good modellability of the sulphate systems Cd - M - SO_4 - H_2O discussed above also shows that explicit consideration of cadmium sulphato complexes can be omitted without loss of predictive accuracy. Because of this, sulphato were not further considered.

9.4.2 Basic cadmium sulphates

The number and composition of basic cadmium sulphates to be considered as a defined compound remains somewhat unclear even after several decades of research (FEITKNECHT and GERBER 1945; BYÉ 1946; URAZOV and KIRAKOSJAN 1954; DENK and DEWALD 1958; SCHINDLER 1956; MARGULIS and BEISEKEEVA 1970; BEN'YASH et al. 1974; WALTER-LEVY et al. 1974a, b). It is certain that the type of solids formed initially in the precipitation of cadmium sulphate solutions with base depends on the $CdSO_4$ concentration of the initial solution. The primary precipitates later transform into more stable compounds. Depending on the environmental conditions, the latter include $Cd(OH)_2$, $CdSO_4 \cdot 3Cd(OH)_2 \cdot xH_2O$, $CdSO_4 \cdot 2Cd(OH)_2$ and $CdSO_4 \cdot Cd(OH)_2$. Especially FEITKNECHT and GERBER (1945) could not find $CdSO_4 \cdot Cd(OH)_2$, while ASPELUND (1933) considered this compound as the only precipitation product. However, the existence of all the compounds mentioned is ultimately proven by the structural chemical work of WALTER-LEVY et al. (1974a, b), LOUËR AND LOUËR (1982), LOUËR ET AL. (1982a, 1982b, 2001), LABARRE et al. (1976a,b).

Tab. 9.12 Systematics of the basic cadmium sulphates according to Feitknecht and Gerber (1945) and others

Formula*	**Conditions of formation**	**Source**
$Cd(OH)_2$	First precipitation product, converts with solution sulphate to higher base sulphate	Denk and Dewald (1958)
$CdSO_4 \cdot 3.5Cd(OH)_2 \cdot 3\text{-}4H_2O$ (IV)	First precipitate with (III), ages to (III)	Schindler (1956)
$CdSO_4 \cdot 3.5Cd(OH)_2 \cdot H_2O$ (III)	First precipitate, converts to $Cd(OH)_2$ in alkaline solution, in sulphatic solution at $c_{CdSO4} < 0.05$ to (II) otherwise to (I)	Moeller and Rhymer (1942), Feitknecht and Gerber (1945), Hartinger (1965)
$CdSO_4 \cdot 2.5Cd(OH)_2 \cdot H_2O$ $CdSO_4 \cdot 3.5Cd(OH)_2 \cdot H_2O$ (IIIα)	First ageing product of (IV)	Schindler (1956)
$CdSO_4 \cdot 2.5Cd(OH)_2 \cdot H_2O$ $CdSO_4 \cdot 3.5Cd(OH)_2 \cdot H_2O$ (IIIβ)	Unstable intermediate of ageing from (III) to (II)	Schindler (1956)
$CdSO_4 \cdot 3Cd(OH)_2 \cdot xH_2O$(II) $x = 0.5$ $x = 1$ $x = 1.5$	Formation at $c_{CdSO4} < 0.05$ M. Unstable, slowly converts to (I)	Feitknecht and Gerber (1945), Denk and Dewald (1958) x = 0.5: Louër et al. (1982) x = 1: Walter-Levy et al. (1974a,b), Feitknecht and Gerber (1945) x = 1.5: Louër et al. (2001)
	Formation at $0{,}002 < c_{CdSO4} < 0{,}035$ M	Walter-Levy et al. (1974a,b)
	Stability limit $5{,}75 \cdot 10^{-5} < c_{CdSO4} < 6{,}1 \cdot 10^{-3}$	Schindler (1956)
$CdSO_4 \cdot 2Cd(OH)_2 \cdot 0.5H_2O$(Iβ)	Formation at $0.05 < c_{CdSO4} < 0.13$ M.	Feitknecht and Gerber (1945)
	Same structure as (I)	Ben'yash et al. (1974)
$1\text{-}2Cd(OH)_2 \cdot CdSO_4$ (Iα)	At higher temperatures only product, probably also at lower temperatures the more stable one, transforms into (I)	Schindler (1956)

* **Bold print** means presence of stable products

Tab. 9.12 [cont.] Systematics of the basic cadmium sulphates according to FEITKNECHT and GERBER (1945) and others

Formula*	**Conditions of formation**	**Source**
$CdSO_4 \cdot Cd(OH)_2$ -(α,β,γ)	Formation at c_{CdSO4} > 0.13 M	DENK and DEWALD (1958)
	Formation at c_{CdSO4} > 0.04 M, but in three modifications (α,β,γ)	WALTER-LEVY et al. (1974a,b), LOUËR et al. (1982), LABARRE et al. (1976a,b),
	Only product	ASPELUND (1933), GRÜTZNER (1898; cited in FEITKNECHT and GERBER 1945).
$Cd_3K_2(OH)_2(SO_4)_3 \cdot 2H_2O$		LOUËR and LOUËR (1982)

* **Bold print** means presence of stable products

9.4.3 Phase sequence

According to FEITKNECHT and GERBER (1945), the compound $CdSO_4 \cdot 3Cd(OH)_2$ is formed at initial concentrations of < 0.05 M $CdSO_4$, $CdSO_4 \cdot CdSO_4 \cdot 2Cd(OH)_2$ at concentrations between 0.05 and 0.13 M and $CdSO_4 \cdot Cd(OH)_2$ at higher concentrations. All compounds are anhydrous. The findings were largely confirmed by DENK (1949) and ASTLER (1962) and KIEßIG and REIMERS (1962). According to DENK (1949), compounds of the type $xCdSO_4 \cdot yCd(OH)_2$ tend towards a mole ratio of one at 60 °C and higher.

DENK and DEWALD (1958) found two basic cadmium sulphates $CdSO_4 \cdot Cd(OH)_2$ and $CdSO_4 \cdot 3Cd(OH)_2$ in agreement with earlier experiments. A more detailed investigation showed that the primary product of precipitation when NaOH is added to cadmium sulphate solution is cadmium hydroxide, which then reacts further with additional sulphate in the solution to form the two basic cadmium sulphates. After prolonged ageing (> 30 days), the basic sulphates decompose to an unidentified cadmium hydroxide or higher basic cadmium sulphate.

MARGULIS and BEISEKEEVA (1970) assume that highly basic cadmium sulphate can contain between 3 and 4 $Cd(OH)_2$, depending on the formation conditions. Other compounds are $CdSO_4 \cdot Cd(OH)_2$ and $CdSO_4 \cdot 2Cd(OH)_2$.

In a follow-up study, BEN'YASH et al. (1974) found three spectroscopically distinguishable preparations at 20 °C: α-$Cd(OH)_2 \cdot CdSO_4$ (final $CdSO_4$ concentration 5.83 - 34.7 wt.-%), β-$Cd(OH)_2 \cdot CdSO_4$ (0.93 - 2.67 wt.-%) and $3Cd(OH)_2 \cdot CdSO_4$ (0.017 - 0.35 wt.-%). Based on the absence of an H_2O deformation vibration in the IR spectrum, the authors concluded that water is not present in the crystal structure. It should be noted that the preparations were dried over concentrated sulphuric acid. The comparison of the XRD diffractograms is interesting. According to this, the data for $CdSO_4 \cdot 2Cd(OH)_2$ (Feitknecht 1945; Margulis et al. 1970), as well as $CdSO_4 \cdot Cd(OH)_2$ (Urazov and Kirakosjan 1954) agree with those for β-$CdSO_4 \cdot Cd(OH)_2$. They found no agreement with the data of Denk and Dewald (1958). The XRD diffractograms of basic cadmium sulphates are very line-rich. Since the preparations are mostly finely dispersed, a clear identification is usually not possible. The IR spectra, on the other hand, are much simpler.

According to Urazov and Kirakosjan (1954), the composition of the product in the reaction of $CdSO_4$ solutions with $Cd(OH)_2$ depends on the pretreatment of the $Cd(OH)_2$. While a compound with $CdSO_4 \cdot 1.2\ Cd(OH)_2$ is formed when air-dried $Cd(OH)_2$ is used as a solid phase, $Cd(OH)_2$ $CdSO_4 \cdot Cd(OH)_2$ is found when freshly precipitated $Cd(OH)_2$ is added. The equilibrium is also established more slowly. In both cases, these compounds form at initial concentrations of 0.44 mol/kg $CdSO_4$ or higher. In contrast, $CdSO_4 \cdot 2Cd(OH)_2$ forms at lower $CdSO_4$ concentrations. The equilibration is the slower the lower the initial concentration of $CdSO_4$ is. It amounts to almost five months at 0.25 wt.-% $CdSO_4$. In two preparations with final concentrations $c_{CdSO4} \leq 0.02$ mol/kg, $CdSO_4 \cdot 3Cd(OH)_2$ was also observed.

9.4.4 Solubility studies

The evaluation of the solubility measurements in Urazov and Kirakosjan (1954) is not possible due to the lack of information on pH values. The solubility investigations presented in Hartinger (1965) can also not be evaluated due to the lack of detailed information. According to Feitknecht (1945) and Feitknecht and Gerber (1945), $CdSO_4 \cdot 3.5Cd(OH)_2 \cdot H_2O$ is in equilibrium with $Cd(OH)_2$ in a solution containing $2.7 \cdot 10^3$ mol/l cadmium sulphate. They obtained $4.4 \cdot 10^{-53}$ as the constant solubility product. Using the concentration data given and the ion interaction parameters derived above, the activity coefficients can be calculated. For freshly precipitated $CdSO_4 \cdot 3.5Cd(OH)_2 \cdot H_2O$ follows:

$$\log K = -54.6 \pm 0.3$$

GROMOV (1948) investigated the solubility of basic cadmium sulphate by adding NaOH at 18 °C to $CdSO_4$ solutions (0.3% to 43 % $CdSO_4$). He specified $3Cd(OH)_2 \cdot CdSO_4 \cdot xH_2O$ as the solid phase in each case. After 24 h, a pH measurement was carried out. It is not clear from the article how much NaOH was added or how the solid phase was analysed. If one neglects the Na_2SO_4 concentration in the solution and calculates the activity coefficients of the ions involved in the phase formation, the solubility constant for the three lowest concentrated solutions (0.1 – 0.35 mol/l Cd) is -48.7. However, this value can only be of orienting character, as important detailed information is missing. At the higher concentrations, a falsification of the pH measurement by diffusion potentials must be assumed. The activity ratios at the other initial $CdSO_4$ concentrations rather refer to compositions with a smaller $Cd(OH)_2:CdSO_4$ ratio, probably $Cd(OH)_2 \cdot CdSO_4 \cdot xH_2O$. With this composition, all measuring points would be explained.

Data on the free enthalpy of formation of $CdSO_4 \cdot 2Cd(OH)_2$ (-1797.3 kJ/mol) and $2CdSO_4 \cdot Cd(OH)_2$ (-2157.9 kJ/mol) can be found in the compilation by WAGMAN et al. (1982). It is unclear on which basis these values were determined. Moreover, the compound $2CdSO_4 \cdot Cd(OH)_2$ is not known from any other literature source. According to SCHINDLER (1956), the compound $CdSO_4 \cdot 2Cd(OH)_2$ is not stable at 25 °C but transforms into the hydrous $CdSO_4 \cdot 2Cd(OH)_2 \cdot 0.5H_2O$. The solubility constants of both compounds should probably differ only slightly, because water is easily split off in all basic cadmium sulphates. Since other data for $CdSO_4 \cdot 2Cd(OH)_2 \cdot 0.5H_2O$ are lacking, the information from WAGMAN et al. (1982) for $CdSO_4 \cdot 2Cd(OH)_2$ serves provisionally as a substitute. The enthalpies of formation correspond to the following solubility constants if the enthalpies of formation of the starting products (Cd^{2+}, SO_4^{2-}, OH^-) are also taken from WAGMAN ET AL. (1982):

$\log K\ [CdSO_4 \cdot 2Cd(OH)_2] = -33.5$

$\log K\ [2CdSO_4 \cdot Cd(OH)_2] = -21.3$

9.4.5 More compounds

The compounds $Cd_3K_2(OH)_2(SO_4)_3 \cdot 2H_2O$ and $Cd_3Cs_2(OH)_2(SO_4)_3 \cdot 2H_2O$ were obtained by LOUËR and LOUËR (1982) when cadmium oxide was mixed with 0.02M $CdSO_4$ and 0.04 M alkali sulphate. In contrast, when sodium, lithium or ammonium sulphate is used, only γ-$Cd(OH)_2 \cdot CdSO_4$ is obtained. Information on the stability of $Cd_3K_2(OH)_2(SO_4)_3 \cdot 2H_2O$ is not available.

9.5 Result overview

The following tables contain an overview of the thermodynamic quantities obtained in this work.

Tab. 9.13 Complex formation constants in the system Cd^{2+} CO_3^{2} – OH^- – H_2O

Reaction	Value (log)	Source
$Cd^{2+} + OH^- \rightleftharpoons [CdOH]^+$	4.16	This work
$Cd^{2+} + 2\ OH^- \rightleftharpoons [Cd(OH)_2]^0$	7.49	This work
$Cd^{2+} + 4\ OH^- \rightleftharpoons [Cd(OH)_4]^{2-}$	9.51	This work
$Cd^{2+} + CO_3^- \rightleftharpoons [CdCO_3]^0$	4.23 ± 0.1	This work
$Cd^{2+} + 2CO_3^- \rightleftharpoons [Cd(CO_3)_2]^{2-}$	6.38 ± 0.1	This work
$Cd^{2+} + HCO_3^- \rightleftharpoons [CdHCO_3]^+$	2.36 ± 0.1	STELLA et al. (1984)
$Cd^{2+} + Cl^- + OH^- \rightleftharpoons [CdClOH]^0$	5.8	GAYER and HAAS (1960)

Tab. 9.14 Binary ion interaction coefficients for cadmium species

Ion pair	$\beta^{(0)}$ or λ	$\alpha^{(1)}$	$\beta^{(1)}$	C^{γ}	Source
$[CdOH]^+$ - $ClO4^-$	0.0279	2	0.0139	-0.05216	Pitzer and Mayorga (1973) for CsBr
$[Cd(OH)_2]^0$-Na+	-0.15	-	-	-	this work
$[Cd(OH)_2]^0$-ClO_4^-	0	-	-	-	this work, set to zero
$[Cd(OH)_4]^{2-}$ - Na^+	0.255		4.286	-	this work
$[Cd(OH)_4]^{2-}$ - K^+	0.505		2.813	-	this work
$[Cd(CO_3)_2]^{2-}$-Na^+	-0.14171				this work
$[Cd(CO_3)_2]^{2-}$-K^+	-0.09614				this work

Tab. 9.15 Solubility constants of basic cadmium-containing compounds

Connection	Reaction	log K	Source
β-$Cd(OH)_2$	β-$Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2\ OH$	-14.39 ± 0.05	This work
$CdCO_3$ (otavite)	$CdCO_{3(s)} + H+ \rightleftharpoons Cd^{2+} + HCO_3^-$	-1.80 ± 0.10	This work
$CdCl_2 \cdot Cd(OH)_2$	$CdCl_2 \cdot Cd(OH)_2 \rightleftharpoons 2Cd^{2+} + 2Cl^- + 2OH^-$	-21.0	Feitknecht and Reinmann (1951)
$3CdCl_2 \cdot 5Cd(OH)_2$	$3CdCl_2 \cdot 5Cd(OH)_2 \rightleftharpoons 8Cd^{2+} + 6Cl^- + 10OH^-$	-46.8	Feitknecht and Reinmann (1951)
$CdCl_2 \cdot 2Cd(OH)_2$ (active)	$CdCl_2 \cdot 2Cd(OH)_2$ (active) $\rightleftharpoons 3Cd^{2+}$ + 2Cl- + $4OH^-$	-34.8	Feitknecht and Reinmann (1951)
$CdCl_2 \cdot 2Cd(OH)_2$ (inactive)	$CdCl_2 \cdot 2Cd(OH)_2$ (inactive) $\rightleftharpoons 3Cd^{2+}$ + 2Cl- + $4OH^-$	-36.0	Feitknecht and Reinmann (1951)
$CdCl_2 \cdot 3Cd(OH)_2$	$CdCl_2 \cdot 3Cd(OH)_2 \rightleftharpoons 4Cd^{2+} + 2Cl^- + 6OH^-$	-50.55	Feitknecht and Reinmann (1951)
$CdSO_4 \cdot 3.5Cd(OH)_2 \cdot H_2O$	$CdSO_4 \cdot 3.5Cd(OH)_2 \cdot H_2O \rightleftharpoons 4.5Cd^{2+} + SO_4^{2-} + 7OH^- + H_2O$	-54.6 ± 0.3	This work based on Feitknecht (1945)
$CdSO_4 \cdot 2Cd(OH)_2$	$CdSO_4 \cdot 2Cd(OH)_2 \rightleftharpoons 3Cd^{2+} + SO_4^{2-} + 4OH^-$	-33.5	Wagman et al. (1982)

10 Thermodynamic properties of hydroxide and carbonate compounds of zinc

10.1 The hydroxo complexes of zinc

10.1.1 Overview and procedure

Zinc forms mononuclear and polynuclear complexes with hydroxide. Besides the mononuclear series $[Zn(OH)_x]^{(2-x)-}$(x=1 ...4), the following polynuclear complexes have been postulated so far: $[ZnOH_2]^{3+}$ and $[Zn_4(OH)_4]^{4+}$ and $[Zn_2(OH)_6]^{2-}$. They occur mainly in zinc-rich solutions (> 0.1 M). Since such can occur in waste leaching processes, they are also considered here.

First, the solubility constant of the most thermodynamically stable zinc hydroxy compound of ε-$Zn(OH)_2$ at 25 °C was determined based on solubility measurements in acidic to neutral solutions in which hydroxo complexes do not occur. On this basis, solubility measurements at high OH concentrations can be evaluated to determine the stability of the highest complex $[Zn(OH)_4]^{2-}$.

From the position of the solubility minimum of ε-$Zn(OH)_2$ under weakly basic conditions, the stability of the prevailing complex $[Zn(OH)_2]^0$ can be derived. This is followed by considerations on the stability of the complexes $[ZnOH]^+$ and $[Zn(OH)_3]^-$.

10.1.2 Type and number of hydroxo complexes of zinc

As in the case of cadmium and lead, there is disagreement in the literature about the type and number of zinc hydroxo complexes relevant at 25 °C. In many cases, the entire range of mononuclear hydroxo complexes $[Zn(OH)_n]^{(2-n)-}$ with n=1…4 was uncritically assumed without providing verifiable evidence for their existence (e.g., REICHLE et al. 1975, SCHORSCH 1964a, 1965; ZHANG and MUHAMMED 2001). POKRIĆ and PUČAR (1971), for example, were able to show that the solubility data (more precisely their tyndallometric findings) can also be described sufficiently well with a model with only two complexes, $[Zn(OH)_2]^0$ and $[Zn(OH)_4]^{2-}$. FERRI and SALVATORE (1988a) came to similar conclusions based on their potentiometric measurements. They showed that a complex $[Zn(OH)_3]^-$ cannot have a significant region of existence, at least in 3 M $NaClO_4^-$. The same conclusion was made in the present study, where numerous measurement data could be explained by assuming only two complexes, especially because the stability fields of $[Zn(OH)]^+$ and $[Zn(OH)_3]^-$ are so narrow that they were not or only slightly covered in many measurement series. However, there are individual solubility studies that provide clear and quantitatively evaluable indications of the two complexes. A closer look is taken below.

The highest hydroxo complex in solution is clearly $[Zn(OH)_4]^{2-}$, as DIRKSE (1954, 1955) was able to show on the basis of potentiometric measurements on strongly alkaline solutions (c to 7 M KOH) with a measuring cell consisting of zinc and HgO/Hg electrodes. In contrast to $[Zn(OH)_3]^-$, there is also strong evidence for this complex from ^{1}H-NMR measurements on zincate solutions (NEWMAN and BLOMGREN 1965).

Multinuclear complexes have also been found or postulated in zinc-rich solutions (> 0.1 M). These include: $[Zn_2OH]^{3+}$ and $[Zn_4(OH)_4]^{4+}$ and $[Zn_2(OH)_6]^{2-}$ (among others ZINEVICH and GARMASH 1975, SCHORSCH 1964a; BURKOV et al. 1978; RAMOS et al. 1983). $[Zn_2(OH)_6]^{2-}$ was also observed in solid calcium zincate (VAPNIK et al. 2019). According to MATIJEVĆ et al. (1962), at least on the basis of coagulation measurements, it is not possible to distinguish between $[Zn_2OH]^{3+}$ and other trivalent species such as $[Zn_3(OH)_3]^{3+}$. Since an analogous beryllium species $[Be_3(OH)_3]^{3+}$ has already been found, the authors considered the latter type more probable.

The determination of complex formation constants is difficult because of several reasons. Solubility experiments with zinc hydroxide are only suitable to a limited extent, since zinc forms at least five different hydroxides, whose different thermodynamic and kinetic stabilities were often not explicitly taken into account. In potentiometric measurements with pH glass electrodes, the influence of the salt content of the solution on the measurement signal was often neglected (liquid junction potential). Furthermore, alkali chlorides were occasionally used as background electrolytes which form chloro complexes with zinc (e.g., SCHORSCH 1964a, 1965). Less prominently, but still disturbingly, nitrato complexes occur in nitrate-rich solutions (cf. HUTCHINSON and HIGGINSON 1973 and the comments in ZHANG and MUHAMMED 2001). The strong changes of hydroxo complex formation when using different background electrolytes and electrolyte concentrations was impressively demonstrated by the experimental work of MILIĆ and JELIĆ (1995).

Structure

The structure of the hydroxo complexes is subject to certain uncertainties. This is explained by the example of the highest complex $[Zn(OH)_4]^{2-}$. LIPPINCOTT et al. (1952) as well as BRIGGS et al. (1974) assumed on the basis of potentiometric results that the highest complex has the composition $[Zn(OH)_4]^{2-}$ and then proved with the help of Raman and NMR measurements that this complex must have a tetrahedral structure. SHARMA (1973), on the other hand, concluded on the basis of identical Raman measurements in concentrated NaOH and KOH solutions that the highest zinc complex should rather be a linear molecule ZnO_2^{2-}. To our knowledge, such a formula was first postulated by FULTON and SWINEHART (1954), but without providing any evidence for it.

The contradiction cannot be clarified. However, since analogous dioxoanions from the series of divalent transition elements of the fourth period are otherwise unknown, it is assumed that $[Zn(OH)_4]^{2-}$ is the correct formula.

Kinetic effects

As an explanation for the wide range of published complex formation constants, CHODAKOVSKIJ and ELKIN (1975) pointed out that the hydrolysis of zinc in dilute aqueous solutions proceeds very slowly and equilibrium may not be reached. In zinc-rich solutions, moreover, polynuclear hydroxo ions are formed that are difficult to quantify. The speed of equilibration seems to decrease with decreasing zinc concentration (ZHANG and MUHAMMED 2001).

It is interesting to note the information by BRIGGS et al. (1974), based on Raman measurements, that in highly concentrated KOH solutions additionally dissolved Zn is only found as $[Zn(OH)_4]^{2-}$ after standing for a longer period of time. Other, intermediate species cannot be identified on the basis of the Raman bands.

10.1.3 The different modifications of zinc oxide and zinc hydroxide

The thermodynamic properties of zinc hydroxides and oxides have been studied in detail by the Bern working group around FEITKNECHT, SCHINDLER and co-workers (FEITKNECHT, 1930 ff.). According to this, at least eight different modifications are to be considered in the Zn-OH(O) system (Tab. 10.1). Precipitation processes from ordinary solutions at standard conditions initially lead to amorphous $Zn(OH)_2$, which begins to transform into crystalline β_1-$Zn(OH)_2$ and ε-$Zn(OH)_2$ via the solution after a few minutes. However, the amorphous phase remains for a long time and controls the zinc concentration. Only when it has completely disappeared, the zinc concentration decreases to a value that results from the solubility constant of the β_1-$Zn(OH)_2$. In the course of 24 h and more, the complete transformation of the solid phase into ε-$Zn(OH)_2$ is often observed.

Further transformation into the thermodynamically most stable ZnO is considerably slower. Published kinetic data differs. According to measurements by SCHOLDER and HENDRICH (1939), at 20°C it is completed after about 150 days . DIETRICH AND JOHNSTON (1927), SCHINDLER et al. (1963, 1964) and ZHANG and MUHAMMED (2001) found no reaction or negligible transformation rates at normal temperature. FRICKE and AHRNDTS (1924) showed that $Zn(OH)_2$ does not transform into ZnO even when stored for one year under alkaline solution (1 – 3 mol/l). ZnO, on the other hand, forms directly during the ageing of highly concentrated zincate lyes or during the storage of $Zn(OH)_2$ in concentrated alkali lyes (> 8 mol/l OH). Only at temperatures of 100°C and more the transformation takes place within hours (DIETRICH and JOHNSTON, 1927). The zinc oxides formed directly during the corrosion of metallic zinc have a high specific surface area and show only a slightly lower solubility compared to ε-$Zn(OH)_2$ (GRAUER, 1980). As expected, the reverse reaction from ZnO to $Zn(OH)_2$ is not observed during storage under water (TOMANEK, 1967).

According to FEITKNECHT (1938), preparations with brucite structure, sometimes called α-$Zn(OH)_2$ in the literature, always and necessarily contain certain amounts of other anions, which are apparently necessary to stabilise the structure. While α-$Zn(OH)_2$ is only a short-lived intermediate under normal conditions, especially since it is always contaminated with anions of the mother solutions, it seems to be the only stable form at higher temperatures (> 400 °C) (BANEYEVA and POPOVA, 1969).

The existence of the various intermediates of the zinc hydroxide was doubted by DIRKSE et al. (1986), since FEITKNECHT (1938) had not carried out a chemical analysis of the preparations obtained. It could not be ruled out that they were basic salts or at least contaminated hydroxides. In our opinion, this cannot be ruled out in individual cases, but the multitude of findings in the literature proves that one can very well speak of different modifications.

ε-$Zn(OH)_2$ is also found in nature as a weathering product of zinc-bearing minerals (wuelfingite: SCHMETZER et al. 1985). Apart from the modifications characterised by

FEITKNECHT, which all have a hexagonal or orthorhombic structure, two tetragonal modifications were found in the 1980s, which occur as secondary minerals of zinc-bearing ores (CLARK et al. 1984; CLARK et al. 1988) or zinc-bearing slags (SCHNORRER-KÖHLER 1988). It has not yet been possible to produce these modifications synthetically. It is possible that the secondary constituents (Cd, Pb, Si) play a decisive role. The phase synthesised by ROY and MUMPTON (1956) under hydrothermal condition also deserves a closer look. Its structure does not correspond to any of the $Zn(OH)_2$ modifications known to date.

Zinc oxide (ZnO, zincite) is distinguished by FEITKNECHT (1938) into active and inactive preparations. However, the crystal structure is the same in both cases, the differences seem to be in the degree of perfection of the crystal lattice and the grain size.

Of the modifications listed in Tab. 10.1 only the kinetically extraordinarily stable ε-$Zn(OH)_2$ (wuelfingite), sweetite, ashoverite and possibly active ZnO are to be regarded as environmentally relevant phases. All other phases do not form at room temperature (inactive ZnO) or transform into ε-$Zn(OH)_2$.

Tab. 10.1 Modifications of zinc hydroxide according to FEITKNECHT (1930, 1938, 1949 ff.) as well as two later findings

Value*	Mineral name	Educational conditions
$Zn(OH)_2$ (amorphous)		First product of precipitation with diluted NaOH
"α-$Zn(OH)_2$“		Preparation always contaminated with anions from the mother liquor
β_1-$Zn(OH)_2$		Precipitate 0.3 M $Zn(ClO_4)_2$ with 70% aq. NaOH at RT. Arises from ageing of α-$Zn(OH)_2$
β_2-$Zn(OH)_2$		is formed by ageing of β_1-$Zn(OH)_2$ in NaOH
γ-$Zn(OH)_2$		FEITKNECHT (1930)
δ-$Zn(OH)_2$		from $Zn(NH_3)_4^{2+}$solution after addition of concentrated H_2SO_4
ε-$Zn(OH)_2$	Wuelfingite (orthorhombic)	Formed by ageing of $Zn(OH)_2$ (am) and ε-$Zn(OH)_2$
$Zn(OH)_2$	Sweetite (tetrahedral)	CLARK et al. (1984). Found mineral. Conditions of formation unknown
$Zn(OH)_2$	Ashoverite (tetrahedral)	CLARK et al. (1988) Found mineral. Conditions of formation unknown
ZnO (active)	Zincite	Precipitate 0.3 M $Zn(ClO_4)_2$ with 100% aq. NaOH at RT. Forms very slowly by ageing of ε-$Zn(OH)_2$
ZnO (inactive)	Zincite	Thermolysis of zinc oxalate at 900°C

* **Bold print** means presence of stable phases

10.1.4 The solubility of the zinc hydroxide ε-$Zn(OH)_2$ (wuelfingite)

To determine the solubility constant of ε-$Zn(OH)_2$, which appears in early works as "crystalline zinc hydroxide" (e.g., DIETRICH and JOHNSTON, 1927), solubility tests as well as polarographic and potentiometric methods were used in the past. An overview can be found in Tab. 10.2. Older work on the formation and solubility of zinc hydroxides not considered here: see GMELIN (1924) or DESHPANDE and KABADI (1952).

A number of investigations had to be discarded before evaluation. MAIER et al. (1926) reported continued drift in their potentiometric experiments, which they attributed to impurities in the preparation they used. The authors considered the measurement results to be less accurate. The derived solubility constant turned out to be too high.

The investigations by FEITKNECHT and HÄBERLI (1950) took place in zinc chloride solutions in which, in addition to chloro complex formation, chloride could also be incorporated into the zinc hydroxide precipitate. FULTON and SWINEHART (1954) published a solubility constant that was an order of magnitude lower than in other works. COLLAT (1958) did not adjust the pH values to the concentration of the background salt solution. In GUBELI and STE-MARIE (1967), the calibration of the pH probe in 1 M $NaClO_4$ is unclear, as is the modification of the hydroxide. REICHLE et al. (1975) worked in solutions of variable ionic strength but used a formula to derive their solubility constant that only applies to constant ionic strength.

The remaining work includes the solubility experiments of SCHINDLER's group and potentiometric measurements on $Zn(OH)_2$-saturated solutions with zinc/mercury oxide electrode chains. They yield values that agree very well with each other. The following mean value was obtained:

$$\log K\ [\varepsilon\text{-}Zn(OH)_2] = -16.42 \pm 0.05$$

It is striking that with this solubility constant some measured values of the neutral pH range in the system $NaOH\text{-}Zn(OH)_2\text{-}H_2O$ cannot be reproduced correctly. The calculated solubility curve is somewhat too high. According to current knowledge, zinc hydroxo complexes do not yet occur here and therefore do not yet have any influence on the result.

10.1.5 The solubility of zincite (ZnO)

As already stated by HÜTTIG and STEINER (1931a), the preparation history of the ZnO has a measurable influence on the solubility of the phase. Both grain size and annealing temperature are reflected in the experimental results. However, the duration (90 min) of their solubility experiments was probably too short to cleanly separate kinetic effects, i.e., the speed of equilibration, from thermodynamic ones, i.e., the level of equilibrium concentration in solution. However, the findings could ultimately be confirmed by SCHINDLER et al. (1965). They showed that the higher the annealing temperature, the lower the specific surface area and thus, according to the OSTWALD-FREUNDLICH relationship, also the solubility. Against this background, it can also be assumed that the distinction between "active" and "inactive" ZnO, as last cited by SCHINDLER et al. (1964), is ultimately based on grain size differences. The solubility differences do not seem large enough to justify the existence of two separate phases.

Tab. 10.2 Solubility constant for ε-$Zn(OH)_2$

log K	log K_S (medium)	Medium / Method	Source
-16.2 ± 0.1		pol. KNO_3 0.02 - 0.17	Collat (1958), no adjustment of pH readings to concentration of background solution
-16.21		pot. (Zn/OH-ISE)	Maier et al. (1926) Cell potential re-evaluated with electrode potentials from
-16.37 ± 0.03	11.75	0.2 M $NaClO_4$	Schindler et al. (1964) re-evaluated with SIT
-16.39	11.75	0.2 M KNO_3	Schindler et al. (1962) re-evaluated with SIT
-16.42 ± 0.03	11.72	0.2 M KNO_3sol.	Pinto et al. (1963) re-evaluated with SIT
-16.42 ± 0.02		pot. (Zn/OH-ISE)	Davies and Staveley (1972)
-16.48		pot. (Zn/OH-ISE)	Dietrich and Johnston (1927)
-16.76		soluble, variable ionic strength	Reichle et al. (1975). Derivation of solubility and complex formation constants with the help of a formula which is only valid for constant ionic strengths
-16.93		Sol. $ZnCl_2$	Feitknecht and Häberli (1950)
-17.2		sol.	Fulton and Swinehart (1954)
-17.5	-16.76	sol. in1M $NaClO_4$	Gubeli and Ste-Marie (1967). Composition of the solid phase unclear (fresh?), pH calibration unclear
-16.42 ± 0.05			**Mean value** (without *italic* values)

An overview of previous measurements of the solubility of ZnO (zincite) is givem in Tab. 10.3. The following studies were not considered in the evaluation:

- Maier et al. (1926) reported continued drift in their potentiometric experiments, which they attributed to impurities in the preparation they used. The derived solubility constant (-16.40) turned out to be too high and reached the value for crystalline zinc hydroxide.

- The preparation annealed at 1000 °C by Feitknecht and Häberli (1950) showed a considerably lower solubility constant than other measured data. It is possible that equilibrium had not yet been reached.

- BARTON and BETHKE (1960) gave ZnO as the product of their titration of zinc sulphate solutions, but this is unlikely to have formed under the experimental conditions they described.
- COLLAT (1958) did not take into account the high ionic strength of the measuring solutions when calibrating the pH probe.
- Earlier work on the determination of the solubility constant or the free enthalpy of formation of zinc oxide and zinc hydroxide was mostly disregarded because they regularly showed quality deficiencies (cf. the discussions in MAIER et al. 1926). Herz (1900) as well as DE WIJS (1925) worked with ammonium-containing solutions in which zinc ammonia complexes form.
- DUPRÉ and BIALAS (1903) omitted important information on the purity of the zinc oxide dissolved in conductometric measurements.

The remaining works agreed well with each other, whereby no distinction was made in the evaluation between so-called "active" and "inactive" ZnO preparations.

The mean value was

$$\log K \text{ (zincite)} = -16.65 \pm 0.09$$

For the further evaluation of solubility measurements, the notice of SCHOLDER and HENDRICH (1939) was helpful. They showed that the solubility of ZnO depends only slightly on temperature. Solubility measurements at temperatures slightly deviating from 25 °C can therefore also be used without further corrections.

Tab. 10.3 Solubility constant of zincite (ZnO)

$\log K_S^0$	Method/Medium	Source
-16.40	pot. (Zn/OH-ISE)	MAIER et al. (1926) Cell potential re-evaluated with electrode potentials from Tab. 7.2
-16.56	Sol. 0.2 M $NaClO_4$	SCHINDLER ET AL. (1964) ZnO "active" re-evaluated with SIT
-16.59	Conductivity.	BOHNSACK (1988) Merck-ZnO, washed.
-16.63	0.02 M $ZnCl_2$	FEITKNECHT and HÄBERLI (1950), "ZnO inactive" dried at 100 °C, re-evaluated with SIT
-16.66	pot. (Zn/OH-ISE)	DIRKSE (1986). ZnO unspecified
-16.73	Sol. 0.2 M $NaClO_4$	SCHINDLER et al. (1964) ZnO "inactive" re-evaluated with SIT
-16.73	Sol. 0.2 M $NaClO_4$	SCHINDLER et al. (1965) ZnO "inactive" coarsest fraction of a measurement series with different grain sizes, re-evaluated with SIT
-16.83	pol. 0.295 M KNO_3	COLLAT (1958) no adjustment of the pH measured values to the concentration of the background solution
-17.05 ± 0.1	variable (Cl,SO_4), titration	BARTON and BETHKE (1958.1960). Solutions contained chloride and sulphate
-17.16	pol. 0.718 M KNO_3	COLLAT (1958) no adjustment of the pH measured values to the concentration of the background solution
-18.11	0.02 M $ZnCl_2$	FEITKNECHT and HÄBERLI (1950), "ZnO inactive" annealed at 1000 °C, re-evaluated with SIT
-16.65 ± 0.09		**Mean value** (without *italic* values)

10.1.6 The solubility of other zinc hydroxides

Besides zincite and ε-$Zn(OH)_2$, other zinc hydroxide phases occur during the basic precipitation of zinc. As already explained above, they are thermodynamically unstable and transform into zincite and ε-$Zn(OH)_2$. The detailed and systematic work of SCHINDLER et al. (1964), in which these phases were subjected to a detailed experimental investigation, can serve as authoritative orientation. For β_1-, β_2-, γ–, and δ-$Zn(OH)_2$ almost no other measured values were available. According to SCHINDLER et al. (1964), the earlier measurements by FEITKNECHT and HÄBERLI (1950) were probably affected by carbonate traces. The only later measurement by BOHNSACK (1988) for a phase assumed to be β_1-$Zn(OH)_2$ confirmed the measured value of SCHINDLER et al. (1964) very well.

The stability of amorphous zinc hydroxide requires closer examination. For the solubility constant, there are numerous measured values in the literature covering a log range from -15 to -16.1. Some literature data that are even lower (-20.2: POKRIĆ and PUČAR (1971); -17.6: KOLTHOFF and KAMEDA (1931)) were probably caused by evaluation errors. FEITKNECHT (1938) already pointed out that the phase, as well as the so-called α-$Zn(OH)_2$, is very difficult to obtain completely pure, since during precipitation other anions are also entrained and incorporated into the lattice. This has a significant effect on the solubility of the phases. In addition, FRICKE and AHRNDTS (1924) showed that the complete transformation into more stable modifications (β, ε) takes place within hours, at most days. It is therefore hardly surprising that the values published in the literature for the solubility and the solubility constant form a continuous series and extend without interruption to the solubility of the most stable phases of ε-$Zn(OH)_2$.

Tab. 10.4 Solubility constant for amorphous $Zn(OH)_2$ (selection)

log K	Method/Medium	Source
-15	I = 0 pot. Titr.	NIKURAŠIN (1938)
-15.42 ± 0.03	0.2 M $NaClO_4$ pot, sol.	SCHINDLER et al. (1963.1964) **Recommended value**
-15.47	Pot. titr.	HAGISAWA (1939)
-15.68 bis -15.95	I = 0 Sol.	FEITKNECHT and HÄBERLI (1950) pH measurement and preparation probably impaired by carbonate traces (cf. SCHINDLER et al. 1964).
-15.74	Pot. titr.	OKA (1938)
-15.90	Solubility / conductivity, $I < 10^{-5}$	BEANBAG (1988)
-16.12	Sol. / conc. of the medium unclear	DE WIJS (1925). Concentration product (Kc)
-16.17	0.17-0.19 M KNO_3	COLLAT (1958). 24 °C Re-evaluated with SIT
-17.33 ± 0.03	pot.	SPIVAKOVSKII and MAYAKOVSKAYA (1968) Freshly precipitated from solutions containing LiCl Preparation designated as $Zn(OH)_2 \cdot 0.1H_2O$
-17.6	Pot. titr. of $ZnSO_4$ solution $I \rightarrow 0$	KOLTHOFF and KAMEDA (1931) preparation contained sulphate
-20.2	Solubility / tyndallometry	POKRIĆ and PUČAR (1971), pH calibration unclear

The data of SCHINDLER et al. (1964) (log K = -15.42) reflects the maximum solubility of freshly precipitated preparations. Depending on the experimental conditions (stirring speed, type of anions, type of addition of lye), the initial solubility of the zinc hydroxide precipitate can also be lower. A generally valid relationship cannot be established.

Tab. 10.5 Solubility constant for the zinc hydroxide modifications β_1, β_2, γ, δ

log K*	Method / Medium	Source
β_1		
-16.65	sol. /I = 0	Feitknecht and Häberli (1950) pH measurement and preparation probably impaired by carbonate traces (cf. Schindler et al., 1964).
-16.14 ± 0.03	0.2 M $NaClO_4$	Schindler et al. (1963.1964), re-evaluated
-16.26	sol., conductivity, I < 10^{-5}	Bohnsack (1988) Zinc hydroxide as a corrosion product on zinc chips, not characterised more precisely, but designated as β_1-$Zn(OH)_2$
β_2		
-16.10 ± 0.03	0.2 M $NaClO_4$	Schindler et al. (1963.1964), re-evaluated
γ		
-16.70	pot., sol. I = 0	Feitknecht and Häberli (1950)
-16.16 ± 0.03	0.2 M $NaClO_4$	Schindler et al. (1963.1964), re-evaluated
δ		
-16.05 ± 0.03	0.2 M $NaClO_4$	Schindler et al. (1963.1964), re-evaluated

* **Bold print** means presence of stable phases

10.1.7 The system NaOH – ZnO/$Zn(OH)_2$ – H_2O

An overview of previous solubility studies in this system is given by Tab. 10.6. In addition to the oxides and hydroxides already mentioned above, sodium zincates occur at high NaOH concentrations. A compound of the composition $NaZn(OH)_3 \cdot 3H_2O$ was observed in precipitation experiments above 9 mol/l NaOH (Scholder and Hendrich 1939). At even higher alkalinity (14 - 19 mol/l), anhydrous $NaZn(OH)_3$ occurs, above that $Na_2Zn(OH)_4$. Urazov et al. (1956) reported $NaZn(OH)_3 \cdot H_2O$ to form at concentrations of 16.9 mol/kg NaOH and above. Goudriaan (1920) - at 30°C - as well as later Haldar (1946), on the other hand, found only $Na_2Zn(OH)_4 \cdot 2H_2O$ or $NaZn_2(OH)_4$.

Tab. 10.6 Overview of previous solubility studies in the system NaOH – ZnO/$Zn(OH)_2$ – H_2O at 25°C

Source	Solid phase	Taken into account	Comments
RUBENBAUER (1902)	$Zn(OH)_2$ (am)		Freshly precipitated $Zn(OH)_2$ from $ZnSO_4$ solution. Test temperature probably room temperature
MOIR (1905)	$Zn(OH)_2$		No indication of temperature, probably room temperature. The stated solubility is an order of magnitude too high. Only molar concentrations.
WOOD (1910)	$Zn(OH)_2$		Molar data. Probably amorphous $Zn(OH)_2$, data would also fit for ε-$Zn(OH)_2$
SMALL (1912)	$Zn(OH)_2$ (am)		Titration experiments probably at room temperature. Since solubility was tested by adding $ZnSO_4$ to KOH solutions, all solutions additionally contained sulphate
GOUDRIAAN (1920)	ε-$Zn(OH)_2$/ ZnO/ zincate	Yes	Measurements at 30 °C. Only the data with crystalline $Zn(OH)_2$ as the solid phase were used.
FRICKE and AHRNDTS (1924)	$Zn(OH)_2$		Temperature probably room temperature, 24 hours, equilibrium not yet reached. Solid phase not precisely characterised
DIETRICH and JOHNSTON (1927)	ε-$Zn(OH)_2$	Yes	Molar concentrations only. Converted to molarities. Only the measuring points with less than 0.1 M $Zn(OH)_2$ solution concentration were used.
MÜLLER (1927)	ZnO		Only the initial concentration of NaOH is given. The zinc solubilities observed at 30 °C depend on the amount of zinc oxide used. Whether equilibrium was reached after 50 days cannot be determined from the experimental data. Molar concentrations
FRICKE (1928)	ε-$Zn(OH)_2$		Solid phase indicated as "crystallised $Zn(OH)_2$". However, the measured value is an order of magnitude too high.
SCHOLDER and HENDRICH (1939)	$Zn(OH)_2$/ ZnO		Measurements at 20 ˚C. Not considered, as only molar concentrations were given
CIŽIKOV and FRENC (1940)	ZnO		A paper mentioned in URAZOV et al. (1956) on the solubility of ZnO in NaOH solutions (temperature?). The citation is incomplete, the cited conference proceedings could not be obtained.
PAKŠER et al. (1950), ARCHIPOV et al. (1950)	$Zn(OH)_2$ (am)		Measurements at 20 °C. Not considered, as only molar concentrations were given
DIRKSE et al. (1954)	ZnO		The data on the solubility of ZnO in NaOH solutions were described as erroneous by the authors themselves
FULTON and SWINEHART (1954)	$Zn(OH)_2$	Yes	
URAZOV ET AL. (1956)	$Zn(OH)_2$/ ZnO/ zincate	Yes	Strongly scattering measured values with $Zn(OH)_2$ as solid phase: not used.

Tab. 10.6 [cont.] Overview of previous solubility studies in the system NaOH – ZnO/Zn(OH)$_2$ – H2O at 25°C

Source	Solid phase	Taken into account	Comments
DEJČMAN (1958)	$Zn(OH)_2$		Investigation of the solubility of zinc sulphate and zinc chloride (0.01 mol/l initial concentration) in sodium hydroxide solutions. However, the measured values are only of limited use, as no information was given about the modification of the zinc hydroxide formed. The incorporation of chloride and sulphate into the solid phase is probable. Above a 30-fold excess of sodium hydroxide, a different zinc hydroxide modification is formed. The temperature during these experiments is unclear
AKESEL'RUD (1960)	$Zn(OH)_2$ (am)		Indication of the measurement data in converted activities, the original data is not available
LANDSBERG et al. (1959-1960)	ZnO		20 °C. The measured values are too high by a factor of 10-50. Test time was probably only about 30 minutes. Solubility data reconstructed from printed diagram
JENKINS et al.(1964)	ZnO		Extraction of ZnO with neutral to slightly basic solutions (produced by adding CaO) probably around 18-22 °C. Values are much too low, probably unsaturated solutions.
GUBELI AND STE-MARIE (1967)	$Zn(OH)_2$		Measurements in weakly acidic to weakly basic solutions. Only molar concentrations. Calibration of the pH electrode unclear
GUBELI AND STE-MARIE (1968)	$Zn(OH)_2$		Solutions contained small amounts of ammonium and thus zinc ammonia complexes possibly present
PONOMAREVA et al. (1973)	ε-$Zn(OH)_2$		Molar concentrations only
REICHLE et al. (1975)	ε-$Zn(OH)_2$		
PATTERSON et al. (1977)	„$Zn(OH)_2$“		Solid phase not characterised more precisely, ionic strength variable. Comparable results were obtained with $ZnCO_3$ as solid phase
BÉNÉZETH et al. (1999)	ZnO	Yes	Only one measuring point

Despite the very large number of experimental investigations, only a few measuring points could be considered reliable and thus evaluable: if it was clear that the solid phase consisted either of "crystalline" $Zn(OH)_2$, i.e., the modification ε-$Zn(OH)_2$, or of zinc oxide. Most of the measurements where the concentrations were only given in molarities had to be eliminated. Up to about 3 mol/l NaOH, the concentrations could be converted into molarities with the help of the density function shown in the appendix. Without having a more precise proof for this, we assumed that the Zn contents occurring at higher NaOH concentrations (above 0.1 mol/l) have a significant effect on the density and make a reliable conversion too difficult.

Based on the findings of SCHOLDER and HENDRICH (1939), it was assumed that the solubility of ZnO in NaOH and KOH solutions changes only slightly with temperature. We therefore also used some measurements at slightly different temperatures (20-30 °C) for evaluation. More detailed description of the individual works and their treatment is given in Tab. 10.6.

10.1.8 The KOH – ZnO/Zn(OH)$_2$ – H$_2$O system and the determination of the formation constant for [Zn(OH)$_4$]$^{2-}$

Tab. 10.7 shows an overview of the available literature on this system. In contrast to the previously discussed system, zinc does not seem to form any or only metastable zincates at 25 °C with potassium. While at 0 °C and concentrations above 8 mol/kg KOH a potassium zincate KHZnO$_2$= KZnO(OH) can be detected as a phase, such a phase is absent at 30°C (IOFA et al. 1949) and also at 25°C (DIRKSE et al. 1954). According to FRICKE and AHRENDTS (1924), a compound KZnO(OH) is found at least as a minor component at very high KOH concentrations. It is probably only metastable.

Only those studies were evaluated in which the solid phase was clearly identifiable as crystalline ε-Zn(OH)$_2$ or ZnO (Tab. 10.7) and the KOH concentration was below 10 mol/kg. In addition, potentiometric measurements of unsaturated zincate solutions (BODEN et al. 1971) were available. However, these could not be evaluated because only molar concentrations were given. The only earlier work on the determination of ion interaction coefficients with [Zn(OH)$_4$]$^{2-}$ unfortunately did not provide any information on the measurement data used and included only incomplete information on the derived parameters (COCKE et al. 1997).

Tab. 10.7 Overview of previous solubility studies in the system KOH-$ZnO/Zn(OH)_2$-H_2O at 25 °C

Source	Solid	Considered for the determination of β_4	Comments
HEART (1901)	$Zn(OH)_2$		20 °C The modification of the $Zn(OH)_2$ finally obtained is unclear, although the author also spoke of a "more difficult to dissolve form".
MOIR (1905)	$Zn(OH)_2$		No indication of temperature, probably room temperature. The solubilities given are an order of magnitude too high. Only molar concentrations.
SMALL (1912)	$Zn(OH)_2$(am)		Titration experiments probably at room temperature. Since the solubility was tested by adding $ZnSO_4$ to KOH solutions, all solutions additionally contained sulphate
HÜTTIG and STEINER (1931a)	ZnO		20 °C. Molar concentrations. The measured value with the coarsest ZnO fraction was selected. Test duration with only 90 min obviously too short: solubility too high.
MALLORY (1948)	$ZnO/Zn(OH)_2$		Molar data presented as solubility curves in FALK and SALKIND (1969, p. 586). No individual data to be taken. No experimental details given.
IOFA et al. (1949)	ε-$Zn(OH)_2$		30 °C. Measurement data digitised from graph. Not taken into account, as significantly higher than other results.
SOČEVANOV (1952)	ε-$Zn(OH)_2$/ ZnO	Yes	18 – 22 °C
DIRKSE et al. (1954)	ZnO	Yes	Measurement data from graph digitised and converted to molalities with density function
DIRKSE (1959)	ZnO	Yes	The measured values at the lowest KOH concentrations (< 2.3 mol/kg) are obviously too high and were not taken into account.
BAKER and TRACHTENBERG (1967)	ZnO		Only the KOH concentrations before the start of the experiments and the Zn molarities after the end of the experiments are mentioned.
DYSON ET AL. (1968)	ZnO	Yes	
HAMPSON et al. (1969)	ZnO	Yes	23 °C. Only molar concentrations. Measurement data digitised from graph, only the lowest two at 1 and 2 mol/l KOH converted to molality. The measuring point at 1 mol/l KOH turned out to be much too high.
DELCO and REMY	ZnO		Private communication in SHARMA (1986). Data presented only in imprecise graphical form
GAGNON and MAHESWARI	ZnO		Private communication in SHARMA (1986). Data presented only in imprecise graphical form

The solubility data from the systems $NaOH - ZnO/Zn(OH)_2 - H_2O$ and $KOH - ZnO/Zn(OH)_2 - H_2O$ were evaluated together to determine in parallel both the complex formation constant β_4 and the Pitzer β parameters for the interactions between

Na^+ and K^+, respectively, with $[Zn(OH)_4]^{2-}$. The same procedure was used as for the complex $[Cd(OH)_4]^{2-}$ (see chapter 0). For the complex formation constant, the following result was obtained

$$\log \beta_4 = 14.90$$

in combination with the interaction coefficients in Tab. 10.12. The experimental data up to a MOH concentration of 10 mol/kg in NaOH solutions (Fig. 10.2) and in KOH solutions (Fig. 10.3) are well reproduced.

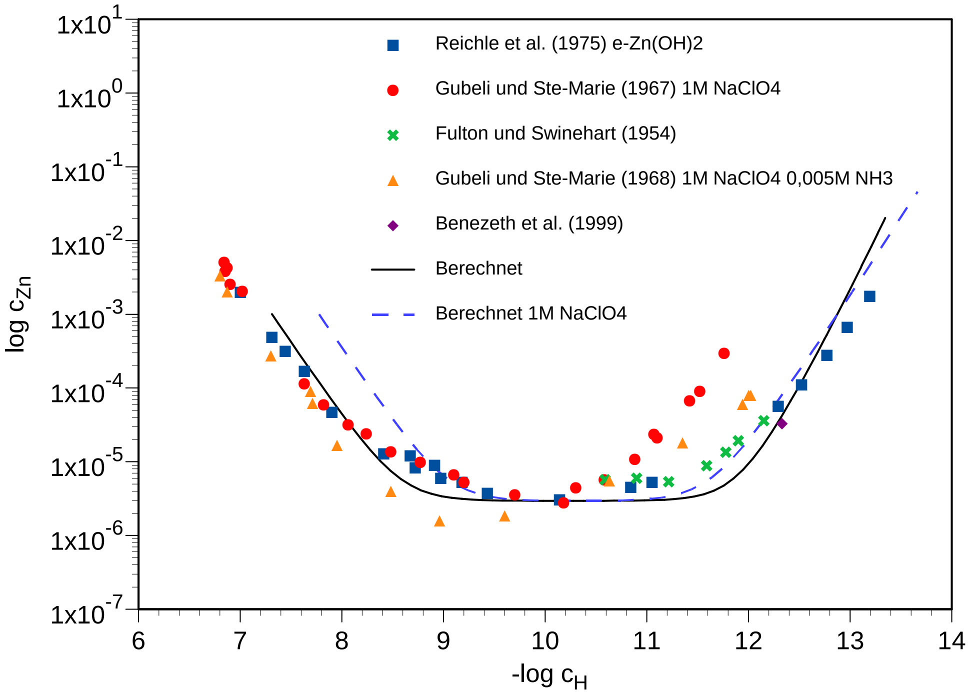
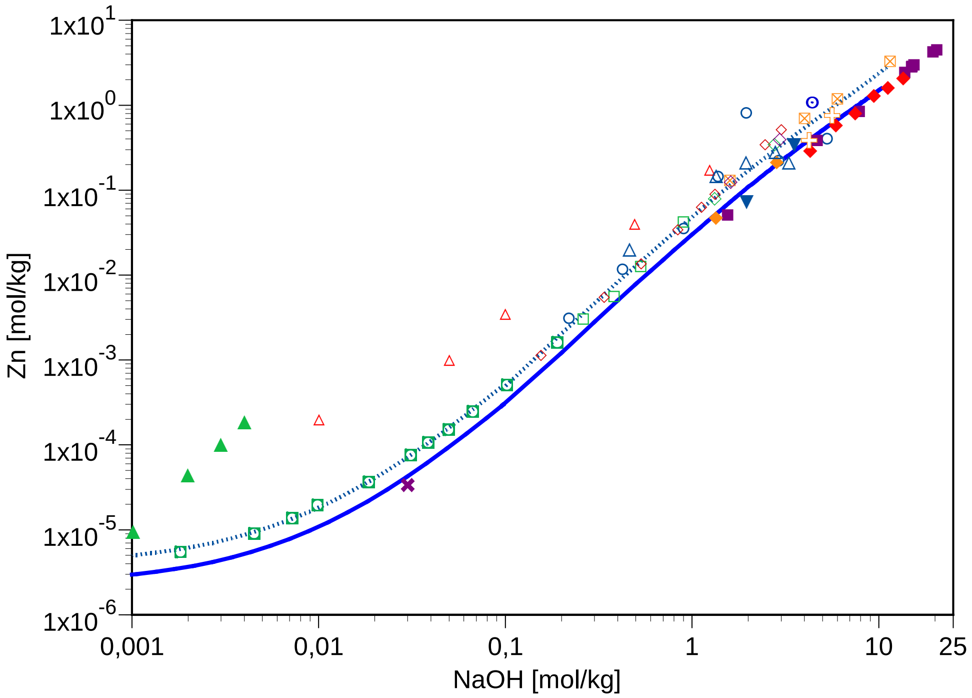
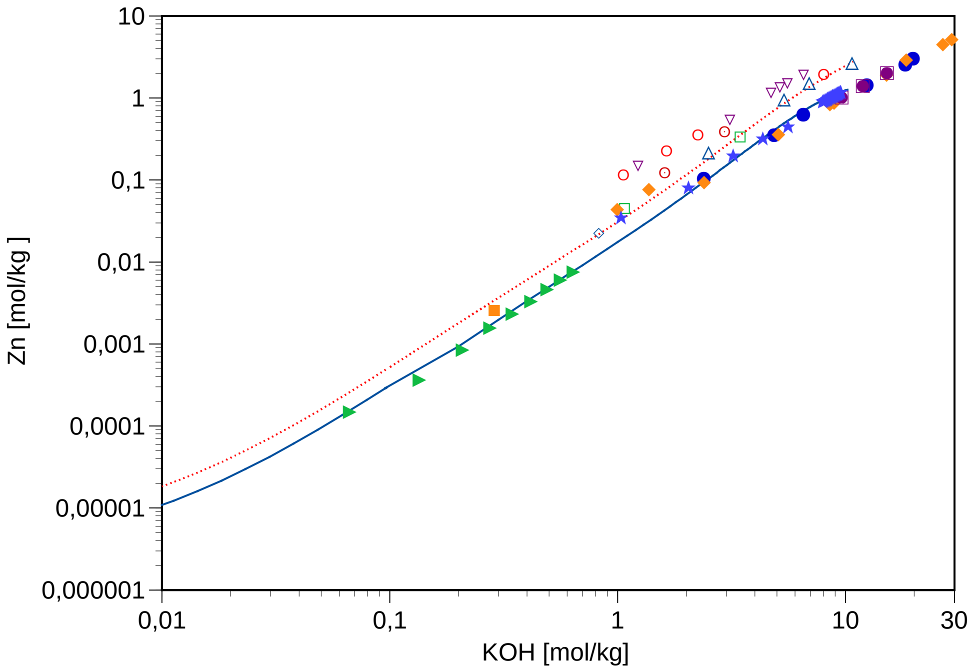


Fig. 10.1 Solubility of $Zn(OH)_2$ in NaOH solutions



filled symbols: measured data zincite, solid line: calculation
open symbols: Measured data ε-$Zn(OH)_2$, dashed line: calculation

Fig. 10.2 Solubility of zincite and ε-$Zn(OH)_2$ in NaOH solutions at 25 °C



filled symbols: measured data zincite, solid line: calculation
open symbols: Measured data ε-$Zn(OH)_2$, dashed line: calculation

Fig. 10.3 Solubility of zincite and ε-$Zn(OH)_2$ in KOH solutions at 25 °C

10.1.9 The formation constants for the complexes $[ZnOH]^+$, $[Zn(OH)_2]^0$ and $[Zn(OH)_3]^-$

The available potentiometric and polarographic measurement data are very contradictory (Tab. 10.8). As an example, the work on the stability of the complex $[ZnOH]^+$ may be mentioned. Study of seemingly equal quality yielded complex formation constants (log β_1) between 5 and 6.6. Such a wide range is quite unusual for the first complex formation constant. Accordingly, the conclusions are also very different. While PERRIN (1962) assumed on the basis of his potentiometric measurements in very dilute KNO_3 solutions (I = 0.0015 to 0.043) that relevant amounts (1 mol.-%) of the complex only occur from pH 7.5, MILIĆ and JELIĆ (1995) conclude that complex formation already begins at pH 3. However, as the evaluation and modelling of the solubility experiments in weakly alkaline solutions showed, no influence of possible complex formation can be detected before about pH 7.5: In a double logarithmic plot, the initially linearly falling solubility curve (a sign of the absence of complex formation) only begins to flatten at this pH (Fig. 10.3).

Unfortunately, the most recent critical evaluation presented by ZHANG and MUHAMMED (2001) did not help. If the set of complex formation constants presented by the authors is taken as a basis, the solubilities of $Zn(OH)_2$ in the pH range 7 to 11 could not be correctly reproduced. The calculated solubilities were consistently about one order of magnitude too high and also did not correctly reflect the shape of the solubility curve.

Tab. 10.8 Previously determined molar formation constants (log $\beta_{m,n}$) of zinc hydroxo complexes at 25 °C (formation reaction m Zn^{2+} + n $OH^{-} \rightleftharpoons [Zn_m(OH)_n]^{2m-n}$), not corrected for activities.

Medium	$[ZnOH]^{+}$ 1.1	$[Zn(OH)_2]^{0}$ 1.2	$[Zn(OH)_3]^{-}$ 1.3	$[Zn(OH)_4]^{2-}$ 1.4	$[Zn_4(OH)_4]^{4+}$ 4.4	$[Zn_2(OH)]^{3+}$ 2.1	**Method**	**Source**
I→0				15.44			sol.	Dietrich and Johnston (1927)
I→0	4.42						pot	Kolthoff and Kameda (1931)
I→0	5.03						pot	Prytz (1931)
I→0	3.81						pot	Hagisawa (1939)
I→0			16.08	15.04			pot	Bernheim and Quintin (1950) 20 °C
0.1M KCl	5.09						pot	Chaberek et al. (1952) 30 °C
I→0				15.15			pot	Dirkse (1954)
I→0			14.23				sol.	Fulton and Swinehart (1954)
I→0	4.64						pot	Achenza (1958)
		12.89					sol.	Aksel'rud and Spivakovsky (1959)
2 M KCl				15.19			pol	Matsuda and Ayabe (1959)
I→0	4.71						pot	Besson and Eckert (1959)
I→0	4.95						pot	Dye et al. (1960)
2 M $NaClO_4$		9.46					pot	Schorsch (1961)
2 M KCl	4.92					6.73	pot	Schorsch (1961)
2 M NaCl	4.75						pot	Schorsch (1961)
3M $LiClO_4$						5.04	pot	Biedermann (1962)
0.1 M $NaClO_4$			13.57				distr.	Bode (1962) 20 °C
0.002 M KNO_3	5.03						pot	Perrin (1962)
0.013 M KNO_3	4.93						pot	Perrin (1962)
0.043 M KNO_3	4.85						pot	Perrin (1962)
I→0	5.04						pot	Perrin (1962)
3 M NaCl				13.24			pot	Schorsch (1964a)
2 M KCl	4.93					6.71	pot	Schorsch (1964a)
3 M NaCl	4.75					6.47	pot	Schorsch (1965)
3 M $NaClO_4$		8.21	13.63	17.89			distr.	Sekine (1965)
0.5 M $NaClO_4$	5.66						pol	Barić and Branica (1967)
1 M $NaClO_4$	6.29	11.15	14.24	17.61			pot	Gubeli and Ste-Marie (1967)
I→0		9.86					pol	Bradford (1973) 20 °C
0.01 M $NaClO_4$	4.81	11.01	14.11				distr.	Okunev (1973)
var.	6.16	11.18	13.88	15.57			sol.	Reichle et al. (1975)
3 M $NaClO_4$					30.42	5.49	pot	Zinevich and Garmash (1975)
3 M $NaClO_4$	3.75					5.37	pot	Burkov et al. (1978)
0.1 M; KNO_3	5.81	11.09					phot	Nazarenko et al. (1978)
0.3 M KNO_3	5.70	10.91					phot	Nazarenko et al. (1978)
0.5 M KNO_3	*						phot	Nazarenko et al. (1978)

Tab. 10.8 **[cont.]** Previously determined molar formation constants (log $\beta m_{,n}$) of zinc hydroxo complexes at 25 °C

Medium	**$[ZnOH]^+$** 1.1	**$[Zn(OH)_2]^0$** 1.2	**$[Zn(OH)_3]^-$** 1.3	**$[Zn(OH)_4]^{2-}$** 1.4	**$[Zn_4(OH)_4]^{4+}$** 4.4	**$[Zn_2(OH)]^{3+}$** 2.1	**Method**	**Source**
1 M KNO_3	5.35	10.32					phot.	NAZARENKO et al. (1978)
3 M $NaClO_4$	6.65	11.39	13.84	16.03			pol	YANG et al, (1983)
3 M $NaClO_4$				14.83			pot	FERRI et al. (1987a)
I→0	5.14	9.94					sol., cond.	BEANBAG (1988)
3 M $NaClO_4$		12.09		15.13			pot	FERRI and SALVATORE (1988a)
0.5 M $NaNO_3$	5.03						pot	MILIC and JELIC (1995)
1 M $NaNO_3$	*						pot	MILIC and JELIC (1995)
1.5 M $NaNO_3$	*						pot	MILIC and JELIC (1995)
2 M $NaNO_3$	4.88						pot	MILIC and JELIC (1995)
2.5 M $NaNO_3$	*						pot	MILIC and JELIC (1995)
3 M $NaNO_3$	4.64						pot	MILIC and JELIC (1995)
0.5 M $NaClO_4$	5.96						pot	MILIC and JELIC (1995)
0.5 M NaCl	5.13						pot	MILIC and JELIC (1995)
0.1 M $NaClO_4$	7.22						pot	SRIVASTAVA and TIWARI (1995) 3°C0
unclear	5.00	9.00	12.70				pot	HANZAWA et al. (1997)
I→0	5.25	10.15	13.88				sol.	BENEZETH et al. (1999)
0.2 M $NaNO_3$	5.90	12.65					pot	PATEL et al. (1999) 30 °C
0.1 M $NaNO_3$	5.90	12.65					pot	MUKHERJEE and SAHU (2000)
I→0	6.50	11.60	13.80	14.70			rev.	ZHANG and MUHAMMED (2001)
I→0	**5.7**	**11.0**	**13.4**	**14.9**				**This work**

phot: photometry, pol: polarographic/ voltammetric, pot: potentiometric, sol.: solubility, cond.: conductivity,

rev: critical review, photom.: photometric, distr.: distribution equilibrium between two phases.

* Data refer to reaction equation with H instead $^+$of OH$^-$. The necessary data for the conversion to a reaction with OH are missing.$^-$

The problem was approached step by step, using the numerous available solubility studies as a guide. In a first step, the formation constant for $[Zn(OH)_4]^{2-}$ was determined in the concentration range in which this complex largely occurs alone based on previous findings (solubility experiments, potentiometric data) (see above).

After that, the formation constant for $[Zn(OH)_2]^0$ was determined on the basis of the consideration that at the minimum concentrations occurring in the investigations in Tab. 10.9 (FULTON and SWINEHART, 1954; GUBELI and STE-MARIE, 1967; REICHLE et al. , 1975) only the complex $[Zn(OH)_2]^0$ occurs - i.e. the solid phase is in equilibrium only with this zinc species. This assumption seems justified on the basis of previous complex formation models and solubility experiments. In fact, the solubility experiments (except those of Gubeli and Ste-Marie (1967,1968) showed a mostly constant zinc solubility between pH 9.5 and pH 11.5. In this case, the following relationships apply:

$$\begin{aligned}
&c_{Zn,tot} \approx c_{[Zn(OH)_2]^0} \approx c_{[Zn(OH)_2]^0}\,\gamma_{[Zn(OH)_2]^0} = a_{[Zn(OH)_2]^0} = \beta_2 a_{Zn^{2+}} a^2_{OH^-} \\
&K[\varepsilon[\,Zn(OH)_2] = a_{Zn^{2+}} a^2_{OH^-} \\
&c_{Zn,tot} \approx \beta_2 K[\varepsilon-Zn(OH)_2] \\
&\beta_2 \approx \frac{c_{Zn,tot}}{K[\varepsilon[\,Zn(OH)_2]}
\end{aligned} \tag{10.1}$$

If one further assumes that the activity coefficient of $[Zn(OH)_2]^0$ also in 1 M $NaClO_4$ deviates only insignificantly from one, then according to the investigations summarised in Tab. 10.9 a complex formation constant of $\log \beta_2 = 11.0 \pm 0.2$ can be derived. This constant is to be regarded as the maximum value. If one of the two complexes $[ZnOH]^+$ or $[Zn(OH)_3]^-$ should occur at this concentration to an appreciable extent, the free concentration of $[Zn(OH)_2]^0$ would have to decrease and so would the complex formation constant. However, at least in the pH range 9.5 to 10.5 this is not the case (see below).

Tab. 10.9 Minimum solubilities of ε-$Zn(OH)_2$

value [mol/kg] x 10^{-6}	Source	Comments
5.8	Fulton and Swinehart (1954)	
2.8	Gubeli and Ste-Marie (1967)	1 M $NaClO_4$. pH calibration unclear, but not relevant for this evaluation.
3.1	Reichle et al. (1975)	pH calibration unclear, but not relevant for this evaluation
3.9 ± 1.5	**Mean value**	

This process leads to the formation constants β_2 and β_4. Fig. 10.4 shows the calculated solubility curve for ε-$Zn(OH)_2$. It agrees well in large parts with the available measured data. In particular, the linear solubility decrease in weakly basic solutions as well as minimum solubilities around pH 9.5 - 11 are well reproduced. There are noticeable deviations in two narrow pH ranges: Both at pH 8-9 and pH 11.5-12.5 the experimental solubilities are up to a factor 2 above the calculated curves. This could be a clear indication that additional species are present here that contribute significantly to the total solution concentration. For further evaluation, it is important to note that in the range of minimum solubility (pH 9.9 - 10.5) no significant deviations can be found, so that the derived constant β_2 is confirmed.

Assuming that the additionally occurring concentrations in the pH ranges 8 - 9 and 11.5 to 12.5 can are caused by the formation of $[ZnOH]^+$ and $[Zn(OH)_3]^-$, a way opens up to calculate the concentration ratios $[ZnOH]^+/[Zn(OH)_2]^0$ and $[Zn(OH)_3]^-/[Zn(OH)_2]^0$ and thus to derive the complex formation constants β_1 and β_3. The solubilities from REICHLE et al. (1975) in the pH range from 8.41 to 9.18 served as the data basis for β_1. For the six measuring points concerned, the solubility of ε-$Zn(OH)_2$ was calculated as a function of pH based on the previously derived complex formation constants β_2 and β_4. The total zinc concentration $c_{Zn,total}$ is then composed of the proportion of the three species Zn^{2+}, $[Zn(OH)]^+$ and $[Zn(OH)_2]^0$:

$$c_{Zn,total} = c_{Zn^{+2}} + c_{[ZnOH]^+} + c_{[Zn(OH)_2]^0} \qquad (10.2)$$

The total concentration results from the experiment, the concentration for $[Zn(OH)_2]^0$ is constant for all pH values ($3.9 \cdot 10^{-6}$ mol/kg, Tab. 10.9), the concentration of Zn^{2+} results from the pH value and the concentration of $[Zn(OH)_2]^0$. The difference between calculated and experimental values was completely assigned to the complex $[ZnOH]^+$.

$$c_{[ZnOH]^+} = c_{Zn,total} - c_{[Zn(OH)_2]^0} - \frac{c_{[Zn(OH)_2]^0}}{\beta_2 \, \gamma_{Zn^{2+}} \, a^2_{OH^-}} \qquad (10.3)$$

The complex formation constant β_1 was calculated from the ratio

$$\beta_1 = \frac{a_{[ZnOH]^+}}{a_{Zn^{2+}} \, a_{OH^-}} \qquad (10.4)$$

where the activity coefficients contained in the activities *a* could be calculated with the Debye-Hückel equation at the low ionic strengths of the experiment (around 10^{-5} mol/l). The result was a complex formation constant of

$\log \beta_1 = 5.7 \pm 0.4$

For the calculation of the constant β_3 the results of FULTON and SWINEHART (1954) in the NaOH concentration range of 0.0018 to 0.067 mol/kg were used. The evaluation was analogous to the above case. The stepwise formation constant k_3 results from the equation[16]

$$k_3 = \frac{c_{[Zn(OH)_3]^-,\mathrm{berech}}}{c_{[Zn(OH)_2]^0}\,\gamma_{[Zn(OH)_2]^0}\,c_{OH^-}}\,\frac{\gamma_{[Zn(OH)_3]^-}}{\gamma_{OH^-}} \cong \frac{c_{[Zn(OH)_3]^-,\mathrm{berech}}}{c_{[Zn(OH)_2]^0}\,c_{OH^-}} \qquad (10.5)$$

The assumption was that in the solutions considered with ionic strengths below 0.067 the following applies approximately: $\gamma_{[Zn(OH)3]}=\gamma_{OH}$ a well as $\gamma_{[Zn(OH)2]}=1$. Then one obtains as mean value:

$\log k_3 = 2.44 \pm 0.03$

and for cumulative complex formation:

$\log \beta_3 = \log \beta_2 + \log k_3 = 13.4 \pm 0.2$

Adding these data to the parameter set, the solubility calculation is given in Fig. 10.4. All the characteristics of the series of measurements between pH 7 and 13.5 are now correctly reproduced. But how do these findings fit in with the statements of FERRI et a. (1988a) and POKRIĆ AND PUČAR (1971), who found no evidence for $[ZnOH]^+$ and $[Zn(OH)_3]^-$ respectively? FERRI and Salvatore (1988a) worked in a medium of 3 M $NaClO_4$. Under these conditions, the formation of the divalent ion $[Zn(OH)_4]^{2-}$ is favoured over the only monovalent $[Zn(OH)_3]^-$ because the activity coefficient of the divalent ion is much lower. As a result, the narrow existence range of the ion $[Zn(OH)_3]^-$ mostly disappeared.

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[16] In the following equation, the index „berech“ means „calculated“

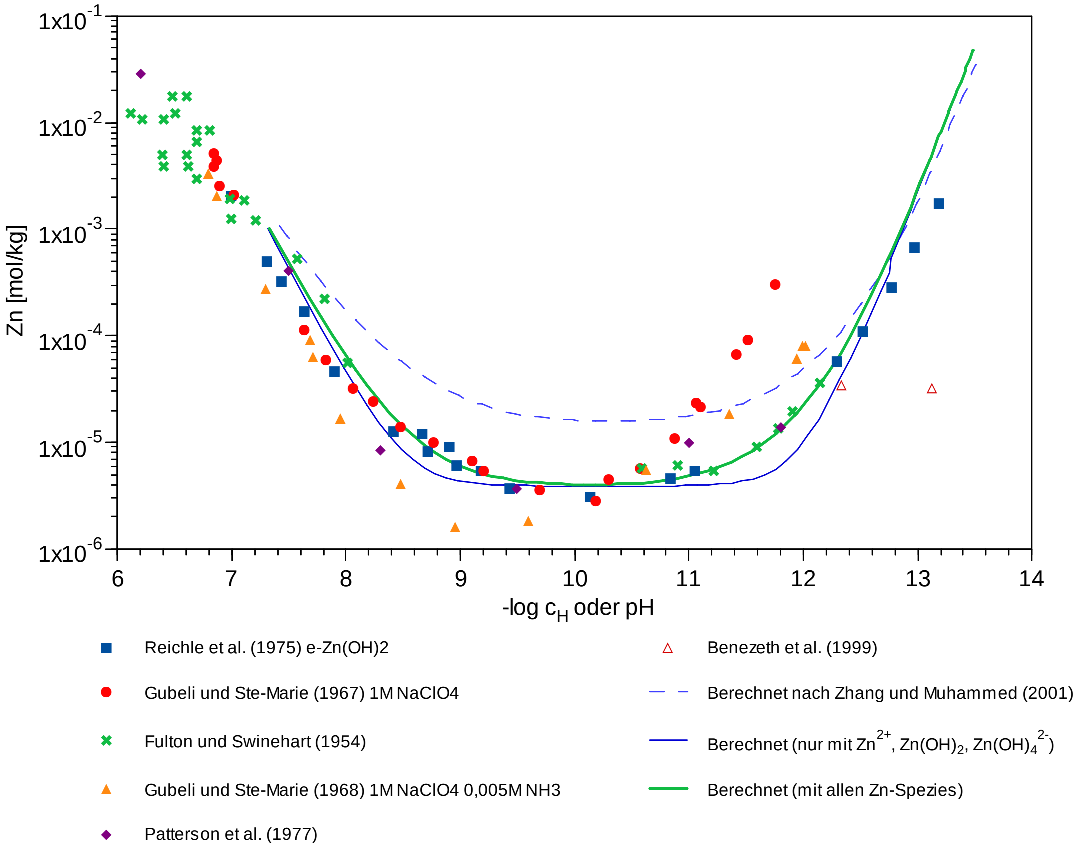

Fig. 10.4 Calculated solubility of ε-$Zn(OH)_2$ in weakly basic solutions

The measurement data of Pokrić and Pučar (1971) are only available in a double logarithmic order. The area in which the two complexes $[ZnOH]^+$and $[Zn(OH)_3]^-$ occur more strongly is only weakly occupied with measurement data. The complex formation constants derived in this work are in the range of previously published values.

10.1.10 Polynuclear hydroxo complexes

Only few reliable data are available on polynuclear zinc hydroxo complexes. The compounds $[Zn_4(OH)_4]^{4+}$ and $[Zn_2(OH)]^{3+}$ have been postulated so far (cf. Tab. 10.8). Some measurements were carried out in concentrated chloride-containing media, in which the formation of chloro complexes is also to be expected (Schorsch 1961, 1964a, 1965). These are omitted for closer consideration. The remaining investigations were carried out in 3 M $NaClO_4$ or 3 M $LiClO_4$ (Biedermann 1962, Zinevich and Garmash 1975, Burkov et al. 1978). Here, the determined molar complexation coefficients are close to each other, but cannot be converted into thermodynamic constants at present because neither SIT nor Pitzer interaction coefficients are available.

10.1.11 Calcium zincate

If calcium is present in addition to zinc at high alkalinities, the formation of a sparingly soluble calcium zincate is observed. It represents an important binding form of zinc in cement-containing systems (Ziegler and Johnson, 2001). The composition is consistently reported as $Ca(OH)_2 \cdot 2Zn(OH)_2 \cdot 2H_2O = CaZn_2(OH)_6 \cdot 2H_2O$ (Bertrand 1892, Bertrand and Javillier 1906, Heise and Schumacher 1932, Sharma 1986). It forms approximately above pH 11 - 12 and is stable relative to ZnO up to hydroxide concentrations around 10 mol/kg. A compound of the same composition has been described as the mineral qatranaite (Vapnik et al. 2019).

In the literature, there have been two experimental studies to determine the solubility constant of this phase. Sharma (1986) determined the solubility of calcium zincate in KOH solutions that were simultaneously saturated with portlandite, $Ca(OH)_2$. Since two phases are saturated at the same time, a simple relationship can be derived to calculate the solubility constant.

It applies:

$$\mathrm{K(Portlandite)} = \mathrm{K_P} = \mathrm{a_{Ca}a_{OH}^2} \qquad (10.6)$$

$$\mathrm{K(Calciumzincate)} = \mathrm{K_Z} = \mathrm{a_{Ca}a_{OH}^2a_{Zn}^2a_{OH}^4a_W^2} \qquad (10.7)$$

and at high OH concentrations as well:

$$c_{\mathrm{Zn,tot}} \approx c_{\mathrm{Zn(OH)_4}} \qquad (10.8)$$

with

$$a_{\mathrm{Zn(OH)_4}} = \beta_4 a_{\mathrm{Zn}} a_{\mathrm{OH}}^4 \qquad (10.9)$$

The formulas can be summarised as:

$$K_Z = \frac{K_P a_{\mathrm{Zn(OH)_4}}^2 a_W^2}{\beta_4^2 a_{\mathrm{OH}}^4} \qquad (10.10)$$

Thus, only the activity coefficients of the ions $[Zn(OH)_4]^{2-}$, OH^- and the water activity in KOH solutions are needed. Due to the very low solubility of portlandite in KOH solutions

(<<0.001mol/kg), the influence of Ca^{2+} on the dissolution properties of these ions is negligible and does not need to be considered. With the help of the complex formation constants derived above, the measured values of SHARMA (1986) were re-evaluated. This resulted in the following solubility constant:

log K (Ca-zincite) = -40.08 ± 0.05

This value agrees very well with the value derived by ZIEGLER and JOHNSON (2001) (-40.08), although the complex formation constants used there do not agree with those derived in this work.

A re-evaluation of the data in ZIEGLER and JOHNSON (2001) is not possible because no measurement data were printed. The measurement data of SHARMA (1986) are reproduced very well. The onset of zincite formation depends on the calcium content of the solution. At a Ca concentration of 0.0001 mol/kg, it starts at about pH 11.9.

COCKE et al. (1997) determined interaction coefficients for the ion pair $Ca^{2+}/ [Zn(OH)_4]^{2-}$. Apparently, the measured values from SHARMA (1986) served as the data basis. However, it is not clear from the explanations how the derivation was carried out, since in SHARMA there is no information on the solubility of Ca^{2+} in calcium zincate-saturated solutions, without which an evaluation is not possible in our opinion. The parameters are not adopted.

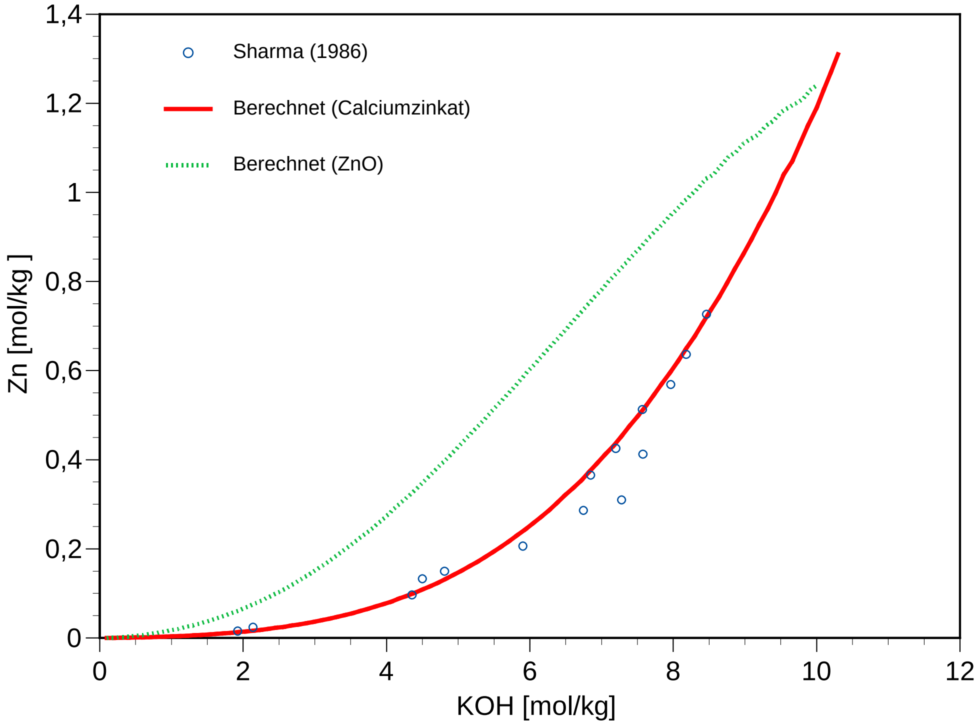

Fig. 10.5 Solubility of calcium zincate and zincite in KOH solutions in the presence of portlandite, $Ca(OH)_2$

Tab. 10.10 Solubility constants of zinc oxide, zinc hydroxides and calcium zincate derived or adopted in this work.

Reaction	**value (log K)**	**Source**
$Zn(OH)_2$ (am) $\rightleftharpoons Zn^{2+} + 2\ OH^-$	-15.42 ± 0.03	SCHINDLER et al. (1963.1964), re-evaluated
β_1-$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2\ OH^-$	-16.14 ± 0.03	SCHINDLER et al. (1963.1964), re-evaluated
β_2-$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2\ OH^-$	-16.10 ± 0.03	SCHINDLER et al. (1963.1964), re-evaluated
γ-$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2\ OH^-$	-16.16 ± 0.03	SCHINDLER et al. (1963.1964), re-evaluated
δ-$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2\ OH^-$	-16.05 ± 0.03	SCHINDLER et al. (1963.1964), re-evaluated
ε-$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2\ OH^-$	-16.42 ± 0.05	This work
$ZnO + H_2O \rightleftharpoons Zn^{2+} + 2\ OH^-$	-16.65 ± 0.08	This work
$Ca(OH)_2 \cdot 2Zn(OH)_2 \cdot 2H_2O \rightleftharpoons$ $Ca^{2+} + 2\ Zn^{2+} + 6\ OH^- + 2\ H_2O$	-40.08 ± 0.05	This work based on SHARMA (1986)

Tab. 10.11 Equilibrium constants in the system Zn^{2+} - OH^- - H_2O

Reaction	value (log K)	Source
$ZnO + H_2O \rightleftharpoons Zn^{2+} + 2\ OH^-$	-16.65 ± 0.08	This work
$Zn^{2+} + OH^- \rightleftharpoons [ZnOH]^+$	5.7 ± 0.4	This work
$Zn^{2+} + 2\ OH^- \rightleftharpoons [Zn(OH)_2]^0$	11.0 ± 0.2	This work
$Zn^{2+} + 3\ OH^- \rightleftharpoons [Zn(OH)_3]^0$	13.4 ± 0.2	This work
$Zn^{2+} + 4\ OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	14.90 ± 0.05	This work

Tab. 10.12 Binary ion interaction coefficients for zinc species

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	C^{γ}	Source
$[Zn(OH)_4]^{2-} – Na^+$	0.29320	2	1.94105	-0.00337	This work
$[Zn(OH)_4]^{2-} – K^+$	0.23432	2	3.59950	0.00617	This work

10.2 Chloridic systems

10.2.1 Basic Zinc Chlorides - Overview

In the literature, especially in older publications, a large number of basic zinc chlorides are described. The Gmelin Handbook (Vol. 32, p. 175) lists about 20. After reviewing the more recent literature, two defined compounds can be identified that can be regarded as thermodynamically stable: $Zn(OH)_2{\cdot}ZnCl_2{\cdot}H_2O$, which forms at extremely high zinc chloride concentrations (> 55 wt.-%), and $4Zn(OH)_2{\cdot}ZnCl_2{\cdot}H_2O$ (simonkolleite), which occurs in less concentrated solutions. Numerous older and more recent works agree on this point (Driot and Le Chatelier 1910; Feitknecht 1930; Aspelund 1933; Sorrel 1977; Ligier et al. 1999). It is unclear whether the compound $3Zn(OH)_2{\cdot}ZnCl_2{\cdot}xH_2O$, which appears in many studies as a precipitation product, is also thermodynamically stable or occurs only as an intermediate product on the way to even more basic compounds. As already Feitknecht (1933) and later Nowacki and Silberman (1961) pointed out, the basic zinc chlorides have a layer structure in which water can be bound "zeolitically". It can be easily removed without changing the X-ray structure.

In addition, there is a wide range of information on other compounds, especially with higher $ZnO/ZnCl_2$ ratios (selection: see Tab. 10.13). What they have in common is that discrete compositions cannot be produced. Thus, Tikhonov et al. (1957) found that during the hydrolysis of zinc chloride solutions, depending on the NaOH: $ZnCl_2$ ratio, an uninterrupted series of basic chlorides is formed, covering the entire conceivable range $ZnCl_{2-n}OH_n$. As soon as the NaOH: $ZnCl_2$ ratio exceeds two, the compounds transform into $Zn(OH)_2$. Thus, there are always bandwidths that are more or less narrow depending on the authors and thus pretend to be discrete compounds. In most cases, they are probably solid solutions based on the layered structure of $4Zn(OH)_2 \cdot ZnCl_2 \cdot H_2O$. Hydroxide and chloride are easily exchangeable for other ions without significantly changing the basic structure of the compound. It is unclear under which conditions these non-stoichiometric compounds are stable. Sometimes a transformation into $Zn(OH)_2$ or simonkolleite was observed, sometimes no change occurred for months. In the following evaluation, the discussed is focussed on simonkolleite.

With magnesium, zinc forms basic double chlorides (García Martínez et al. 1966), but nothing is known about their stability.

Tab. 10.13 Basic zinc chlorides (compounds thermodynamically stable at 25°C are shown in bold)

Phase	Source/ Comment
$Zn(OH)_2 \cdot ZnCl_2 \cdot xH_2O$	Driot and Le Chatelier (1910) for dissolution of ZnO in $ZnCl_2$ solutions >10 mol/kg (x = 0.5) Holland (1930) for dissolution of ZnO in ZnCl solutions$_2$ (x = 1 /x = 2); Aspelund (1933), Sorrell (1977) in the system $ZnO\text{-}ZnCl_2\text{-}H_2O$ (x=1). Also in Feitknecht (1930), Aspelund (1933), Feitknecht and Petermann (1943), Sorrel (1977).
$2Zn(OH)_2 \cdot ZnCl_2 \cdot 0.5H_2O$	Miljutina and Tarabaev (1958) When dissolving ZnO in 5.1 M NaCl solution.
$3Zn(OH)_2 \cdot ZnCl_2 \cdot xH_2O$	Aksel'rud and Spivakovskij (1958) Precipitate in potentiometric titrations.
$4Zn(OH)_2 \cdot ZnCl_2 \cdot xH_2O$	Driot and Le Chatelier (1910) on dissolution of ZnO in $ZnCl_2$ solutions (x = 2). Aspelund (1933), Mannooret-tonnil and Glibert (1973), Sorrell (1977) in the system $ZnO\text{-}ZnCl_2\text{-}H_2O$ (x = 1).
$5Zn(OH)_2 \cdot ZnCl_2 \cdot 3H_2O$	Holland (1930) after dissolution of ZnO in $ZnCl_2$ solutions
6 – 9 $Zn(OH)_2 \cdot ZnCl_2 \cdot 2H_2O$	Häberli (1950), Feitknecht and Häberli (1950) 20 °C, precipitate aged below mother liquor. Also Feitknecht and Weidmann (1943), Grauer and Schindler (1972),

10.2.2 Simonkolleite - $4Zn(OH)_2 \cdot ZnCl_2 \cdot H_2O$

The compound $4Zn(OH)_2 \cdot ZnCl_2 \cdot H_2O$ is found in nature as a simonkolleite, a weathering product on zinc-bearing minerals (Schmetzer et al. 1985). It is also a corrosion product frequently observed in the presence of chloride in humid air containing NaCl (SVENSSON and JOHANSSON 1993) and in $NaCl/NaHCO_3/H_2O$ solutions (FEITKNECHT 1952; LIGIER et al. 1999). It is also formed when carbonate is present and hydrozincite would be the thermodynamically more stable phase. GRAUER (1970) found that simonkolleite is always found under a "bonnet" of hydrozincite, whereby the covering layer acts as a semi-permeable membrane for chloride ions and water, but not for hydrogen carbonate. Different water contents are found for simonkolleite. This may be due to the preparation method used in each case (partly washing with acetone, drying in vacuum, leaving to stand in air).

The study of HÄBERLI (1950) and GRAUER and SCHINDLER (1972) was used as basis for the evaluation. Despite different experimental conditions, consistent solubility constants can be derived from both works, which are on average

$$\log K = -73.8 \pm 0.5$$

The results of the titration published by LARCIN et al. (1997) could not be used. The experiments were carried out in solutions of high zinc chloride concentration (1 - 6 m), which additionally contained large amounts of ammonium chloride. The speciation of zinc in such solutions is not known and was not considered in detail by the authors. Based on numerous assumptions, which will not be further discussed here, the authors derived a free enthalpy of formation of -2.896 kJ/mol. This corresponds to a solubility constant of $\log K = -70.6$.

Tab. 10.14 Experimental determinations of the solubility constant of simonkolleite - $4Zn(OH)_2 \cdot ZnCl_2 \cdot H_2O$ (hydroxychloride II)

Medium	log Kc	log K	log *K	Source/ Remarks
0.02 M $ZnCl_2$	-71.1	-74.0 ± 0.2		Häberli (1950), Feitknecht and Häberli (1950) 20 °C, dissolution in 0.02 M-$ZnCl_2$ solution until pH constant. In the experiments with zinc hydroxides mentioned in the same paper, the pH measurement was probably affected by traces of carbonate (cf. Schindler et al., 1964).
0.2 M Na(Cl,ClO_4)	41.10 (K_H)	73.5 ± 0.5		Grauer and Schindler (1972) with new parameter model converted to I = 0. The value converted to I = 0 by the authors is -72.65 ± 0.5. The same value was also found in Lehniger and Rüfenacht (1969).
1 – 2 M	-71			Limpo et al. (1995) 30 °C derived based on solubility measurements in NH_3/NH_4Cl solutions. Chloro and ammino complex formation taken into account. Unclear to which ionic strength the value refers.
1 – 6 M $ZnCl_2$		*-70.6*		Larcin et al. (1997). Calculated from the free enthalpy of formation given there (-2.896kJ/mol).
I = 0		**-73.8 ± 0.5**		**This work** (mean value without *italic* data)

10.3 Sulphatic systems

10.3.1 Sulphato complexes

The existence of sulphato complexes was first demonstrated by Brinziger and Ostwald (1934) on the basis of dialysis measurements on sulphate-rich solutions. Although some information on the stability of zinc sulphato complexes is available in the literature (e.g., Aruga 1978), an explicit consideration in thermodynamic models has not appeared necessary so far. Therefore, sulphato complexes won’t be discussed in any more detail at this place.

10.3.2 Basic zinc sulphates – Overview

Similar to the basic zinc chlorides, a wide range of basic zinc sulphates has been described in the literature. A good overview is given by BRÖNNIMANN (1959, see also Tab. 10.15). He describes five groups of compounds with a ratio of $Zn(OH)_2$ to $ZnSO_4$ between 1.0 and 6.1. Anong these compounds, $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$ seems to be the most stable. It is found both in precipitation reactions and in atmospheric corrosion of zinc. In addition, many publications also report the occurrence of compounds up to about $4Zn(OH)_2 \cdot ZnSO_4 \cdot 3H_2O$ in stable preparations. The water content of both compounds is somewhat unclear (see also discussion on basic zinc chlorides). According to BRÖNNIMANN (1959_2), the most hydroxide-rich compound $(5.7\text{-}6.1)Zn(OH)_2 \cdot ZnSO_4 \cdot 2H_2O$ is only found at very small sulphate concentrations (< 0.003 M). It may be assumed that, as in the case of similar hydroxide-rich chlorides, these solid phases are contaminated or partially substituted zinc hydroxide, rather than defined compounds. The sulphate-rich hydroxides I and II form only at higher temperatures. The discussion of the thermodynamic data therefore concentrates on the compounds $3Zn(OH)_2 \cdot ZnSO_4 \cdot xH_2O$ and $4Zn(OH)_2 \cdot ZnSO_4 \cdot xH_2O$.

10.3.3 The compound $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$ (namuwite)

A basic zinc sulphate with the ratio $Zn(OH)_2$: $ZnSO_4$ of 3 was found by many authors zinc when NaOH or ammonia was added to zinc sulphate solutions (overview: cf. Tab. 10.15). It has also been found as a product of corrosion in humid air (QU et al., 2002) as well as corrosion in seawater (MOR and BECCARIA, 1975).

The solubility constant of $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$ was studied by several authors (Tab. 10.16). The work of QUIMBY and MCCUNE (1957), for which essential information was not available, was not taken into account. The mean value is

$$\log K = -56.0 \pm 1$$

Similar compounds with three or five hydrate water molecules have been described as the minerals lahnsteinite and osakaite.

Tab. 10.15 Basic zinc sulphates: Roman numerals for findings by Brönnimann (1959); bold: stable phases.

Connection	Source/ Comment
$ZnO\cdot 2ZnSO_4$ (glikinite)	Described as a mineral (Nazarchuk et al. 2020)
$Zn(OH)_2\cdot ZnSO_4$ bis $1.5Zn(OH)_2\cdot ZnSO_4$ (I)	Brönnimann (1959); during prolonged storage of $3Zn(OH)_2\cdot ZnSO_4\cdot 4H_2O$ (III) at high temperatures.
$Zn(SO_4.2OH)\cdot xH_2O$	Evdokimova and Ceidler (1959), Margulis et al. (1965a,b), Jacob and Riquier (1969)
$2.5Zn(OH)_2\cdot ZnSO_4$ (II)	Brönnimann (1959); during prolonged storage of $3Zn(OH)_2\cdot ZnSO_4\cdot 4H_2O$ (III) at high temperatures.
$3Zn(OH)_2\cdot ZnSO_4\cdot(2\text{-}2.25)H_2O$	Stanimoriva et al. (2018) in transformation reactions of other basic Zn salts.
$3Zn(OH)_2\cdot ZnSO_4\cdot 3H_2O$ (lahnsteinite)	Described as a mineral by Chukanov et al. (2013)
$3Zn(OH)_2\cdot ZnSO_4\cdot 4H_2O$ (III) (namuwite)	Brönnimann (1959), Fridman (1935), Copeland and Short (1940), Gromov (1948); without a water content: Werner (1907), Feitknecht (1933), Nikurašin and Nikol'skij (1949), Jacob and Riquier (1969), Zubkovskaja (1907), Evdokimova and Ceidler (1959), Odnevall and Westdahl(1993), Liegier et al. (1999), Gromov (1948); with 5 H_2O: Bear et al. (1986, 1987), Odnevall and Leygraf (1994); with 3 H_2O: Qu et al. (2002) on atmospheric corrosion of zinc in the presence of SO_2
$3Zn(OH)_2\cdot ZnSO_4\cdot 5H_2O$ (osakaite)	Described as a mineral by Ohnishi et al. (2007)
$3.5ZnO\cdot ZnSO_4\cdot 3H_2O$	Fridman (1935)
$3.8Zn(OH)_2\cdot ZnSO_4\cdot 3H_2O$ to $4Zn(OH)_2\cdot ZnSO_4\cdot 3H_2O$ (IV)	Brönnimann (1959); mixture of 3-4 $Zn(OH)_2$ per $ZnSO_4$: Margulis et al. (1965a,b), Čalyj (1972); without indication of water content: Pickering (1907), Heubel (1945), Tananaev and Mzareulishvili (1956), Brönnimann (1959). develops from $3Zn(OH)_2\cdot ZnSO_4\cdot 4H_2O$ as intermediate stage
$5Zn(OH)_2\cdot ZnSO_4\cdot 5H_2O$ (guarinoite)	Described as mineral with traces of Ni and Co (Sarp 1993)
$5.7Zn(OH)_2\cdot ZnSO_4\cdot 2H_2O$ bis $6.1Zn(OH)_2\cdot ZnSO_4\cdot 2H_2O$ (VI)	Brönnimann (1959). Develops from $3Zn(OH)_2\cdot ZnSO_4\cdot 4H_2O$ as an intermediate.

10.3.4 The compound $4Zn(OH)_2 \cdot ZnSO_4 \cdot 3H_2O$

Information on the stability of this compound at 20 °C is only available from TANANAEV and MZAREULIŠVILI (1956) and BRÖNNIMANN (1959) (Tab. 10.17). The first-mentioned authors always found only this compound in their titrations, but not $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$. This is a rather unusual finding and may explain why their solubility data differs so much from BRÖNNIMANN. The results of the latter author are preferred. The solubility constant is log K = -75.

Tab. 10.16 Experimental determinations of the solubility constant of $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$

Medium	log Kc	log K	Source/ Remarks
variable		-55.0± 0.1	GROMOV (1948) Solubility experiments in $ZnSO_4$ solutions at 18 °C. Water content not determined in GROMOV BUT set to 4 according to FEITKNECHT (1930) et al. Conversion to 25 °C under the assumption that solubility remains unchanged.
variable	-52	-55.1	NIKURAŠIN (1938) Incomplete titration of $ZnSO_4$ solutions with KOH at 20 °C. Conversion to 25 °C assuming solubility unchanged.
I=0		*-55.6*	DOBROKHTOV (1954) Derived from literature data, although it is unclear from which of the given places the value originates
variable		-56.1 ± 0.6	EVDOKIMOVA and CEJDLER (1959) Solubility experiments in $ZnSO_4$ solutions at 30 °C. Used under the assumption that solubility remains unchanged at 25 °C.
I by 0.15	-53.6	-57.8	BRÖNNIMANN (1959) 20 °C. Composition of the medium unknown, pH unknown, therefore influence of hydroxo complexes unknown (set to zero). Conversion to 25 °C under the assumption that solubility remains unchanged.
0.0038 to 0.382 M $ZnSO_4$		*-63.8*	LECOCQ et al. (1971) Authors' statement
0.0038 to 0.382 M $ZnSO_4$		*-64.4*	LECOCQ et al. (1971) re-evaluated with new parameters for zinc. Only data up to 0.12 M $ZnSO_4$ were used, since the calculated activity product is no longer constant at higher $ZnSO_4$ concentrations.
		-56.0 ± 2	**Mean value (without *italic* data)**

Tab. 10.17 Experimental determinations of the solubility constant of $4Zn(OH)_2 \cdot ZnSO_4 \cdot 3H_2O$

Medium	**log Kc**	**log K**	**log *K**	**Source/ Remarks**
I by 0.15	-70.0	**-75.2**		BRÖNNIMANN (1959) 20 °C. Composition of the medium unknown, pH unknown, therefore influence of hydroxo complexes unknown (set to zero). Conversion to 25°C under the assumption that solubility remains unchanged.
variable		*-85 ± 1*		TANANAEV and MZAREULIŠVILI (1956) Incomplete titration of $ZnSO_4$ solutions with NaOH at 20°C , values not constant.

10.4 Basic zinc chloride sulphates

The formation of basic chlorosulphato compounds of zinc is reported by CRUZ CUMPLIDO et al. (1964), MAC EWAN et al. (1966a, b). These are compounds of variable composition in which the $OH/Cl/SO_4$ ratio can vary between 3 : 1 : 2 and 7 : 1 : 2. Formulas result between

$$Zn_5(OH)_{6.25}Cl_{1.25}(SO_4)_{1.25} \cdot 2H_2O \qquad (10.11)$$

and

$$Zn_{12}(OH)_{15}Cl_3(SO_4)_3 \cdot 5H_2O \qquad (10.12)$$

Structural investigations showed that two types with different layer thicknesses can be distinguished. The structural basis is formed by triple $Zn(OH)_2$ layers, the anions OH^-, Cl^- and SO_4^{2-} are distributed in the intermediate layers. The phase was also identified by QU et al. (2002) via XRD in the atmospheric corrosion of zinc in the presence of SO_2 and NaCl. More detailed information on the stability of these compounds is not available.

Under suitable conditions, $Zn_4Na(OH)_6SO_4Cl \cdot 6H_2O$ forms as a product of aerobic corrosion in marine atmospheres (SVENSSON and JOHANSSON 1993; ODNEVALL and WESTDAHL 1993, ODNEVALL and LEYGRAF 1993). The compound was first found in nature in 1995 and named gordaite (SCHLÜTER et al. 1997).

A corresponding product with potassium does not form in aqueous solution in the presence of free potassium ions (LIGIER et al. 1999). However, a Ca analogue was synthesised: $CaZn_8(OH)_{12}(SO_4)_2Cl_2\cdot 9H_2O$ (STANIMIROVA et al. 2018), which has also been found as a mineral in historical slags (BURNS et al. 1998, so far unnamed).

If sodium is not available in sufficient quantities, the reaction stalls at $Zn_4(OH)_4Cl_2SO_4\cdot 5H_2O$ (ODNEVALL and WESTDAHL 1993, ODNEVALL and LEYGRAF 1994b; LIGIER et al. 1999). The presence of SO_2 and NaCl-containing solutions are required for formation (SVENSSON and JOHANSSON 1993). Dissolved sulphates may also lead to the same solid. Corrosion first leads to the formation of hydrozincite, then simonkolleite and finally ends with gordaite (ODNEVALL and LEYGRAF 1993).

In gordaite, part of the zinc can also be exchanged for Cu(II), as found as a weathering product on a copper shale dump (JAHN and WITZKE 1999) or in a deep-sea sediment (NASDALA et al. 1998).

ZHU et al. (1997) found that gordaite $Zn_4Na(OH)_6SO_4Cl\cdot 6H_2O$ has exactly the same X-ray diffraction pattern as the compounds $Zn_4(OH)_5Cl(SO_4)\cdot 1.6H_2O$ to $Zn_4(OH)_5Cl\ (SO_4)\cdot 5/3H_2O$. Possibly one of the two underlying elemental analyses has an error. However, it is also conceivable that small variations in the elemental ratio are possible.

Other compounds from the chlorosulphate group are the minerals thérèsemagnatite, $(Co,Zn,Ni)_6(SO_4)(OH,Cl)_{10}\cdot 8(H_2O)$ and guarinoite, $(Co,Zn,Ni)_6(SO_4)(OH,Cl)_{10}\cdot 5(H_2O)$ (SARP 1993). However, thérèsemagnatite was later redefined as $NaCo_4(SO_4)(OH)_6Cl\cdot 6H_2O$, thus representing the cobalt-rich analogue of gordaite (KASATKIN et al. 2018).

10.5 Carbonate systems

10.5.1 Zinc carbonate - Smithsonite

Zinc forms the compound $ZnCO_3$ with carbonate, which occurs in nature as smithsonite. Under atmospheric conditions with CO_2 partial pressures around $3\cdot 10^{-5}$ bar, $ZnCO_3$ is not stable but withers to hydrozincite ($Zn_5(OH)_6(CO_3)_2$, see below). Accordingly, $ZnCO_3$ can only be produced from ZnO by applying high CO_2 pressures (TOMANEK, 1967).

Tests under defined CO_2 pressures are particularly suitable for determining the solubility constant. Up to about 10 bar CO_2, constant results are achieved (SMITH, 1918). At higher pressures, the solution concentration of the CO_2, which increases to over 1 mol/kg, has an effect.

Different series of measurements lead to corresponding results. The data of SMITH (1918) newly evaluated in the present study coincides very well with the solubility constants derivable from SCHINDLER et al. (1969) and determined by PREIS et al. (2000). They also agree well with the value determined from potentiometric measurements by SAHLI (1953). The results of REINERT (1965), who also found excessive values for hydrozincite, are too high, as are those of KELLEY and ANDERSON (1935), which are based on thermochemical data. The values of AGENO and VALLA (1911) are about two orders of magnitude higher. It was not possible to find indications for the reasons for this large deviation.

Other investigations in which the CO_2 partial pressure and thus the actual carbonate concentration in the measuring solution was not controlled were not considered further in the evaluation. A list can be found in CLEVER et al. (1992). An overview is given in Tab. 10.18.

Tab. 10.18 Experimental determinations of the solubility constant of smithsonite ($ZnCO_3$)

Medium	log Kc	log K	log *K	Source/ Remarks
var.		*-8.28 ± 0.06*	2.06 ± 0.06	AGENO and VALLA (1911), Solubility measurements under CO_2 atmosphere, re-evaluated
var.		-10.90	-0.56	SMITH (1918), Solubility measurements under CO_2 atmosphere, re-evaluated
I = 0		*-10.00*		KELLEY and ANDERSON (1935): thermochemical data, converted to log K by SILLÉN and MARTELL (1964, p. 140).
?		*-10.15*		SAEGUSA (1950). Potentiometric measurement on a preparation described as "$ZnCO_3$-H_2O". Derivation partly on the basis of thermochemical data
I = 0		-10.99	-0.65	SAHLI (1953) potentiometric measurements on saturated solutions (Zn and pH electrodes) at 20 °C [log K(20 °C) = -10.84], corrected to 25 °C
0.2 M $NaClO_4$		*-10.26*	*0.08*	REINERT (1965), solubility test, converted with SIT to I = 0.
0.2 M $NaClO_4$		-10.86	-0.52 ± 0.03	SCHINDLER et al. (1969), Solubility measurements under CO_2 atmosphere, re-evaluated with SIT
Var. $CaCO_3$ solutions		*-10.53*		ZACHARA et al. (1989) Measurement on natural smithsonite. Evaluation there with hydroxo complex formation constants that do not correspond to the present model.
1 M $NaClO_4$		-10.91	-0.57 ± 0.1	PREIS et al. (2000); PREIS and GAMSJÄGER (2001a)
		-10.92 ± 0.03	**-0.58 ± 0.03**	**Mean value without *italic* data**

For the reaction

$$ZnCO_3 \rightleftharpoons Zn^{2+} + CO_3^{2-} \tag{10.13}$$

the mean value of the works considered is a solubility constant of

$$\log K = -10.92 \pm 0.03$$

10.5.2 Other neutral and acidic zinc carbonates

A sodium zinc carbonate of the formula $3ZnCO_3 \cdot Na_2CO_3 \cdot 8H_2O$ was found by KRAUT (1897) when a $ZnSO_4$ solution was mixed with $NaHCO_3$. It is possibly identical to the compound designated as $8ZnCO_3 \cdot 3Na_2CO_3 \cdot 8H_2O$ (= $2.7ZnCO_3 \cdot Na_2CO_3 \cdot 2.7H_2O$), which was previously found by SAINTE CLAIRE-DEVILLE (1851) and WÖHLER (1833) by different routes, and which was later also found by HUBER (1943b) during the cathodic attack of Zn in Na_2CO_3-$NaHCO_3$ baths.

A poorly soluble potassium zinc carbonate of the formula $4K_2O{\cdot}6ZnO{\cdot}11CO_2{\cdot}8H_2O$ = $K_8H_2Zn_6(CO_3)_{11}{\cdot}7H_2O$ is formed according to WITTGEN and CUNO (1882) and WAESER (1930) in concentrated potassium chloride or potassium sulphate solutions when high CO_2 pressures are allowed to act on zinc oxide, zinc hydroxide or zinc carbonate. In hot water, the compound decomposes into potash (K_2CO_3) and zinc carbonate. A compound of the same composition was also found by SAINTE-CLAIRE DEVILLE (1851). When a saturated $ZnCl_2$ solution was mixed with $KHCO_3$ or K_2CO_3, KRAUT (1897) could not obtain a potassium-containing carbonate. No thermodynamic information is available on these Na and K compounds.

Natural zinc carbonate always contains some magnesium, corresponding preparations can also be synthesised. Solid solutions therefore exist between the two carbonates (FERRARI and COLLA, 1936).

Zinc traces can be incorporated into the lattice during the formation of calcite (orthorhombic $CaCO_3$) as well as aragonite (rhombohedral $CaCO_3$) (DARDENNE 1967; RACHINSKII and ZHUKOVA 1973; PINGITORE 1980; TEMMAM et al. 2000). If only traces of zinc are present, ideal solid solutions are formed at temperatures around 50°C . However, equilibration is so slow at 25°C that only logarithmic distributions are found (CROCKET and WINCHESTER 1966). A dolomite analogue $CaZn(CO_3)_2$ called minrecordite was described by TAREEN et al. (1995).

If, on the other hand, solutions containing zinc meet calcite, hydrozincite is formed or, depending on the type and concentration of the zinc salt, other basic compounds such as simonkolleite - $Zn_5(OH)_8Cl_2$ (KAUSHANSKY and YARIV, 1986).

The partition coefficient for the incorporation of zinc in calcite

$$\left(\frac{m_{Zn}}{m_{Ca}}\right)_{Calcite} = k_{Calcite}^{Zn^{2+}}\left(\frac{m_{Zn}}{m_{Ca}}\right)_{solution} \qquad (10.14)$$

was determined by CROCKET and WINCHESTER (1966) as DARDENNE (1967) at temperatures slightly above 25 °C (Tab. 10.19). The recommended value of 5.5 (PINTIGORE, 1980) is taken as a reference, which, assuming an uncertainty of 0.5, includes both previously mentioned works.

Tab. 10.19 Partition coefficients for Zn in calcite

Value	Temperature	Source
5.2 ± 0.2	35 °C	CROCKET and WINCHESTER (1966)
5.6 ± 0.6	28 - 30 °C	DARDENNE (1967)
5.5		recommended value by PINGITORE (1980)
5.5 ± 0.5		**This work**

10.5.3 Basic carbonates

Hydrozincite

Zinc forms a broad group of basic carbonates. Systematic studies were first carried out by FEITKNECHT (1933), later by SAHLI (1953), FEITKNECHT and OSWALD (1966) and GRAUER and FEITKNECHT (1967). Under atmospheric conditions, only $Zn_5(OH)_6(CO_3)_2$ (hydrozincite) seems to be stable. It is also found as a corrosion product of metallic zinc as well as a weathering product of $ZnCO_3$, $Zn(OH)_2$ and ZnO. However, the weathering of ZnO is very slow. A systematic overview is given in Tab. 10.21.

Depending on the chemical conditions at the time of formation, the composition of hydrozincite can deviate from the ideal formula. The observed products reach compositions of $3Zn(OH)_2 \cdot 2ZnCO_3$ to $3.33Zn(OH)_2 \cdot 1.67ZnCO_3$, but still have the structure of hydrozincite. Obviously, only some carbonate positions are replaced by hydroxide. Moreover, they are still thermodynamically stable (GRAUER and FEITKNECHT 1967; GRAUER 1980,).

Based on the large number of analytically proven compounds, JAMBOR (1964), in agreement with FEITKNECHT (1933), assumed that basic zinc carbonates are not to be regarded as defined compounds of discrete composition, but rather as a group of compounds which, depending on the formation conditions, are transformed into each other by incorporation of water in intermediate layers or by mutual exchange of hydroxide and carbonate. Water can be thermally removed from these compounds without changing the basic structure. The higher water content found in some compounds can be attributed to water molecules that are very loosely (absorptively) bound.

JAMBOR derived the formula $Zn_5(OH)_6(CO_3)_2 = 5ZnO \cdot 2CO_2 \cdot 3H_2O$ (ideal hydrozincite formula), which had already been derived by FEITKNECHT, as the central compound. Two structural types belong to this formula, which are called "Dorchester" and "Constantine" type according to two localities. According to GHOSE (1964) and ZABINSKI (1966), both types consist of layers with $Zn_3(OH)_6O_2^{4-}$ with additional Zn^{2+} and CO_3^{2-} groups above and below these layers. Deficiencies of carbonate lead to a disorder ("Dorchester"). Ageing in the presence of CO_2 may lead to an ordered structure ("Constantine"). The two types differ clearly from each other in IR and XRD spectra.

According to JAMBOR, hydrozincites of the ‘Dorchester’ type, contains four instead of three molecules of water per formula unit: $5ZnO \cdot 2CO_2 \cdot 4H_2O$. This non-stoichiometric type includes all synthetic and many naturally occurring compounds of the composition $Zn_5(OH)_6(CO_3)_2$. They differ chemically from the ‘Constantine’ type in that they are able to absorb water.

JAMBOR therefore assumes that the "Dorchester" type represents an independent mineral, a dimorph of hydrozincite. Deviating from this, GHOSE (1964), FEITKNECHT and OSWALD (1966) and GRAUER and FEITKNECHT (1967) assume that the synthetic hydrozincites are partially disordered due to the formation conditions and therefore have more room for absorption or incorporation of water.

EHSANI et al. (2021) reported on a hydrozincite-like compound, in which part of the zinc is replaced by magnesium: $Mg_5Zn_3(CO_3)_2(OH)_{12} \cdot H_2O$.

Stability of hydrozincite

Hydrozincite has a larger area of existence than its thermodynamic solubility constant would allow. At lower carbonate contents, carbonate ions are increasingly replaced by hydroxide ions, whereby the zinc-related solubility drops significantly. Kinetic effects may also play a role (SAHLI 1953, GRAUER and FEITKNECHT, 1967).

According to ZACHARA et al. (1989), hydrozincite is also formed when calcite suspensions were treated with solutions containing zinc. However, the resulting precipitate had a higher solubility than natural hydrozincite.

More recent investigations (from 1969 onwards) on the solubility of hydrozincite throughout show consistent results. Significantly higher solubilities were found by SAHLI (1953), who worked with freshly precipitated solids. The even higher values of REINERT (1965) cannot be explained. ZACHARA et al. (1989) investigated the solubility of natural hydrozincite, which, as described above, does not have the same structure as synthetic preparations. Natural hydrozincite is considerably less soluble. However, it is unknown if and when newly formed hydrozincite transforms into the less soluble phase type.

Tab. 10.20 Experimental determinations of the solubility constant of hydrozincite - reaction $2ZnCO_3{\cdot}3Zn(OH)_2 \rightleftharpoons 5Zn^{2+} + 2CO_3^{2-} + 6OH^-$ (K) and $2ZnCO_3{\cdot}3Zn(OH)_2 + 8\,H^+ \rightleftharpoons 5Zn^{2+} + 2HCO_3^- + 6H_2O$ (*K), respectively.

Medium	log K	log *K	Source/ Remarks
about 0.059 M	*-73.27*	*31.39*	Sahli (1953) Solubility determinations at 20 °C on freshly precipitated preparations, experimental details not available. Mean composition $3.2Zn(OH)_2{\cdot}1.8ZnCO_3$ but evaluated as ideal hydrozincite. Kc = -72.10 Described by Schindler et al. (1969) as "orienting". Converted to I = 0 with SIT ($\log K_{20}^{\dagger}$ = -75.19). Corrected to T =25 °C with ΔH_f = -3584 kJ/mol (Preis and Gamsjäger 2001a, b).
0.2 M $NaClO_4$	*-71.54*	*33.12*	Reinert (1965), Solubility measurement, With SIT converted to I = 0
0.2 M $NaClO_4$	-74.59 ± 0.05	30.07 ± 0.05	Schindler et al. (1969), solubility measurement, with SIT converted to I = 0
var	-74.5 ± 0.5	30.2 ± 0.5	Alwan and Williams (1979) based on solution compositions in a Pb/Zn mine.
?	*-77.6 ± 0.5*	*27.09*	Zachara et al. (1989) Measurement on natural hydrozincite. Solubility constant increases with increasing pH
I = 0	-74.96	29.70	Mercy et al. (1998) Potentiometric measurement. Value there converted for G_f (-3163.3 kJ/mol).
1-3 M $NaClO_4$	-75.3 ± 0.1	29.4 ± 0.1	Price and Gamsjäger (2001a,b)
	-74.8 ± 0.4	**29.8 ± 0.4**	**Mean value (synthetic preparations)** (without *italic* data)

Basic zinc carbonates with increased carbonate content compared to hydrozincite

Hydrozincite converts to the more carbonate-rich compound $ZnO{\cdot}ZnCO_3{\cdot}xH_2O$ when high CO_2 partial pressures are applied, with x predominantly around 0.5 to 1. This also includes a preparation reported by Jambor (1964). In a corked container with commercial zinc carbonate that had been stored for 30 years, the original product was no longer found after closer analysis, but the hydrolysed form $ZnO{\cdot}ZnCO_3{\cdot}0.8H_2O$. Based on thermogravimetric results, part of this water is to be considered as absorbed. It transforms into $ZnO{\cdot}ZnCO_3{\cdot}0.5H_2O$ when heated to 200 °C.

According to Grauer and Feitknecht (1967), the compound cannot be obtained in pure form and is therefore not accessible to thermodynamic investigations. Since it only ever appears in small quantities next to hydrozincite in corrosion experiments, it is assumed that it is a metastable phase under atmospheric conditions without its own predominant region.

According to investigations by TERADA (1931 cited in HUBER 1943b), hydrozincite is initially obtained when CO_2 is passed through a zinc hydroxide suspension. However, the precipitate slowly absorbs further CO_2 and transforms into $ZnO·ZnCO_3·xH_2O$. A compound of similar composition was obtained by KRAUT (1897) and MIKUSCH (1908). It is formed when alkali carbonate or hydrogen carbonate solution is poured into a zinc sulphate solution. The composition determined by HUBER (1943b) is

$ZnO·(ZnCO_3)_{0.96\text{-}1.06}·(H_2O)_{1.20\text{-}1.35}$.

Thermodynamic data is not available for any of these compounds.

Even more carbonate-rich compounds are also found in the precipitation of zinc salts with alkali hydrogen carbonates (HUBER, 1943b). According to FEITKNECHT and OSWALD (1966), the ideal formula $Zn_4(OH)_2(CO_3)_3·4H_2O = ZnO·3ZnCO_3·5H_2O$ can be assigned to them. In water, the compound converts rapidly into hydrozincite.

Basic zinc carbonates with increased hydroxide content compared to hydrozincite

When precipitating zinc salt solutions with alkali carbonate or carbonate/hydroxide mixtures, SAHLI (1953) found hydroxide-rich products with $2.3ZnO·ZnCO_3·xH_2O$ to $3ZnO·ZnCO_3·xH_2O$. The precipitates transform into hydrozincite-like products. Only at high hydroxide concentrations of the mother solutions the precipitates remain stable. According to their X-ray diagrams, they are to be regarded as strongly disordered hydrozincites. The conclusions of NECZAJ-HRUZEWICZ et al. (1977) are similar: the higher-basic carbonates are to be regarded as solid solutions between hydrozincite and zinc hydroxide.

FEITKNECHT and OSWALD (1966) obtained different types of highly basic carbonates by introducing CO_2 into suspensions of amorphous $Zn(OH)_2$. Their structure is oriented towards α-$Zn(OH)_2$. With further introduction of CO_2, they rapidly transform into the carbonate-rich forms.

Tab. 10.21 Basic zinc carbonates, compounds that are thermodynamically stable at 25 °C are shown in bold.

Phase	**Alternative formula**	**Source/ Comment**
$ZnCO_3$ (smithsonite)	**$ZnCO_3$**	
$Zn_5(OH)_2(CO_3)_3\cdot H_2O$	$ZnO\cdot 3ZnCO_3\cdot 5H_2O$	Feitknecht and Oswald (1966) In the precipitation of zinc salt solution with hydrogen carbonate excess. Converts to hydrozincite or smithsonite in aqueous solution.
$3Zn(OH)_2\cdot 8ZnCO_3\cdot$	$3ZnO\cdot 8ZnCO_3\cdot 3H_2O$	Alwan and Williams (1979), Mercy et al. (1998)
$Zn_2(OH)_2(CO_3)\cdot xH_2O$	$ZnO\cdot ZnCO_3\cdot xH_2O$ (x = 0...1)	Terada (1931), Huber (1943b), Sahli, (1953); Grauer and Feitknecht (1967): unstable intermediate in the conversion of hydrozincite to $ZnCO_3$ by reaction with excess CO_2 and in the carbonation of -$Zn(OH)_2$. Occurs as an intermediate product in the corrosion of zinc in hydrogen carbonate solutions. Jambor (1964) Hydrolysed commercial zinc carbonate. Water content x = 0.8 (without absorbed water x = 0.5). Terminal member of the rosasite series - $(Cu,Zn)_2(CO_3)(OH)_2$ (cf. Jambor 1976).
$Zn_5(OH)_6(CO_3)_2$ (hydrozincite)	**$3ZnO\cdot 2ZnCO_3\cdot 3H_2O$**	Sahli (1953), also as corrosion product on zinc metal
	$3ZnO\cdot 2ZnCO_3\cdot 4H_2O$	Jambor (1964) in many natural mineral samples. Additional water is absorbed. Structure other than hydrozincite
	$3Zn(OH)_2\cdot 2ZnCO_3$ to $3.33Zn(OH)_2\cdot 1.67ZnCO_3$	Sahli (1953), Grauer (1980). Disturbed hydrozincite. Composition varies depending on manufacturing conditions
	$2ZnO\cdot ZnCO_3\cdot xH_2O$	Taboury and Gray (1937) as a corrosion product on zinc (x = 2).
	$2.3ZnO\cdot ZnCO_3\cdot xH_2O$ bis $3ZnO\cdot ZnCO_3\cdot xH_2O$	Taboury and Gray (1937) as a corrosion product on zinc ($3ZnO\cdot ZnCO_3\cdot 3H_2O$). Anderson and Fuller (1939) as a corrosion product on zinc ($3ZnO\cdot ZnCO_3\cdot 4H_2O$) after treatment with distilled water and air. Sahli(1953) in the precipitation of a zinc salt solution with Na_2CO_3/NaOH mixture with 50 to 80 % NaOH. Feitknecht and Oswald (1966) when precipitating zinc salt solutions with excess hydrogen carbonate, converts to hydrozincite.

Highly basic carbonates are also observed as corrosion products on zinc (cf. Tab. 10.21). That hydroxide-rich phases exist in nature is shown by sclarite and loseyite, first described by Grice and Dunn (1989). Its composition is described as $(Zn,Mg,Mn)_4Zn_3(CO_3)_2(OH)_{10}$ which would correspond to $5ZnO\cdot 2ZnCO_3\cdot 5H_2O$ in the case of a pure zinc compound. The same applies to losyeite, $(Mn^{2+},Zn,Mg)_4Zn_3(CO_3)_2(OH)_{10}$ (Bauer and Berman 1929, Hill 1981). No thermodynamic information is available for these compounds.

As a weathering product of primary zinc ores, the rare mineral brianyoungite $Zn_3(CO_3,SO_4)(OH)_4$ occurs, which is easily confused with the similarly looking hydrozincite and with which it also occurs together (LIVINGSTONE and CAMPNESS 1993; WITZKE 1994).

10.5.4 Carbonato and hydrogen carbonato complexes

Compared to the other elements dealt with in this work, only a few experimental studies are available on zinc carbonato complexes (Tab. 10.22). Both hydrogen carbonate and carbonato complexes have been detected so far, while mixed hydroxocarbonato complexes have only been postulated on the basis of analogies with corresponding Cd and Pb compounds (FERRI et al., 1987a).

The measured values for the first hydrogen carbonato complex agree satisfactorily with each other. BAUMAN et al. (1975) and EMARA et al. (1985) and later STANLEY and BYRNE (1990) derived for the equilibrium

$$Zn^{2+} + HCO_3^- \rightleftharpoons [ZnHCO_3]^+ \qquad (10.15)$$

values around 1.4 (log K) using potentiometric, spectrophotometric and polarographic methods. FERRI et al. (1985) found around 0.7 with the help of potentiometric titrations and extraction procedures. The evaluation of the data of FERRI et al. (1985) is complicated because of the high ionic strength used (3 M $NaClO_4$). In BAUMANN et al. (1975) as well as in STANLEY and BYRNE (1990) chloride-containing solutions were used, so that chloro complex formation could have falsified the result. In all cases, no primary measuring data were published that would allow a re-evaluation.

Strongly deviating from all other results is the experimental value of VEGA et al. (1995), which was determined by measurements in natural river water samples. The boundary conditions of this experiment are only insufficiently defined, so that there is little confidence in this value. For the complex formation constant of the first hydrogen carbonato complex the following mean value is derived from the other measurements:

$$\log \beta_1 = 1.5 \pm 0.2$$

The second complex, $[Zn(HCO_3)_2]^0$, was only described by VEGA et al. (1995). Since the data for the first complex already deviated considerably from other publications, the value determined for $[Zn(HCO_3)_2]^0$ is not considered reliable either. BAUMANN et al. (1975) managed without an additional complex when evaluating their measurement data, which was based on solutions with up to 0.3 mol/kg HCO_3^-. Since the carbonate concentration in natural waters is considerably smaller, the postulated complex $[Zn(HCO_3)_2]^0$ in VEGA et al. (1995) is probably a misinterpretation.

The first measured value for the carbonato complex $[ZnCO_3]^0$ was determined voltammetrically by BILINSKI et al. (1976) under different CO_2 pressures and pH values. The evaluation of this work is complicated by the fact that in the pH range they used (4.8 - 9.1) CO_3^{2-} plays a subordinate role compared to HCO_3^-. In addition, zinc hydroxo complexes have to be taken into account above from pH 6, which obviously did not take place in the authors' work. Nevertheless, the derived complex formation constant (4.76) agrees surprisingly well with the value of STANLEY and BYRNE (1990). They investigated the complex formation using distribution equilibria between organic phases and a seawater-like medium ($NaCl/NaClO_4$). At the background concentration of NaCl used (0.55 m NaCl), complex formation with chloride already occurs, but is[17] considered explicitly.

The stability of the second carbonato complex $[Zn(CO_3)_2]^{2-}$ was determined by FERRI et al. (1987a) and by STANLEY and BYRNE (1990). The results agree well and result in a well-supported mean value of

$$\log \beta_2 = 6.75 \pm 0.1$$

For the binuclear carbonato complex $[Zn_2CO_3]^{2+}$, only one potentiometrically obtained measured value by FERRI et al. (1985) is available. The determined complex formation constant (5.1) is doubtful, since the complex formation constant for $[ZnHCO_3]^+$ determined in the same work was too low by 0.6 log units. One reason could be the very high zinc concentration of the test solutions. In extreme cases, the solutions consisted of 3 M $ZnClO_4$ or of 0.3 M $ZnClO_4$+2.7 M $NaClO_4$. Under such circumstances, one can no longer speak of a constant background medium. The value of FERRI et al. (1985) should therefore be regarded as a rough orientation only.

FERRI et al. (1987a) as well as BRUNO (1990) concluded on the basis of their potentiometric measurements the existence of zinc carbonatohydroxo complexes, which can

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[17] A more recent study by SAVENKO and SAVENKO (2017) provides a value of log K =5.0 at 0.1 M $NaClO_4$. It was not considered here.

account for the main part of the speciation in non-saline carbonate-containing natural waters. Only for the complex $[Zn(OH)_2CO_3]^{2-}$ experimental data are available (FERRI et al., 1987a). It was found next to $[Zn(CO_3)_2]^{2-}$ in the solutions examined. However, if the published values are used as a basis for modelling, $[Zn(CO_3)_2]^{2-}$should not occur in any appreciable quantity under the selected experimental conditions ($c_{Na2CO3} = 1$, $c_{OH} = 10^{-3.6}$ up to $10^{-0.9}$ mol/l), since $[Zn(OH)_2CO_3]^{2-}$ is very dominant. On the other hand, the $[Zn(OH)_3]^-$ complex is likely to play a significant role, especially in concentrated carbonate solutions, whose buffering produce a pH around 11.5. But this was not considered by the authors. For these reasons, a complex $[Zn(OH)_2CO_3]^{2-}$ was not included in the model.

The existence of the complex $[Zn(OH)CO_3]^-$ was postulated by BRUNO (1990) on the basis of a comparison with other divalent cations. It was explicitly excluded by FERRI et al. (1987a). The value given by BRUNO already appears to be too high at first glance if one relates it to the complexes $[ZnOH]^+$and $[ZnCO_3]^0$:

$\log \beta_{1.1.1} = 13.5$	$[Zn(OH)CO_3]^-$	(BRUNO, 1990)
$\log \beta_{1.0.1} = 4.75$	$[ZnCO_3]^0$	(BILINSKI et al..1976; STANLEY und BYRNE, 1990)
$\log \beta_{1.1.0} = 5.65$	$[ZnOH]^+$	(This work)
$\log \beta_{1.2.0} = 11.00$	$[Zn(OH)_2]^0$	(This work)

Based on these values the reaction between [ZnOH]+ and carbonate

$$[ZnOH]^+ + CO_3^{2-} \rightleftharpoons [Zn(OH)CO_3]^- \quad \log K = 7.85$$

would by more than two orders of magnitude stronger than

$$[ZnOH]^+ + OH^- \rightleftharpoons [Zn(OH)_2]^0 \quad \log K = 5.35$$

although the formation reactions of the simple complexes $[ZnCO_3]^0$ and $[ZnOH]^+$ already shows that the affinity of zinc to carbonate is significantly weaker than to hydroxide.

The hypothetical equilibrium constant for the reaction

$$[Zn(OH)CO_3]^- + OH^- \rightleftharpoons [Zn(OH)_2CO_3]^{2-}$$

$\log K = -1.16$ (!)

also shows that $[Zn(OH)CO_3]^-$ is unlikely to exist $^-$alongside $[Zn(OH)_2CO_3]^{2-}$. There is therefore considerable doubt as to whether $[Zn(OH)CO_3]^-$ occurs in appreciable quantities. The postulate of BRUNO (1990) cannot be supported at the present time.

This discredits both zinc hydroxocarbonato complexes for the time being. This does not mean that such complexes do not exist. On the contrary, it is likely that they play an important role for entropic reasons. However, further investigations are necessary for a more detailed characterisation.

Tab. 10.22 Previously determined molal formation constants, corrected for activities (log $\beta_{m,x,y}$) of zinc carbonato complexes at 25 °C (formation reaction $m\,Zn^{2+} + x\,HCO_3^- \rightleftharpoons [Zn_m(HCO_3)_x]^{2m-x}$ or $m\,Zn^{2+} + x\,OH^- + y\,CO_3^- \rightleftharpoons [Zn_m(OH)_x(CO_3)_y]^{2m-x-2y}$)

Medium	**$[ZnHCO]_3^+$ $\beta_{1.1}$**	**$[Zn(HCO_3)_2]^0$ $\beta_{1.2}$**	**$[ZnCO]_3^0$ $\beta_{1.0.1}$**	**$[Zn(CO_3)_2]^{2-}$ $\beta_{1.0.2}$**	**$[Zn_2(CO_3)]^{2+}$ $\beta_{2.0.1}$**	**$[Zn(OH)CO_3]^-$ $\beta_{1.1.1}$**	**$[Zn(OH)_2CO_3]^{2-}$ $\beta_{1.2.1}$**	**Method**	**Source**
0.1 M KNO_3			4.76					Pol.	BILINSKI et al. (1976) converted with SIT
0.55 M NaCl/ 0.13M $NaClO_4$	1.64		4.76	7.3 ± 0.6				Pot. titr.	BAUMANN et al. (1975), RYAN and BAUMAN (1978), BAUMANN (1981)
0.01 M $NaHCO_3$ / 0.05 M $Zn(ClO_4)_2$	1.42							Spectr.	EMARA et al. (1985) converted by authors to I=0
3 M $NaClO_4$	*0.71*				*5.1*			Pot. titr.	FERRI et al. (1985) conversion with SIT to I =0; carbonate dissociation from HARVIE et al. (1980); the authors themselves determined log K to be 0.8
3 M $NaClO_4$				6.69			*12.34*	Pot. titr	FERRI et al. (1987a) measured in 1 M $NaClO_4$/Na_2CO_3; by authors on activity scale 3 M $NaClO_4$. Converted with SIT to I = 0
0.68 M Na (Cl, ClO_4, HCO_3)	1.55		4.75	6.81				Distr.	STANLEY and BYRNE (1990) with SIT converted.
var	*2.90*	*4.03*						Pol.	VEGA et al. (1995) in natural river water
Estimated values									
	2.10		*5.30*						ZIRINO and YAMAMOTO (1972)
	2.20		*4.80*						FOULLIAC and CRIAUD (1984)
						13.50			BRUNO (1990)
	1.5 ± 0.2		**4.75 ± 0.1**	**7.0 ± 0.3**	***5 ± 1***				**Mean value** (without *italic* data)

10.6 Result overview

Tab. 10.23 Equilibrium constants of basic zinc species determined in this work

Reaction	**Value (log β)**	**Source**
$Zn^{2+} + OH^- \rightleftharpoons [ZnOH]^+$	5.7 ± 0.4	This work
$Zn^{2+} + 2\ OH^- \rightleftharpoons [Zn(OH)_2]^0$	11.0 ± 0.2	This work
$Zn^{2+} + 3\ OH^- \rightleftharpoons [Zn(OH)_3]^-$	13.4 ± 0.2	This work
$Zn^{2+} + 4\ OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	14.9	This work
$Zn^{2+} + CO_3^- \rightleftharpoons [ZnCO_3]^0$	4.75 ± 0.1	This work
$Zn^{2+} + 2CO_3 \rightleftharpoons [Zn(CO_3)_2]^{2-}$	7.0 ± 0.3	This work
$Zn^{2+} + HCO_3^- \rightleftharpoons [ZnHCO_3]^+$	1.5 ± 0.2	This work

Tab. 10.24 Binary ion interaction coefficients for zinc species

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	C^{γ}	**Source**
$[Zn(OH)_4]^{2-} – Na^+$	0.29320	2	1.94105	-0.00337	This work
$[Zn(OH)_4]^{2-} – K^+$	0.23432	2	3.59950	0.00617	This work

Tab. 10.25 Solubility constants of basic zinc-containing compounds

Solid phase	Reaction	log K	Source
$Zn(OH)_2$ (am)	$Zn(OH)_2 \rightleftharpoons Zn^{2+} \pm 2OH^-$	-15.42	SCHINDLER et al. (1964)
β_1-$Zn(OH)_2$	$Zn(OH)_2 \rightleftharpoons Zn^{2+} \pm 2OH^-$	-16.14 ± 0.03	SCHINDLER et al. (1963.1964)
β_2-$Zn(OH)_2$	$Zn(OH)_2 \rightleftharpoons Zn^{2+} \pm 2OH^-$	-16.10 ± 0.03	SCHINDLER et al. (1963.1964)
γ-$Zn(OH)_2$	$Zn(OH)_2 \rightleftharpoons Zn^{2+} \pm 2OH^-$	-16.16 ± 0.03	SCHINDLER et al. (1963.1964)
δ-$Zn(OH)_2$	$Zn(OH)_2 \rightleftharpoons Zn^{2+} \pm 2OH^-$	-16.05 ± 0.03	SCHINDLER et al. (1963.1964)
ε-$Zn(OH)_2$	$Zn(OH)_2 \rightleftharpoons Zn^{2+} \pm 2OH^-$	-16.42 ± 0.05	This work
ZnO (zincite)	$ZnO + H_2O \rightleftharpoons Zn^{2+} \pm 2OH^-$	-16.65 ± 0.09	This work
$Ca(OH)_2 \cdot 2Zn(OH)_2 \cdot 2H_2O$ (qatranaite)	$Ca(OH)_2 \cdot 2Zn(OH)_2 \cdot 2H_2O \rightleftharpoons$ $2Zn^{2+} \pm Ca^{2+} \pm 6OH^- \pm 2H_2O$	-40.08 ± 0.05	This work
$4Zn(OH)_2 \cdot ZnCl_2 \cdot H_2O$ (simonkolleite)	$4Zn(OH)_2 \cdot ZnCl_2 \cdot H_2O \rightleftharpoons$ $5Zn^{2+} + 2\,Cl^- + 8OH^- + H_2O$	-73.8 ± 0.5	This work
$3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$ (namuwite)	$3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O \rightleftharpoons$ $4Zn^{2+} + SO_4^{2-} + 6OH^- + 4H_2O$	-56.0 ± 1	This work
$4Zn(OH)_2 \cdot ZnSO_4 \cdot 3H_2O$	$4Zn(OH)_2 \cdot ZnSO_4 \cdot 3H_2O \rightleftharpoons$ $5Zn^{2+} + SO_4^{2-} + 8OH^- + 3H_2O$	-75.2	This work
$ZnCO_3$ (smithsonite)	$ZnCO_3 \rightleftharpoons Zn^{2+} + CO_3^{2-}$	-10.92 ± 0.03	This work
$2ZnCO_3 \cdot 3Zn(OH)_2$ (hydrozincite, synthetic, Dorchester type)	$2ZnCO_3 \cdot 3Zn(OH)_2 \rightleftharpoons$ $5Zn^{2+} + 2CO_3^{2-} + 6OH-$	-74.8 ± 0.4	This work
$2ZnCO_3 \cdot 3Zn(OH)_2$ (Hydrozincite, natural, Constantine type)	$2ZnCO_3\ 3Zn(OH)_2 \rightleftharpoons$ $5Zn^{2+} + 2CO_3^{2-} + 6OH-$	-77.6 ± 0.5	This work

11 Thermodynamic properties of compounds of lead

11.1 Additions to the model by HAGEMANN (1999)

As described above, no changes were made to the original model (HAGEMANN 1999) for describing the properties of Pb^{II} in saline neutral and acidic solutions. The following sections deal with basic compounds that occur at elevated pH values. At this point, only a few further findings on lead-containing non-basic solid phases are listed (Tab. 11.1).

Tab. 11.1 Mineral names and other lead compounds

Solid phase	Mineral name	Source	Note
K_2PbCl_4	Pseudocotunnite	BELLANCA and SGARLATA (1952)	Mount Vesuvius, also in combustion processes (NIEMI et al. 2018)
$KCl\cdot 2PbCl_2 = KPb_2Cl_5$	Chalacolloite	SCHLÜTER et al. (2005)	
$2MgCl_2\cdot PbCl_2\cdot 13H_2O$	-	OTTO and DREWES (1890), COURT (1913)	After adding lead acetate or PbO to a technical, concentrated $MgCl_2$ solution
$Na_3Pb_2(SO_4)_3Cl$	Caracolite	SCHNEIDER (1969)	
$K_3Pb_2(SO_4)_3Cl$			As a product of combustion processes (NIEMI et al. 2018)

11.2 Formation of hydroxo complexes, oxides and hydroxides

11.2.1 Type and number of hydroxo complexes of lead

The formation of lead hydroxo complexes has been known for a long time. The first hint was probably given by HANTZSCH (1902), who concluded on the basis of conductivity measurements of lead hydroxide solutions that there was an incompletely dissociated "lead formic acid" H-PbOOH. Based on solubility measurements, BERL and AUSTERWEIN (1907) deduced the existence of a "monoplumbite" ion HO-Pb-ONa (= $[PbO(OH)]^-$) in concentrated NaOH solutions.

Assumptions about the composition of many lead hydroxo complexes were initially based mainly on derivations from potentiometric measurements. Over time, the existence and structure of some of the derived complexes could be established by XRD measurements in solids and also in solutions (Tab. 11.2). Quantum mechanical structure/stability calculations, which have only become possible in the last two decades, gave further valuable insights.

In the course of time, the group of probably occurring complexes was extended by numerous candidates. Due to the analogy to other complexes of lead or to hydroxo complexes of other metals, the existence of a continuous series of mononuclear compounds $[Pb(OH)_n]^{2-n}$ first up to n = 4 (AKSEL'RUD 1960).

FERRI et al. (1989) concluded on the basis of potentiometric measurements in solutions with more than 1 M NaOH that detectable amounts of the complexes $[Pb(OH)_4]^{2-}$ and $[Pb(OH)_6]^{4-}$ occur. However, it should be noted that the authors used a solution with 4.8 M $NaClO_4$ and 0.137 M NaBr as medium, so that complex formation with ClO_4 or Br^- could no longer be excluded.

Raman measurements by PERERA et al. (2001) in 7 M NaOH showed, according to the authors, only one complex with two strongly polarised bands. According to the UV measurements in the same article, the authors interpreted the peak as $[Pb(OH)_4]^{2-}$ or PbO_2^{2-}. However, the single spectrum of $Pb(OH)_4^{2-}$ shown is almost the same as that of $Pb(OH)_3^-$ so that an overinterpretation of the measurements is likely. On the other hand, PERERA et al. excluded a higher complex $[Pb(OH)_6]^{4-}$, as found by FERRI et al. (1989).

EXAFS measurement on lead-containing concentrated NaOH solutions showed in agreement with quantum mechanical calculations that only $Pb(OH)_3^-$ is present as the highest complex (BAJNÓSCZI 2015)

In addition, potentiometric titrations indicated the presence of polynuclear compounds in acidic to slightly basic solutions of higher lead concentrations. Starting with PEDERSEN (1945), the importance of the complex $[Pb_4(OH)_4]^{4+}$ became clear. OLIN (1960a) continued these investigations and could clearly identify the complexes $[Pb_4(OH)_4]^{4+}$, $[Pb_6(OH)_8]^{4+}$ and $[Pb_3(OH)_4]^{2+}$. A new evaluation of his results by SYLVA and BROWN (1980) also made the existence of $[Pb_3(OH)_5]^+$ probable. The conclusion on certain species was made in this work by varying the OH concentration *and* the lead concentration and is therefore well comprehensible. Similar results were obtained by ultracentrifugation analyses (ESVAL and JOHNSON 1965). In a similar investigation, KAWAI et al. (1980) concluded an additional complex $[Pb_3(OH)_3]^{2+}$. In concentrated lead solutions, $[Pb_2(OH)]^{3+}$ probably occurs (PEDERSEN, 1945, OLIN, 1960b).

The conclusions were partially supported by spectroscopic evidence of multinuclear lead hydroxo complexes in solids and in solution.

More types of polynuclear complexes can be found in solid phases, especially in basic nitrates and perchlorates. An overview was given by KOLITSCH and TILLMANNS (2003). According to them, there is so far no evidence for the existence of $[Pb_3(OH)_4]^{2+}$ or $[Pb_3(OH)_5]^{2+}$. The composition of compounds suspected of containing $[Pb_3(OH)_5]^{2+}$ must be corrected according to recent investigations. The structure-forming lead cluster rather consists of $[Pb_6O(OH)_6]^{4+}$. The complex $[Pb_3(OH)_4]^{2+}$ only occurs in very small concentrations during the hydrolysis of lead-containing solutions (OLIN 1960b). The perchlorate compound with the composition $Pb_3(OH)_4(ClO_4)_2$ contains $[PbO_6(OH)_6]^{4+}$ according to spectroscopic investigation (SPIRO et al. 1969b). This should also be the case with the analogously composed phase $Pb_3(OH)_4(NO_3)_2$, although GRIMES et al. (1995) assumed[18] the cluster $[Pb_3(OH)_4]^{2+}$.

BREZA and MANOVÁ (2002) concluded, based on quantum mechanical considerations, that two hexanuclear lead hydroxo complexes could exist in solution, which cannot be distinguished from each other by usual analytical methods: $[PbO_6(OH)_6]^{4+}$ and $[Pb_6(OH)_8]^{4+}$. They considered it very likely that both forms exist in parallel.

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[18] Their derivation is also based on an error. Their solid analyses cannot be interpreted as $Pb_3(OH)_4(NO_3)_2$, but rather as $Pb_6O(OH)_6(NO_3)_4 \cdot H_2O$

Tab. 11.2 Spectroscopic evidence of polynuclear lead hydroxo complexes

Complex	Source
$[Pb_2(OH)]^{3+}$ or $[Pb_2(OH)(H_2O)_2]^{3+}$	EIDEN-AßMANN et al. (2000), KRIVOVICHEV and BURNS (2000c)
$[Pb_3(OH)_3]^{3+}$	No evidence so far
$[Pb_3(OH)_4]^{2+}$	No evidence so far
$[Pb_3(OH)_5]^{+}$	At least in solids, the real composition is probably $[Pb_{13}O_8(OH)_6]^{4+}$ (KOLITSCH and TILLMANNS, 2003)
$[Pb_4(OH)_4]^{4+}$	ESVAL (1962), MARONI and SPIRO (1967.1968), JOHANSSON and OLIN (1968),
$[Pb_6(OH)_8]^{4+}$ or $[Pb_6O(OH)_6]^{4+}$	SPIRO et al. (1969a,b), JOHANSSON and OLIN (1968), OLIN and SÖDERQUIST (1972)
$[Pb_8(OH)_{12}]^{4+}$	TSAI and COONEY (1976B), KOLITSCH and TILLMANNS (2003)
$[Pb_{13}O_8(OH)_6]^{4+}$	KOLITSCH and TILLMANNS (2003)

11.2.2 Calculation method for the determination of the complex formation constants

First, the formation constants of all complexes were determined based on available literature data. Subsequently, the solubility constants for lead oxides and hydroxides were determined on the basis of solubility measurements in strongly basic solutions. At the same time, the ion interaction coefficients for the ion combinations $Na/^{+}[Pb(OH)_3]^{-}$and $K/^{+}[Pb(OH)_3]^{-}$ were determined. On this basis, it was then possible to derive an improved complex formation constant for $[Pb(OH)_2]^0$ that is consistent with the solubility data.

11.2.3 Mononuclear complexes in basic solutions

Ultracentrifugation experiments proved that only mononuclear compounds occur in basic solutions (JOHNSON and KRAUS, 1959). In contrast to slightly acidic to weakly basic solutions, the solubility of lead is strongly limited due to the formation of lead oxides or hydroxides, so that the conditions for the formation of polynuclear complexes are no longer fulfilled. Until recently, there has been no agreement on the maximum number of hydroxide ions that can be bound in a mononuclear lead hydroxo complex. Thus, the complexes $[PbOH]^{+}$, $[Pb(OH)_2]^0$ and $[Pb(OH)_3]^{-}$ could be unambiguously detected polarographically, potentiometrically, UV spectroscopically and with solubility experiments (e.g. GARRETT et al. 1939; CARELL and OLIN 1960; PERERA et al. 2001). Especially the solubility measurements of GARRETT et al. (1939) gave an important indication of the number of OH molecules bound per Pb^{2+} nucleus. The solubility curve in the NaOH-PbO-H_2O system shows a linear increase in the range 0.01 to 1 mol/kg. It can simply be expressed by the formula

$$c_{Pb,tot} = kc_{OH^-} \qquad (11.1)$$

That is a similar case as with $Cd(OH)_2$ described above. From the linear increase of the solubility curve of PbO in NaOH it can be deduced that

a) one species predominates in this concentration range,

b) this species has one more hydroxide molecule than the solid phase.

Thus, for a solid phase PbO or $Pb(OH)_2$, $[Pb(OH)_3]^-$ must be the predominant species.

The thermodynamically correct formulation of the solubility curve would then be obtained in the following way:

The complex formation equilibrium for the third hydroxo complex is described by

$$a_{[Pb(OH)_3]^-} = \beta_3 a_{Pb^{2+}} a^3_{OH^-} \qquad (11.2)$$

If this complex is predominant, its concentration corresponds to the total Pb concentration:

$$c_{Pb,tot} \approx c_{[Pb(OH)_3]^-} = \frac{\beta_3 \; a_{Pb^{2+}} \; a^3_{OH^-}}{\gamma_{[Pb(OH)_3]^-}} \qquad (11.3)$$

or

$$c_{Pb,tot} \approx \frac{\beta_3 \; a_{Pb^{2+}} \; a^2_{OH^-} \; a_{OH^-}}{\gamma_{[Pb(OH)_3]^-}} \qquad (11.4)$$

If the solubility-determining phase is PbO, the following relation is valid

$$K(PbO) = \frac{a_{Pb^{2+}} \; a^2_{OH^-}}{a_{H_2O}} \qquad (11.5)$$

Substituting this expression into the previous formula for $c_{Pb,tot,}$ leads to

$$c_{Pb,tot} \approx \frac{\beta_3\ K(PbO)\ c_{OH^-}\ \gamma_{OH^-}\ a_{H_2O}}{\gamma_{[Pb(OH)_3]^-}} \qquad (11.6)$$

As long as the activity coefficients of OH^- and $[Pb(OH)_3]^-$ develop about the same with the NaOH concentration and the NaOH concentration does not yet have a significant effect on the water activity, the expression can be simplified to:

$$c_{Pb,tot} \approx k\ c_{OH^-} \qquad (11.7)$$

whereby:

$$k = \beta_3\ K(PbO) \qquad (11.8)$$

This formula applies to NaOH concentrations of up to 1 mol/kg. After that, the solubility curve flattens out as the water activity entering the formula decreases. If species such as $[Pb(OH)_4]^{2-}$ (PERERA et al. 2001) or even $[Pb(OH)_6]^{4-}$ (SCHOLDER and PÄTSCH 1934; FERRI et al. 1989) were present, an increase would be more likely. Based on the solubility curve, it is therefore not possible to conclude that the complex is higher than $[Pb(OH)_3]^-$.

In our model, we will therefore initially limit ourselves to the species $[PbOH]^+$, $[Pb(OH)_2]^0$ and $[Pb(OH)_3]^-$.

11.2.4 The complexes $[PbOH]^+$, $[Pb(OH)_2]^0$ and $[Pb(OH)_3]^-$.

A large number of studies are available on the characterisation of these complexes. An overview is given by Tab. 11.3. The overall picture is inconsistent for a 1-1 complex. All complex formation constants determined in nitrate-containing media tend to be higher in their results. Since Pb^{2+} forms[19] nitrato complexes with nitrate, measurements in nitrate media are unsuitable. Equally problematic are investigations in systems with relatively high lead contents. Although these are well suited for characterising polynuclear

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[19] The complexation constant for $[PbNO_3]^-$ is about log β_1=1 (NYMAN et al. 1961). Nothing is known about complex formation with perchlorate.

complexes such as $[Pb_4(OH)_4]^{4+}$, the monohydroxo complex only occurs in traces here, so that the determination of its stability is afflicted with a relatively high uncertainty.

Furthermore, the UV spectroscopic measurements of PERERA et al. (2001) were not taken into account, whose derived complex formation constants were in each case one and a half to two log units higher than the remaining values. The maxima of the UV spectra of the lead species in neutral to basic solutions lie in the very narrow wavelength range from 209 nm (Pb^{2+}) to 239 nm ($[Pb(OH)_3]^-$ (BECHT 1994) and are difficult to separate into discrete spectral species. The investigations of OLIN (1960b) and PAJDOWSKI and OLIN (1962) are based on solutions with high lead concentration (up to 1 M). A correction to zero ionic strength is not possible here. The measurements by SCHORSCH and INGRI (1967) were carried out in 3 M NaCl, a medium in which lead is largely bound in chloro complexes.

The strongly deviating complex formation constant for $[Pb(OH)_3]^-$ of KANEKIYO et al. (2000, log β_3=16.1) and the data of FERRI et al. (1989), which belong to a model with the discarded complexes $[Pb(OH)_4]^{2-}$ and $[Pb(OH)_6]^{4-}$, were not taken into account. The early polarographic measurements of HEYROVSKÝ (1923) could not be included because it is unclear to which ionic strength the given complex formation constant refers. The polarographic measurements by KARNAUCHOV et al. (1984) were carried out in a medium for which the autoprotolysis equilibrium of water is currently unknown (2 M KNO_3). This property is needed to ensure the conversion of their complex equilibrium constant K_{H3} (2 M KNO_3) for $[Pb(OH)_3]$- into β_3.

In the evaluation, we restricted ourselves to the remaining measurements in perchlorate media. Here we obtained the following mean values:

$$\log \beta_{11} = 6.73 \pm 0.23$$

$$\log \beta_{12} = 11.44 \pm 0.23$$

$$\log \beta_{13} = 13.80 \pm 0.25$$

However, it turned out that solubility experiments with lead hydroxides could not be reproduced satisfactorily with this, so that minor corrections were necessary. These are presented in the following sections.

Tab. 11.3 Previously determined molal formation constants (log $\beta_{m,n}$) of lead hydroxo complexes (formation reaction m Pb^{2+}+n $OH^- \rightleftharpoons [Pb_m(OH)_n]^{2m-n}$), not corrected for activities.

Medium log	$[PbOH]^+$ $\beta_{1.1}$	$[Pb(OH)_2]^0$ $\beta_{1.2}$	$[Pb(OH)_3]^-$ $\beta_{1.3}$	$[Pb_4(OH)_4]^{4+}$ $\beta_{4.4}$	$[Pb_6(OH)_8]^{4+}$ $\beta_{6.8}$	$[Pb_3(OH)_4]^{2+}$ $\beta_{3.4}$	$[Pb_3(OH)_5]^+$ $\beta_{3.5}$	$[Pb_2(OH)]^{3+}$ $\beta_{2.1}$	Method	Source
0.0 M									pol	Heyrovský (1924)
→ I = 0	6.22	0.00		35.07				6.70	pot	Pedersen (1945)
KNO_3 1.0 M	6.88	10.73	13.25						pot	Goward (1954)
$(Pb,Ba)(NO_3)_2$ 0.2 M	4.79			35.04					pot	Faucherre (1954) 20 °C
→ I = 0									pol	Vlcek (1955)
$NaClO_4$ 2.0 M			12.49						pol	Olver and Hume (1959)
$NaClO_4$ 3.0 M	6.25			37.17	70.76	33.61			pot	Olin, A (1960a)
$NaClO_4$ 0.3 M	5.95			35.09	67.32	31.65			pot	Olin, A (1960a)
$NaClO_4$ 3.0 M		10.77	13.46						pot	Carell and Olin (1960)
$NaClO_4$ 0.3 M		10.33	13.27						pot	Carell and Olin (1960)
$NaClO_4$ 3.0 M	6.21			37.16	70.77	33.53			*pot*	*Olin, A (1960a) recalc. Sylva and Brown (1980) without*$_{35}$
$NaClO_4$ 3.0 M	6.26			37.16	70.77	33.47	39.02		*pot*	*Olin, A (1960a) recalc. Sylva and Brown (1980) without*$_{35}$
$NaClO_4$ 0.3 M	5.95			35.04	67.20	31.85			*pot*	*Olin, A (1960a) recalc. Sylva and Brown (1980) without*$_{35}$
$NaClO_4$ 0.3 M	5.96			35.05	67.22	31.82	36.48		*pot*	*Olin, A (1960a) recalc. Sylva and Brown (1980) without*$_{35}$
→ I = 0									pol	Nyman et al. (1961) from the data of Vlcek (1955)
$NaNO_3$ 2.0 M	4.98			33.49				6.69	pot	Hugel (1964)
$NaClO_4$ 2.0 M	5.91			35.86					pol	Hugel (1965)
$Pb(NO_3)$ 0.0 M	6.08	10.86							pol	Udovenko et al. (1974)
KNO_3 0.1 M	6.77	11.49							pol	Bilinski et al. (1976)
KNO_3 0.1 M	6.77	12.04		37.62					ISE	Birraux et al. (1977)
$NaClO_4$ 0.0 M	6.57	10.80	13.63						pol	Lind (1978)
KNO_3 0.1 M	5.91			34.67	66.76	31.16	37.09		*pot*	Sylva and Brown (1980)
$LiClO_4$ 3.0 M	6.16			35.89	67.81	32.35			*pot*	Kawai et al. (1980)
$LiClO_4$ 3.0 M				36.13	68.45	32.07			pot	Kogure et al. (1981)
$NaClO_4$ 3.0 M	6.80	10.47	12.60						pol	Yang et al. (1983)
$NaClO_4$ 0.7 M	6.23	10.44							pot	Turner and Vukaden (1983)
$NaNO_3$ 5.0 M	5.97								pot	Mulla et al. (1985)
$NaClO_4$ 1.0 M			13.10						pot	Ferri et al. (1987)
$NaClO_4$ 4.1 M			14.07						pot	Ferri et al. (1989)
$NaClO_4$ 1.0 M	5.99			35.51	67.76	32.42	38.10		*pot*	Cruywagen and van der Water (1993)
$NaClO_4$ 0.1 M	6.03	11.07	15.46	34.88	67.08	31.44		7.48	*pot*	*Kanekiyo et al. (2000)*
$NaClO_4$ 1.0 M	6.59	11.48	14.86						UV	Perera et al. (2001)
$NaClO_4$ 5.0 M	7.58	13.37	17.65						UV	Perera et al. (2001)

Tab. 11.4 Previously determined molal formation constants (log $\beta^{\dagger}_{m,n}$) of lead hydroxo complexes (formation reaction m Pb $^{2+}$+n OH [$^{-}\rightleftharpoons Pb_m(OH)_n]^{2m-n}$) corrected to zero ionic strength

Medium log	$[PbOH]^+$ $\beta_{1.1}$	$[Pb(OH)_2]^0$ $\beta_{1.2}$	$[Pb(OH)_3]^-$ $\beta_{1.3}$	$[Pb_4(OH)_4]^{4+}$ $\beta_{4.4}$	$[Pb_6(OH)_8]^{4+}$ $\beta_{6.8}$	$[Pb_3(OH)_4]^{2+}$ $\beta_{3.4}$	$[Pb_3(OH)_5]^+$ $\beta_{3.5}$	Meth	Source
0.0 M								pol	Heyrovský (1924)
→ I = 0	6.22			35.07				pot	Pedersen (1945)
KNO_3 1.0 M	7.29	12.13	14.86					pot	Goward (1954)
$(Pb,Ba)(NO_3)_2$ 0.2 M	5.80			35.65				pot	Faucherre (1954) 20 °C
0.0 M			13.95					pol	Vlcek (1955)
$NaClO_4$ 2.0 M			13.37					pol	Olver and Hume (1959)
$NaClO_4$ 3.0 M	6.93							pot	Olin, A (1960a)
$NaClO_4$ 0.3 M	6.54			33.41	67.36	33.03		pot	Olin, A (1960a)
$NaClO_4$ 3.0 M		11.74	14.13					pot	Carell and Olin (1960)
$NaClO_4$ 0.3 M		11.20	14.12					pot	Carell and Olin (1960)
$NaClO_4$ 3.0 M	6.89							pot	Olin, A (1960a) recalc. Sylva and Brown (1980) without$_{35}$
$NaClO_4$ 3.0 M	6.94							pot	Olin, A (1960a) recalc. Sylva and Brown (1980) without$_{35}$
$NaClO_4$ 0.3 M	6.54			33.36	67.24	33.23		pot	Olin, A (1960a) recalc. Sylva and Brown (1980) without$_{35}$
$NaClO_4$ 0.3 M	6.55			33.37	67.26	33.20	38.70	pot	Olin, A (1960a) recalc. Sylva and Brown (1980) without$_{35}$
→ I = 0			13.90					pol	Nyman et al. (1961) from the data of Vlcek (1955)
$NaNO_3$ 2.0 M	6.24							pot	Hugel (1964)
$NaClO_4$ 2.0 M	6.64							pol	Hugel (1965)
$Pb(NO_3)$ 0.0 M								pol	Udovenko et al. (1974)
KNO_3 0.1 M	7.22	12.16						pol	Bilinski et al. (1976)
KNO_3 0.1 M	7.22	12.71		37.12				pot	Birraux et al. (1977)
$NaClO_4$ 0.0 M	6.76	11.09	13.91					pol	Lind (1978)
KNO_3 0.1 M	6.36			34.17	67.62	32.43	38.89	pot	Sylva and BROWN (1980)
$LiClO_4$ 3.0 M	6.98							pot	Kawai et al. (1980)
$LiClO_4$ 3.0 M								pot	Kogure et al. (1981)
$NaClO_4$ 3.0 M	7.48	11.44	13.27					pol	Yang et al. (1983)
$NaClO_4$ 0.7 M	6.92	11.47						pot	Turner and Vukaden (1983)
$NaNO_3$ 5.0 M	7.94							pot	Mulla et al. (1985)
$NaClO_4$ 1.0 M			13.77					pot	Ferri et al. (1987)
$NaClO_4$ 4.1 M			14.17					pot	Ferri et al. (1989)
$NaClO_4$ 1.0 M	6.71							pot	Cruywagen and van der Water (1993)
$NaClO_4$ 0.1 M	6.46	11.72	16.10	34.20	67.67			pot	Kanekiyo et al. (2000)
$NaClO_4$ 1.0 M	7.31	12.55	15.24					UV	Perera et al. (2001)
$NaClO_4$ 5.0 M	8.04	13.87	17.77					UV	Perera et al. (2001)
→ I = 0	**6.77**	**11.08**	**13.80**	**34.78**	**67.51**	**32.81**	**(38.79)**		**Recommended values**

11.2.5 Lead oxides and hydroxides

In basic solutions, three different oxo compounds of lead are observed depending on the experimental conditions and the preparation used. If one titrates a solution containing lead, e.g., lead perchlorate or lead acetate, one obtains a white precipitate which is commonly called lead hydroxide. However, closer examination reveals that it is an oxide hydrate whose water content depends on the conditions of formation and decreases with increasing age.

Thus, DURTSCHI et al. (1969) found $PbO \cdot Pb(OH)_2 = 2PbO \cdot H_2O$ as the primary precipitation product. In the analyses, one often finds somewhat less water than the formula shows (HÜTTIG and STEINER 1931b). RANDALL and SPENCER (1928) found $3PbO \cdot H_2O$. A preparation of this formula was also obtained by OSWALD et al. (1968) as a single crystal on corroded lead.

CLARK and TYLER (1939) as well as TODD and PARRY (1964) always found only $5PbO \cdot 2H_2O$ under different preparation conditions. However, the X-ray diagrams of this compound are identical with preparations of the formula $PbO \cdot Pb(OH)_2$ (DURTSCHI et al. 1969). HOWIE and MOSER (1968) assumed a formula $3PbO \cdot H_2O$, since the X-ray diffraction pattern is largely identical to the analogous tin(II) oxide hydrate $3SnO \cdot H_2O$. Preparations with a higher water content can be traced back to sorbed water (HOWIE and MOSER 1973). This could also include the formula $3PbO \cdot H_2O$ described by GLEMSER AND LIN (1971).

Whether a stable hydroxide exists at all or is only a metastable intermediate on the way to yellow PbO and then to red PbO is unclear. What is certain is that the compound $5PbO \cdot 2H_2O$ can be synthesised reproducibly and thus represents a defined substance (EDWARDS et al. 1992). For our evaluations, we follow the somewhat more water-rich formulation of DURTSCHI et al. (1969), but without ruling out the existence of other stages.

If precipitation takes place in the presence of chloride, nitrate or sulphate, basic mixed salts of different composition are formed. This was not taken into account in many early investigations and led to erroneous results (NEWKIRK and HUGHES 1970, TAYLOR and LOPATA 1984).

Dehydration produces yellow PbO (massicot) at low temperatures and red PbO at high temperatures. The latter is more stable (FEITKNECHT and SCHINDLER 1963). Red PbO is also obtained by thermal decomposition of $PbCO_3$ (CLARK and TYLER (1939). The opinion sometimes found in the literature that the colour is solely due to a different grain size (GLASSTONE 1921) was already refuted by APPLEBEY and REID (1922) by growing crystals of the same size with different colours.

The thermodynamically most stable form at room temperature is the red, tetragonal PbO (lithargite). The rate of conversion from white hydrated oxide to red PbO increases with OH concentration. Above certain alkalinities (> 1 mol/kg), which vary from experimenter to experimenter, the red form is formed immediately (MÜLLER 1925). The transition from yellow to red PbO is inhibited by small amounts of some oxoanions, which form sparingly soluble compounds with lead (KWESTROO et al. 1967).

11.2.6 The solubility of the lead oxides in NaOH and KOH solutions and the determination of the complex formation constants log $\beta_{1.3}$

The solubility curve of lead oxide or lead oxide hydrate in NaOH shows a minimum at about 0.001 mol/kg OH concentration (about pH 11), which has so far only seldom been recorded experimentally. This minimum is followed by a long-lasting, almost straight increase in solubility, which slowly levels off at about 1 mol/kg. The experimental data above this mark scatter and vary by about a factor of two.

$$c_{Pb,tot} \approx \beta_3 K \frac{\gamma_{OH^-}\, a_{H_2O}}{\gamma_{[Pb(OH)_3]^-}} c_{OH^-} \qquad (11.9)$$

Tab. 11.5 shows a list of all works found in the literature on the solubility of lead oxides in NaOH solutions.

The large differences in the observed solubilities, especially at high alkalinities, were already discussed in detail by TÖPELMANN (1929). The crushing of the used crystals by too strong stirring, the slow reaction of PbO preparations and the reaction of dissolved lead with the glass of the experimental vessels with the release of alkali and lead silicates come into question.

Interesting is also the hint of BECHT and VOGLER (1993) that in the presence of air the complex $Pb^{II}(OH)_3^-$ is oxidised in 0.1 M NaOH to $[Pb^{IV}(OH)_6]$. If oxygen is absent in the solution, a photoreduction to colloidal lead occurs.

To determine the solubility constants of red and yellow lead oxide, solubility measurements at NaOH concentrations between 0.1 and 1 mol/kg are particularly suitable. The solubility curve is a straight line in this range. As mentioned above, this is an indication of a single predominant species, here $[Pb(OH)_3]^-$.

$$c_{Pb,tot} \approx \beta_3 K \frac{\gamma_{OH^-}\, a_{H_2O}}{\gamma_{[Pb(OH)_3]^-}} c_{OH^-} \qquad (11.9)$$

Tab. 11.5 Solubility tests in the system NaOH-PbO/$Pb(OH)_2$-H_2O at 25 °C unless otherwise noted

Earlier work	Preparation / product used	Comment
RUBENBAUER (1902)	PbO hydrate	Room temperature
BERL and AUSTERWEIL (1907)	unclear	18 °C
WOOD (1910)	"$Pb(OH)_2$"	
APPLEBEY and REID (1922)	PbO (red, yellow)	20 °C
GLASSTONE (1921)	PbO (red)	"not far from" 20 °C
GLASSTONE (1922)	PbO hydrate	
MÜLLER (1925)	PbO hydrate	Room temperature
TÖPELMANN (1929)	PbO (olive yellow)	Presumed room temp.
APPLEBEY and POWELL (1931)	PbO (red, yellow, black)	20 °C
GARRETT et al. (1939)	PbO (red, yellow), PbO hydrate	
PATTANAIK AND PANI (1957)	PbO hydrate	35 °C
SOKOLOVA and ČIŽIKOV (1957)	PbO (red)	18 °C
BRUJLE AND DOMBROVSKIJ (1959)	PbO (yellow)	
KUL'BA et al. (1961)	PbO hydrate	Graphics only
HARTINGER (1965)	$Pb(NO_3)_2$	Presumed room temp.
PATTERSON et al. (1977)	PbO hydrate	Presumed room temp.

Because of the variable and high ionic strengths, an evaluation is only possible in connection with the determination of ion interaction coefficients. From the extensive body of data in the literature, we selected those measuring points where the NaOH concentration was greater than 0.1 and less than 10 mol/kg . In this range, the trihydroxo complex occurs almost exclusively. The following works were not considered:

In BERL and AUSTERWEIL (1907), the type of preparation used was unclear. The values of APPLEBEY and REID (1922), APPLEBEY and POWELL (1931) and SOKOLOVA and ČIŽIKOV (1957) show a large scatter. PATTERSON et al. (1977) used solutions containing nitrates and did not analyse the solid phase.

For the only documented solubility measurements in the weakly acidic to weakly acidic range (around pH 6), no species/parameter combination could be used to reproduce the saturation of a lead oxide hydrate phase.

In the first step of the calculation, the complex formation constants for $[Pb(OH)_3]^-$ from the previous section were set and the solubility constants for lithargite, massicot as well as $Pb(OH)_2 \cdot PbO$ were calculated together with the ion interaction coefficients

$\beta^{(0)}$ (Na^+, $[Pb(OH)_3]^-$) und C^γ (Na^+, $[Pb(OH)_3]^-$).

This resulted in the solubility constants shown in Tab. 11.6. It is noticeable that there are no significant differences between the solubilities of yellow lead oxide and lead oxide hydrate. This is also expressed in the solubility curves, which practically overlap.

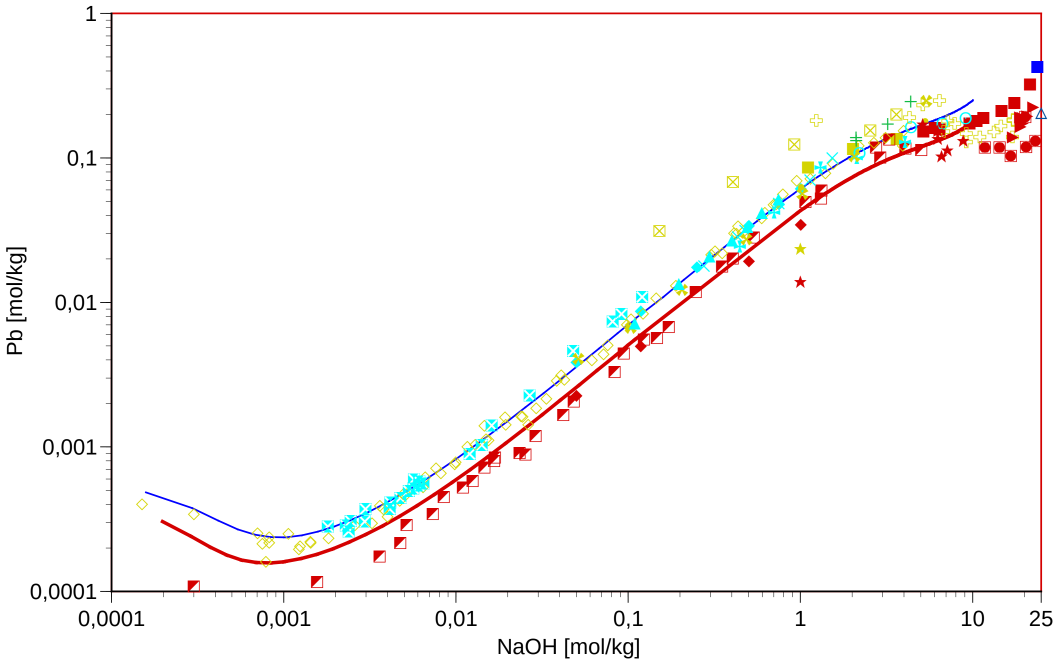
Tab. 11.6 Equilibrium constants determined in this work in the system Pb^{2+}-OH^--H_2O

Reaction	**value (log K)**	**Source**
PbO (red, lithargite) + $H_2O \rightleftharpoons Pb^{2+} + 2\,OH^-$	-15.09	This work. Basis: Solubility measurements
PbO (yellow, massicot) +$H_2O \rightleftharpoons Pb^{2+} + 2\,OH^-$	-14.93_5	This work. Basis: Solubility measurements
½ $(PbO \cdot Pb(OH)_2)$ +½ $H_2O \rightleftharpoons Pb^{2+} + 2\,OH^-$	-14.93_2	This work. Basis: Solubility measurements
$Pb^{2+} + OH^- \rightleftharpoons [PbOH]^+$	6.77	This work. Basis: Potentiometric and polarographic measurements
$Pb^{2+} + 2\,OH^- \rightleftharpoons [Pb(OH)_2]^0$	11.08	This work. Basis: Solubility measurements
$Pb^{2+} + 3\,OH^- \rightleftharpoons [Pb(OH)_3]^-$	13.80	This work: derived from solubility measurements with simultaneous determination of Pitzer coefficients.

After adjusting the solubility constants, it was noticed that the solubilities were not correctly reproduced at small NaOH concentrations. The calculated solubilities were too high at NaOH concentrations of less than about 0.01 mol/kg. Above this level, the complex $[Pb(OH)_2]^0$ has a noticeable contribution to the total lead concentration. To obtain an improved value for its complex formation constant, solubility data for NaOH concentrations between 0.0007 and 0.02 mol/kg were used. Using the previously determined complex formation constant for $[Pb(OH)_3]^-$, it was calculated what solubility would be expected in the exclusive presence of this complex. The difference to the experimental value was assumed to be the proportion of $[Pb(OH)_2]^0$. This consideration resulted in a complex formation constant corrected from the above value of

$$\log \beta_{12} = 11.08$$

With this data set determined in this way, the experimental solubility data could be reproduced well to very well (Fig. 11.1).



Symbols: Lithargite (red) , massicot (yellow-olive), lead oxide hydrate (light blue), sodium plumbite (dark blue)
Lines: calculated values for lithargite (red) and lead oxide hydrate (blue)

Fig. 11.1 Solubility of lithargite, massicot, lead oxide hydrate and sodium plumbite in NaOH solutions

Once the complex formation constants were established, the analogous interaction coefficients $\beta^{(0)}$ and C^{γ} for the ion pair K^+ - $[Pb(OH)_3]^-$ were determined on the basis of the solubility experiments in Tab. 11.7. The agreement between experimental and calculated solubilities is very good up to a concentration of about 3 mol/kg KOH. Above this value, the calculated solubility curve starts to drop sharply. It is possible to construct a parameter set where this drop does not occur, but the parameter values calculated (Tab. 11.8) are unusual: $\beta^{(1)}$ strongly negative and C^{γ} is also negative and comparatively very high. Possibly, there are ternary interactions between K^+, OH^- and $[Pb(OH)_3]^-$ or ion pair formation between K^+ and $[Pb(OH)_3]^-$.

Tab. 11.7 Solubility studies in the system KOH – PbO/Pb(OH)$_2$ – H$_2$O

Earlier work	**Preparation or end product used**	**Comment**
GLASSTONE (1922)	PbO hydrate	
RANDALL and SPENCER (1928)	PbO (red, yellow), PbO hydrate	
KUL'BA et al. (1961)	PbO hydrate	
YUSUPOV et al. (2000)	PbO (red, yellow), PbO hydrate	Formation of basic nitrates cannot be ruled out

Tab. 11.8 Binary ion interaction coefficients for lead hydroxo species

Ion pair	**$\beta^{(0)}$**	**$\alpha^{(1)}$**	**$\beta^{(1)}$**	**C^{γ}**	**Source**
$[Pb(OH)_3]^-$ - Na^+	0.20538	2	0	-0.00663	this work
$[Pb(OH)_3]^-$ - K^+	0.25725	2	0	0.00214	this work[20]

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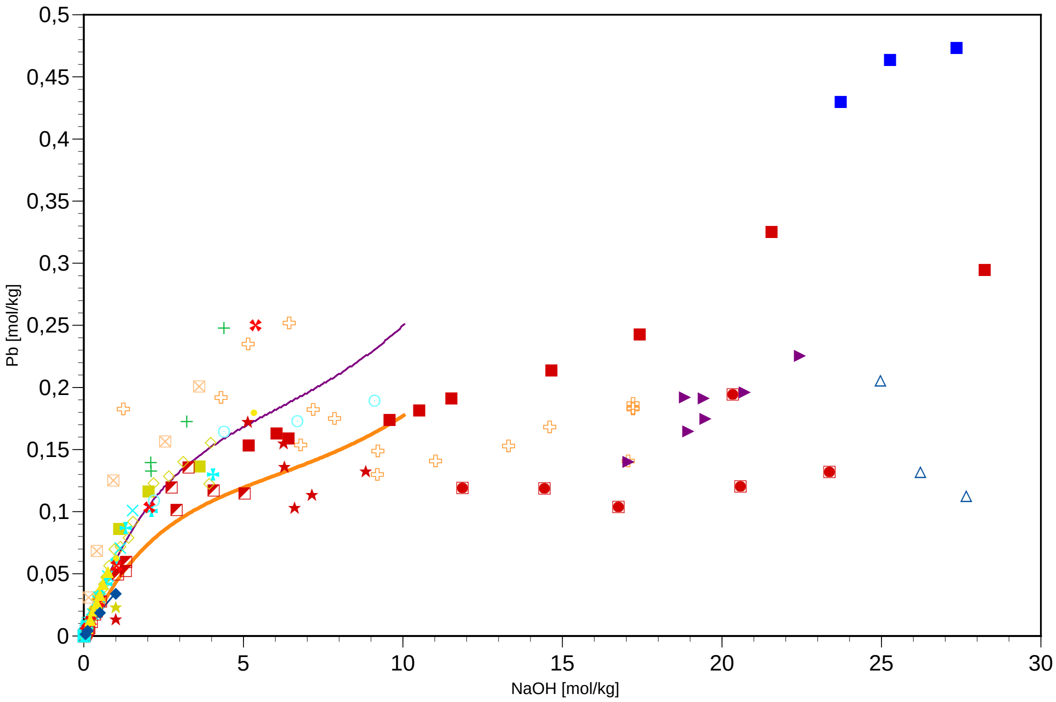
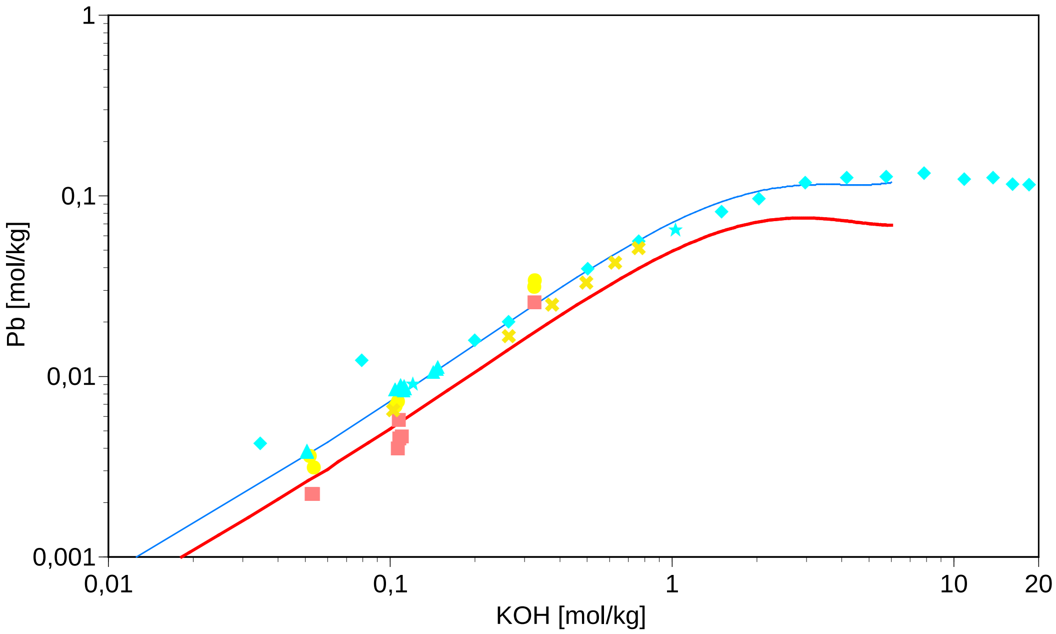
[20] The original version of this report contained a different set of coefficients



Symbols: Lithargite (red), massicot (yellow-olive), lead oxide hydrate (light blue, black lead oxide (black), sodium plumbite (dark blue).

Lines: calculated values for lithargite (red) and lead oxide hydrate (blue)

Fig. 11.2 Solubility of lead oxy- and lead hydroxy-compounds in NaOH solutions



Symbols: Lithargite (red) , massicot (yellow-olive), lead oxide hydrate (light blue), sodium plumbite (dark blue)

Lines: calculated values for lithargite (red) and lead oxide hydrate (blue)

Fig. 11.3 Solubility of lithargite, massicot, lead oxide hydrate and sodium plumbite in KOH solutions

11.2.7 The complexes $[PbOH_2]^{3+}$ $[Pb_3(OH)_4]^{2+}$, $[Pb_3(OH)_5]^{+}$, $[Pb_4(OH)_4]^{4+}$and $[Pb_6(OH)_8]^{4+}$

In slightly acidic to weakly basic solutions with a lead content above about $1 \cdot 10^{-5}$ mol/kg, both mononuclear and polynuclear hydroxo complexes occur. In broad agreement, PEDERSEN (1945), OLIN (1960a, b), KAWAI et al. (1980), KOGURE et al. (1981), KANEKIYO ET AL. (2000) and others found the following group of compounds occurring in significant amounts $[PbOH_2]^{3+}$$[Pb_3(OH)_4]^{2+}$, $[Pb_4(OH)_4]^{4+}$and $[Pb_6(OH)_8]^{4+}$. We restrict ourselves to measurements in perchlorate media and to those with an ionic strength of up to 0.3 mol/l. Under these conditions we can calculate the ion activity coefficients of the polynuclear ions approximately with the extended Debye-Hückel approach. As mean values we obtained the values given in Tab. 11.4 (p. 313) below. In the same way, the complex formation constant for $[Pb_3(OH)_5]^{+}$ was calculated. This species has so far only been identified by CRUYWAGEN and VAN DER WATER (1993) and SYLVA and BROWN (1980). This complex was found to be so stable that the solubility curves of lead oxide or lead oxide hydrate in NaOH below pH 10 can no longer be traced. The calculated lead solubilities become much too high. We have therefore discarded this complex.

11.2.8 Plumbite

As already mentioned above, lead oxide forms a sodium plumbite at very high NaOH concentrations (> 20 mol/kg), lead oxide forms a sodium plumbite. There is hardly any information available on analogous compounds with potassium or calcium. According to ROPP (2013), $CaPbO_2$ does form when $CaCl_2$ is mixed with a sodium plumbite solution, but it converts to calcium plumbate(IV) $CaPbO_3$ in air. Stable compounds of the type $M(II)PbO_2$ and $M(II)Pb_2O_3$ (among others M=Ca, Mg) were predicted by LI et al. (2017) based on structure-theoretical calculations.

11.2.9 Hydroxochloro complexes

If NaOH (to about 1 - $2 \cdot 10$ mol/l^{-5} OH^{-}) is carefully added to a concentrated NaCl solution containing $1 \cdot 10^{-5}$ mol/l Pb, the UV absorption band at 273 nm becomes weaker and a signal at about 250 nm emerges. This band is clearly different from the hydroxo complex band at 239 – 240 nm and can be attributed to a hydroxochloro complex (LÉBL 1966; BECHT 1994).

On the basis of polarographic investigations, CYRANOWSKA (1977) showed that with increasing chloride content of the solution, the pH affects the reduction potential of the Pb^{2+} later, i.e., hydroxochloro complexes form later (Tab. 11.9). The complex formation constants derived by the author for six different hydroxochloro complexes are likely to be of little value due to the lack of spectroscopic evidence, also because the existence of five-fold complexes is postulated, for which there is no other evidence. Moreover, the measurements were carried out in ammoniacal solution, which could itself form complexes with lead. The qualitatively most important statement of the measurements is that the two complexes $[PbCl_3(OH)]^{2-}$ and $[PbCl_2(OH)]^-$ at pH 9.7 have more than 80% share of all lead species at all chloride concentrations examined.

Tab. 11.9 Onset of hydroxochloro complex formation in chloride solutions (CYRANOWSKA 1977)

NH_4Cl concentration mol/l	Formation of hydroxochloro complexes from pH
0.5	> 6.5
2	> 7.0
4	> 8.0

The spectroscopic investigations of TSAI and COONEY (1976a) are essentially based on the evaluation of the position of the high-frequency "bands" at 210 - 220 nm, which, however, are only truncated band edges. Nevertheless, it is clear from the figures that the low-frequency main bands in 4 M NaCl practically do not change during the transition from pH 3 to pH 7, while the high-frequency band edges lose considerable height. The assignment of this band to $[Pb(OH)Cl_n]^{1-n}$ is not comprehensible. The authors even evaluate the fundamental band of Pb^{2+} at 209 nm as $PbOH^+$, which, according to them, should form during the strong dilution of solutions containing $[Pb_4(OH)_4]^{4+}$.

Overall, an inconsistent picture emerges, which could not be clarified at first even by our own orienting measurements. At least in acidic to neutral saline solutions, hydroxochloro complexes do not seem to play a significant role. For chloride-rich palladium solutions, for example, two mixed complexes, $PdCl_3(OH)^{2-}$ and $PdCl_2(OH)_2^{2-}$, are discussed between $PdCl_4^{2-}$ und $Pd(OH)_3^-$ (BOILY et al. 2007, RAI et al. 2012). It would be plausible if similar complexes also exist with Pb(II).

11.3 Chloridic systems

11.3.1 Overview

The phase sequence in the system PbO-$PbCl$-H_2O_2 has most recently been investigated and evaluated in detail by TAVERNIER and de JAEGER (1976) and EDWARDS et a. (1992). In general, the observed phases can be described by the formula $xPbO \cdot yPbCl_2 \cdot yH_2O$, with a large number of compounds known from the literature between $PbO : PbCl_2 = 6:1$ to $PbO : PbCl_2 = 1:3$ (Tab. 11.10 f.). At 25 °C, only three compounds proved to be thermodynamically stable.

a) The compound $6\,PbO \cdot PbCl_2 \cdot 2H_2O$ was first found by CLOUTIER (1933) during a titration experiment, was later also identified by KIYAMA et al. (1976) and by EDWARDS ET al. (1992) during the hydrolysis of $PbCl_2$ solutions. According to EDWARDS et al. (1992), on drying the compound transforms into $6\,PbO \cdot PbCl_2$, a mineral provisionally named chubutite. A mineral of the same composition was described by WELLS and LARSEN (1916, cited in EDWARDS et al. 1992) as the mineral "lorettoite", but was later exposed by WHITE (1979, cited in Edwards et al. 1992) as being man-made. Nevertheless, it was found in the 1980s by SCHNORRER-KÖHLER (1986) in the ancient slags of Lavrion (Greece) next to hydrocerussite and was more recently synthesised again by KRIVOVICHEV and BURNS (2002).

b) Blixite has the idealised formula $3PbO \cdot PbCl_2 \cdot 3H_2O$. Experimentally, it always contains slightly less water (EDWARDS et al., 1992: 2 hydrate water). PLEIßNER (1907) as well as TAVERNIER and de JAEGER (1976) obtained $3\,PbO \cdot PbCl_2 \cdot H_2O$ instead. The minerals mereheadite (WELCH et al. 1998) and yeomanite (TURNER ET AL. 2015) also have this composition. In contrast to blixite, they could not be synthesised so far.

c) Finally, there is laurionite, whose formula is usually expressed as $Pb(OH)Cl$ or $PbO \cdot PbCl_2$. It is the first compound to be formed during the careful titration of neutral solutions containing lead chloride. Paralaurionite has the same composition but a different structure. It has not yet been possible to synthesise it in the laboratory.

Tab. 11.10 Basic lead chlorides (compounds thermodynamically stable at 25 °C are shown in bold)

Phase	Alternative formula	Mineral name	Source/ Comment
$Pb_7O_6Cl_2\cdot 2H_2O$	**$6PbO\cdot PbCl_2\cdot 2H_2O$**		Strömholm (1904), synthesised by Krivovichev and Burns (2002), Also found by Edwards et al. (9192), also as a corrosion product on lead-containing cable sheaths (Shrier, 1963 cited by Edwards et al., 1992). Structure: Krivovichev and Burns (2002)
$Pb_7O_6Cl_2$	β-$6PbO\cdot PbCl_2$	Chubutite (not yet acknowledged)	Formed during drying of $6PbO\cdot PbCl_2\cdot 2H_2O$ Edwards et al. (1992)
	α-$6PbO\cdot PbCl_2$	Lorettoite (discredited as a mineral)	Wells and Larsen (1916, cited in Edwards et al., 1992). Recovered in Lavrion slags (Edwards et al..1992).
$Pb_3O_2(OH)Cl$	$5PbO\cdot PbCl_2\cdot H_2O$ old: “$3PbO\cdot PbCl_2$”	Damaraite	First description: Criddle (1990, cited in Schnorrer et al., 1992). In Lavrion: Schnorrer et al. (1992) Chemical formula corrected and structure redetermined by: Keller et al. (2000, 2001), Krivovichev and Bruns (2001).
$5\,PbO\cdot PbCl_2$	$5\,PbO\cdot PbCl_2$		Döbereiner (n.d.) cit. In Pleißner (1907)
$Pb_{13}O_{10}Cl_6$	$10\,PbO\cdot 3\,PbCl_2$		Siidra et al. (2008), High temperature synthesis
$Pb_2Cl(O,OH)_{2-x}$ $x \sim 0.3$ $Pb_{16}Cl_8(O,OH)_{16-x}$ $x\sim 2.6$ (Gabrielson et al., 1958)	**$3\,PbO\cdot PbCl_2\cdot H_2O$** $3PbO\cdot PbCl_2\cdot 2H_2O$ (idealised formula after Edwards et al. 1992) $3PbO\cdot PbCl_2\cdot H_2O$ (formula after Pleißner, 1907)	Blixite (orthorhombic)	Deschamps and Charreton (1950), Charreton (1956a,b,c), Gabrielson et al. (1960), Tsai and Cooney (1976b), Edwards et al. (1992).
$Pb_2O(OH)Cl$	$3PbO\cdot PbCl_2\cdot H_2O$	"Mereheadite" (monoclinic), Yeomanite (orthorhombic)	In the laboratory: Pleißner (1907), First descriptions: Welch et al. (1998), Turner et al. (2015)
$Pb_6Cl_4(OH)_8$	$2PbO\cdot PbCl_2\cdot 2H_2O$		Tsai and Cooney (1976b)
$Pb_3O_2Cl_2$	$2PbO\cdot PbCl_2$	Mendipite	Symes and Embrey (1977), Krivovichev and Bruns (2001), after Edwards et al. (1992)

Tab. 11.10 [cont.] Basic lead chlorides (compounds thermodynamically stable at 25 °C are shown in bold)

Connection	Alternative formula	Mineral name	Source/ Comment
Pb(OH)Cl	**$PbO\cdot PbCl_2\cdot H_2O$**	Laurionite (orthorhombic)	Pleißner (1907), Charreton (1956a) Forms preferentially to paralaurionite according to Kiyama et al. (1976) and Edwards et al., 1992). First description: Köchlin (1887) and vom Rath (1887) both cited in Merlino et al., (1993) Structure: Venetopoulos and Rentzeperis (1975)
Pb(OH)Cl	$PbO\cdot PbCl_2\cdot H_2O$	Paralaurionite (monoclinic)	First description: Smith (1899 cit. Merlino et al., 1993). Structure: Merlino et al. (1993)
Pb_2Cl_2O	$PbO\cdot PbCl_2$	Matlockite	Ruer (1906) on the fusion of $PbCl_2$ and PbO quoted by Cloutier (1933)
"$Pb_3Cl_4(OH)_2$" $Pb_3Cl_4F(OH)\cdot H_2O$	$PbO\cdot 2\,PbCl_2.H_2O$	Fiedlerite	According to Edwards et al. (1992) metastable phase. According to Merlino et al. (1994) fluorine-containing.
$Pb_2Cl_3(OH)$	$PbO\cdot 3PbCl_2\cdot H_2O$	Penfieldite	Charreton (1956a), According to Edwards et al. (1992) metastable phase
Basic chlorides with additional cations			
$Pb_7O_4[Mg(OH)_4](OH)Cl_3$	$4PbO\cdot 3PbCl_2\cdot 2MgO\cdot 5H_2O$	Rickturnerite	Rumsey et al. (2012)
Basic mixed lead chloride sulphates			
$Pb_{10}(SO_4)Cl_2O_8$	$8PbO\cdot PbSO_4\cdot PbCl_2$	Sundiusite	Dunn and Rouse (1980)
$Pb_4(Cl,SO_4)_2O_3$	$3PbO\cdot PbSO_4\cdot PbCl_2$	Mineral, still unnamed, monoclinic	Rouse and Dunn (1990)
$Pb_{10}(SO_4)O_7Cl_4\cdot H_2O$	$7PbO\cdot PbSO_4\cdot 2PbCl_2\cdot H_2O$	Symesite	First description: Welch et al. (2000)

11.3.2 Laurionite Pb(OH)Cl

The solubility of laurionite has been determined several times in the past. The methods chosen were solubility measurements and pH titrations. An overview of all the work known to us is shown in Tab. 11.11. In all titration studies, important information on the calibration of the pH electrode in chloride-containing solutions as well as on the type of consideration of chloro complex formation is missing. The stabilisation of the pH value was typically used as a measure for reaching equilibrium, which meant waiting times of a few minutes at most - rather short for the formation of homogeneous precipitates. Solubility experiments agree well in their results (Pleißner 1907; Karaoglanov and

Zagorcev 1932; Švedov 1947: 3.8 to 5.7·10 mol/l^{-4}) and, assuming the complex formation constants derived above, give solubility constants for hydroxo complexes in the range of -13.7 to -13.9. The level of these derivations is strongly dependent on the model used to describe the hydroxo complexes, which account for up to 85 % of the speciation at the pH around 7.5.

Tab. 11.11 Solubility constant for laurionite (reaction $Pb(OH)Cl \rightleftharpoons Pb^{2+} + OH^{-} + Cl^{-}$)

Medium	Log K	Source/ Comment
18 °C, solubility $3.8 \cdot 10^{-4}$ mol/l (3 days)	**-13.93**	Pleißner (1907) re-evaluated under the assumption that the solubility at 25 °C is the same.
17 °C, solubility $4.37 \cdot 10^{-4}$ mol/l	**-13.83**	Karaoglanov and Zagorcev (1932) re-evaluated under the assumption that solubility at 25 °C is the same
25 °C, solubility $5.47 \cdot 10^{-4}$ mol/l (6 hours)	**-13.68**	Švedov (1947) re-evaluated
Room temp.	*-13.7*	Deschamps and Charreton (1951) Titration: pH calibration
17 °C, I = 0.1-0.7	**-13.7**	Charreton (1956a, b, c) Titration: pH calibration
var I→0	*-13.27 ± 0.07*	Danilov et al. (1974) Calculated from the onset of precipitation at pH titration. Poorly documented
I= 1 M $NaClO_4$, var I →0	-13.377 ± 0.014	Näsänen and Lindell (1976), With I = 1 M $NaClO_4$ and variable ionic strength.
	-12.67	Toptygina et al. (1984). After precipitation with $Ca(OH)_2$ and waiting a few hours. Hydroxocomplex formation not considered. Re-evaluation not possible, as experimental data not given.
var (0.01 to 0.09 M NaCl) at 22°C	**-13.6 ± 0.1**	Savenko and Šatalov (2000) CO_2 exclusion not documented, but also without significance at observed pH values.
	-13.7 ± 0.1	**Mean value** (without data in italics)

The range of values also agrees well with values derived by the other authors (Deschamps and Charreton 1951; Charreton 1956a,b,c; Savenko and Šatalov 2000) from titrations and solubility experiments in NaCl solutions.

This is contradicted by the value of Näsänen and Lindell (1976) of -13.377 ± 0.014. They determined the hydrogen concentration in slightly acidic 1 M $NaClO_4$ solutions which were in equilibrium with PbCl(OH). Ultimately, the solubility constant at I = 0 given by them is based on an extrapolation of their solubility constant also determined at other ionic strengths. The value derived from a titration by Danilov et al. (1974) is similarly low. It is not taken into account because of the very sparse documentation of the measurement data. Due to the lack of measurement data, the much lower constant of TOPTYGINA et al. (1984) is also not included.

The mean value for laurionite is a solubility constant of

$$\log K = -13.7$$

There is another compound of the same composition but different structure, the monoclinic paralaurionite (cf. MERLINO et al. 1993). It is found in nature partly next to, partly without laurionite. A synthesis has not yet been successful, so that it remains unclear whether paralaurionite is possibly the more stable phase of the two dimorphs. The only reaction pathway that also produces paralaurionite, among others, is the photochemical decomposition of mendipite (EDWARDS et al. 1992).

11.3.3 Blixite, mereheadite and yeomanite - $3\,PbO \cdot PbCl_2 \cdot x\,H_2O$

The titration experiments carried out so far have clearly shown that after laurionite, a basic bleach chloride with a PbO:$PbCl_2$ ratio of 3:1 is formed when further hydroxide is added. The water content remains controversial. PLEISSNER (1907), TAVERNIER and DE JAEGER (1976) and KIYAMA et al. (1976) found between 1.2 %, 1.69 % and 1.9 wt.-% H_2O per formula unit, respectively, corresponding to about 0.6 - 1.0 mol H_2O. GABRIELSON et al. (1960), who first described the mineral blixite, on the other hand, reported about 0.8 wt.-% or 0.4 H_2O per formula unit. An analogue of blixite was synthesised in the laboratory by KRIVOVICHEV and BURNS (2006). It has the formula $Pb_8O_5(OH)_2Cl_4$ or $3PbO \cdot PbCl_2 \cdot \frac{1}{2}H_2O$.

Later, a mineral of almost the same chemical composition but with a slightly higher water content, yeomanite, was found (TURNER et al. 2015). Its ideal formula is expressed as $3\,PbO \cdot PbCl_2 \cdot H_2O$ or $Pb_2O(OH)Cl$.

According to WELCH et al. (1998), the same water content (0.7 wt.-%) is found in mereheadite, a very rare mineral of the same chemical composition. It has not been found in laboratory tests so far (EDWARDS et al. 1992).

In the case of blixite and mereheadite, the character of the bound water is not clearly clarified (at discrete lattice positions or diffusely distributed in the lattice). Both WELCH et al. (1998) and GABRIELSON et al. (1960) could not exclude that the pure form of mereheadite or blixite is actually anhydrous. In our considerations, based on the measurement data of Pleißner (1907), Gabrielson et al. (1960), Tavernier and de Jaeger (1976) and Kiyama et al. (1976) and in agreement with the findings of Krivovichev and Burns (2006), we assume that the phases found in the titration experiments are blixite with the formula $3\,PbO{\cdot}PbCl_2{\cdot}H_2O$.

Later crystal chemical investigations by Krivovichev et al. (2009) showed that, in addition to chloride, mereheadite also contains borate and carbonate, which make an essential contribution to the structure of the mineral. The correct formula is therefore given by them as $Pb_{47}O_{24}(OH)_{13}Cl_{25}(BO_3)_2(CO_3)$.

In the literature there are a total of five papers dealing with the solubility of compounds of the $3\,PbO{\cdot}PbCl_2{\cdot}nH_2O$ type (Tab. 11.12). The documentation of the measurement data is quite poor in all cases. There are always uncertainties about the identity of the solid phase in equilibrium, the solution concentration, or the temperature.

Tab. 11.12 Solubility constant for blixite (reaction $3\,PbO{\cdot}PbCl_2{\cdot}H_2O + H_2O \rightleftharpoons 4\,Pb^{2+} + 6\,OH^- + 2\,Cl^-$)

Medium	log K	Source/ Comment
18 °C, solubility 2.5-10 mol/l^{-5} 3d	*-62.6*	Pleißner (1907) re-evaluated under the assumption that solubility at 25°C equals.
17 °C	*-66.4*	Charreton (1956a,b,c) Solubility and potentiometric (Cl)
Room temp.	*-68*	Deschamps and Charreton (1950.1951) Determination of solubility and Cl activity
0.14-0.19 mol/kg NaCl	**-61.8**	Näsänen and Lindell (1978) re-evaluated. The authors give $3\,PbO{\cdot}PbCl_2{\cdot}3\,H_2O$ as composition and for I = 0 for log K = -67.8.
0.43-0.46 mol/kg NaCl	*-64.5 ± 0.2*	Edwards et al. (1992): Equilibrium laurionite-blixite. pH calibration unclear. Stated pH values converted to -log c_H
	-61.8	**Recommended value**

The most important evidence was provided by Edwards et al. (1992), who showed that in a solution containing about 0.43 to 0.46 mol/kg NaCl, the simultaneous presence of laurionite and blixite produces a measured pH around 8.4 to 8.6. At this NaCl concentration, the "pH" measured with a common single-rod pH electrode corresponds approximately to the -log c_H value. Under these circumstances, the solubility constant for blixite K_B can be calculated according to the relationship

$$\frac{K_B}{K_L^4} = \frac{a_{Pb^{2+}}^4\ a_{OH^-}^6\ a_{Cl^-}^2}{a_{Pb^{2+}}^4\ a_{Cl^-}^4\ a_{OH^-}^4\ a_W^2} = \frac{a_{OH^-}^2}{a_{Cl^-}^2\ a_W^2} \qquad (11.10)$$

$$K_B = \frac{a_{OH^-}^2\ K_L^4}{a_{Cl^-}^2\ a_W^2} \qquad (11.11)$$

which leads to

$-\log K_B = -64.5 \pm 0.2$

With other solubility constants (Tab. 11.12) it is not possible to explain the experimental results of EDWARDS et al. (1992). Similar measurements were carried out by NÄSÄNEN and LINDELL (1976). A new evaluation of their measurement results leads to a solubility constant of

$-\log K_B = -61.8 \pm 0.1$

This solubility constant explains the measurements of NÄSÄNEN and LINDELL (1976) very well, but not those of EDWARDS (1992). It does not make sense to take an average here, as there must be fundamental differences between the two works, which could possibly be due to the pH measurement. Because of the larger experimental basis and the better documentation, we opt for the value of NÄSÄNEN and LINDELL (1976).

11.3.4 $6PbO \cdot PbCl_2 \cdot 2H_2O$

$6\,PbO \cdot PbCl_2 \cdot 2\,H_2O$ is the basic lead chloride with the highest $PbO:PbCl_2$ ratio (KIYAMA et al. 1976, TAVERNIER and DE JAEGER 1976 and EDWARDS et al. 1992). It is thermodynamically stable at pH values above 11. In nature, it has so far only been found in the anhydrous form as chubutite (cf. Tab. 11.10). A mineral phase of the same composition, formerly called lorettoite, was apparently an artificial product (WHITE 1979).

The first solubility determinations were carried out by KIYAMA et al (1976) with aged solid suspensions. Unfortunately, their article lacks essential information on the composition of the equilibrium solutions obtained at different pH values. This can only be derived indirectly from the textual data and the graphical representations of the results. Under these circumstances, the solubility constant of $6\,PbO \cdot PbCl_2 \cdot 2\,H_2O$ results in a value around

$\log K(6\,PbO \cdot PbCl_2 \cdot 2H_2O) = -108 \pm 2$

The only other solubility determination is available from EDWARDS et al. (1992). A re-evaluation of their given measured values, using the complex formation constants derived above for the lead hydroxo complexes, leads to a solubility constant of

$$\log K(6\,PbO \cdot PbCl_2 \cdot 2\,H_2O) = -108.7$$

Both derivations thus lead to mutually consistent results. Because of the better documentation, we give preference to the value from EDWARDS et al. (1992). With this, the solubility experiments of KIYAMA et al. (1976) and EDWARDS et al. (1992) can be well reproduced, but not the position of the equilibrium pH in the presence of blixite and $6PbO \cdot PbCl_2 \cdot 2H_2O$. Their solubility experiments gave a pH around 11.28 at a background salt concentration of 0.025 mol/kg NaCl, at which $6\,PbO \cdot PbCl_2 \cdot 2\,H_2O$ should convert to blixite. KIYAMA et al. (1976) gave a transformation pH of about 11.2 for a solution containing about 0.034 mol/l NaCl. With our solubility constants, the equilibrium pH in the presence of both phases would be about 11.8. The equilibrium blixite-$6\,PbO \cdot PbCl_2 \cdot 2\,H_2O$ therefore requires further investigation.

11.3.5 Other basic lead chlorides

Especially in the mineralogical literature, further basic lead chlorides are reported. For the most part, these are naturally occurring compounds that are usually very rarely found. Many basic lead chlorides were found as weathering products of ancient lead slags in Lavrion (Greece) and later also in Baratti (Italy; FRANZINI et al. 1992a, b). They are also frequently encountered as corrosion products on lead in marine environments. An overview is given in Tab. 11.10. The conditions of formation of these compounds are often unclear. In many cases, kinetic inhibition may also contribute to the fact that these phases have not yet been transformed into other, more stable ones. A good example is mendipite. It does not occur in the titration of lead-containing, chloride-rich solutions at 25 °C, but it does occur at 60 °C. Direct synthesis is only possible from 29 °C on. Once the material has been produced, however, it does not transform further at 25°C , which makes thermochemical investigations at this temperature possible (see EDWARDS et al. 1992).

Some other compounds were found by MILYUTINA and TARABAYEV (1958), who observed phase compositions between $PbO \cdot 5PbCl_2 \cdot H_2O$, $3\,PbO \cdot 4PbCl_2 \cdot 3H_2O$ as well as $4PbO \cdot 3PbCl_2 \cdot 4H_2O$ when titrating a solution of $PbCl_2$ (0.064 mol/kg) in NaCl (300 g/l, about 5.5 mol/kg). However, these data are to be doubted, as the authors assumed only six hours as the equilibrium setting time in each case. It is more likely that the authors had mixtures of the phases already determined by Pleißner (1907) in hand.

Equally questionable is the compound $Pb_6Cl_4(OH)_8 = 2PbO\cdot PbCl_2\cdot 2H_2O$ synthesised by Tsai and Cooney (1976b) It is said to contain the complex ion $[Pb_6(OH)_8]^{4+}$. Its yellow colour possibly indicates contamination with nitrate used in the synthesis of the underlying lead hydroxide.

Penfieldite and fiedlerite have occasionally been found as mineral phases on ancient lead objects, but their synthesis in the laboratory has so far failed. For these and other reasons, Edwards et al. (1992) assume that laurionite is thermodynamically stable in comparison to penfieldite and fiedlerite.

Merlino et al. (1994) were able to show that fiedlerite from Laurion additionally contains fluorine and does not have the previously assumed formula $Pb_3Cl_4(OH)_2$, but $Pb_3Cl_4F(OH)\cdot H_2O$. This could be a reason why earlier synthesis attempts failed.

According to Scholder and Pätsch (1934), well-defined hydroxoplumbites can be produced from highly concentrated alkalis (> 50 wt.-% NaOH) in which one hydroxide is replaced by chloride: $Pb_2Na_4Cl(OH)_7$. Thus, 3 or 4 hydroxyl ions are bound per lead atom. From this, Scholder and Pätsch concluded the existence of an ion $Pb(OH)_4^{2-}$ at least in highly concentrated solutions. In another compound with barium, even a coordination number of six is achieved.

A similar compound with a lower hydroxide content was found by Rumsey et al. (2012) in the form of the mineral Rickturnerite - $Pb_7O_4[Mg(OH)_4](OH)Cl_3$.

11.4 Sulphatic systems

11.4.1 Basic lead sulphates: overview

Basic lead sulphates play a special role in the production of lead accumulators (curing process). They significantly influence the performance of the batteries. While tribasic lead sulphate ($3PbO\cdot PbSO_4$) is the main component of the negative grid plates, tetrabasic lead sulphate ($4PbO\cdot PbSO_4$) is the desired starting product for finishing the positive grid plates. While $4PbO\cdot PbSO_4$ can be oxidised to PbO_2 in a solid-state reaction and at the same time retain the crystal lattice, the oxidation of neutral lead sulphate leads to irreversible crystal lattice destruction and thus to capacity losses or passivation of the positive electrode.

In a careful study, PLEIßNER (1907) found only two compounds stable at 18°C: $PbO\cdot PbSO_4$ (lanarkite) and $3\,PbO\cdot PbSO_4\cdot H_2O$. CHARRETON also found the same salts at 17°C, but for the latter he found the formula $3PbO\cdot PbSO_4$ (but interpretable as $3PbO\cdot PbSO_4\cdot H_2O$: see BODE and VOSS 1959). $3PbO\cdot PbSO_4\cdot nH_2O$ is also found in the corrosion of lead in marine sediments (e.g., BECCARIA et al., 1982: on ancient lead plates).

Tetrabasic lead sulphate only occurs above approx. 60 °C. Below this temperature, $3PbO\cdot PbSO_4$ forms together with PbO (SCHAUMBERG, 1987). Furthermore, there is a dibasic lead sulphate $2PbO\cdot PbSO_4$, which is unstable below 450°C and decomposes into $PbO\cdot PbSO_4$ and $4PbO\cdot PbSO_4$ (LANDER 1949; ESDAILE 1966; JONES and ROTHSCHILD 1958; BILLHARDT 1970).

It is interesting to note that at 80 °C the type of lead modification added (tetragonal or orthorhombic PbO) determines the type of basic lead sulphate formed first in the reaction with H_2SO_4. $3PbO\cdot PbSO_4\cdot H_2O$ forms in the case of tetragonal lead oxide, but $PbO\cdot PbSO_4$ in the case of orthorhombic PbO. In both cases, $4\,PbO\cdot PbSO_4$ is the ultimately stable phase (ILIEV and PAVLOV 1979).

Tab. 11.13 Basic lead sulphates, compounds thermodynamically stable at 25 °C are shown in bold

Solid Phase	Source/ Comment
$4PbO\cdot PbSO_4$	ILIEV and PAVLOV (1979), STEELE and PLUTH (1998). Forms only above 60 °C.
$3PbO\cdot PbSO_4\cdot H_2O$	STRÖMHOM (1904), PLEIßNER (1907). STEELE et al. (1997)
$3PbO\cdot PbSO_4$	
$2PbO\cdot PbSO_4$	LANDER, 1949. Stable only above 450 °C.
$PbO\cdot PbSO_4$ (lanarkite)	PLEISSNER (1907), CHARRETON (1956a,b)

11.4.2 $PbO\cdot PbSO_4$ (lanarkite) and $3\,PbO\cdot PbSO_4\cdot H_2O$

The solubility of $PbO\cdot PbSO_4$ was first investigated by PLEIßNER (1907). Assuming that the solubility determined by him at 18°C does not differ significantly from that at 25°C, a solubility constant of -26.9 can be derived from his measured values.

CHARRETON (1956a,b) presented a more far-reaching investigation at 17°C. He determined the pH value of solutions that were in equilibrium with both anglesite ($PbSO_4$) and $PbO\cdot PbSO_4$. Here, the following relationship is valid:

$$\frac{K_{1:1}}{K_A^2} = \frac{a_{Pb^{2+}}^2 a_{OH^-}^2 a_{SO_4^{2-}}}{a_{Pb^{2+}}^2 a_{SO_4^{2-}}^2 a_W} = \frac{a_{OH^-}^2}{a_{SO_4^{2-}} a_W} \qquad (11.12)$$

If a value of -7.843 is used as the solubility constant for anglesite (K_A) (HAGEMANN 1999), the solubility constant for $PbO\cdot PbSO_4$ is as follows$_4$

log $K_{1:1}$= -27.49.

Data on the solubility of $3PbO\cdot PbSO_4\cdot H_2O$ are available from the same authors. From the solubility experiments of PLEIßNER (1907), a solubility constant of -58.6 can be derived analogous to the above case. CHARRETON (1956a, b) investigated the phase equilibrium $PbO\cdot PbSO_4$/ $3PbO\cdot PbSO_4$. However, BODE and VOSS (1959) already pointed out that the analytical data of CHARRETON (1956A, b) indicate a composition $3PbO\cdot PbSO_4\cdot H_2O$.

If the newly determined solubility constant for $PbO\cdot PbSO_4$ (see above) is taken into account in the calculation carried out by him, the following is obtained for $3\,PbO\cdot PbSO_4\cdot H_2O$

log $K_{3:1}$= -63.7

We adopt the values of CHARRETON (1956A, b) in both cases because of the larger body of measurement data and the greater reliability of three-phase equilibria compared to simple solubility experiments. The exact knowledge of the speciation of lead is not required for the evaluation of experiments with several solid phases as with Charreton. Data derived from high temperature thermochemical data by DERRICHE and PERROT (1976), NORWISZ (1984) and KELLOGG (1989) were not considered.

Tab. 11.14 Solubility constant for $PbO \cdot PbSO_4$ (reaction $PbO \cdot PbSO_4 + H_2O \rightleftharpoons 2\,Pb^{2+} + 2\,OH^- + SO_4^{2-}$)

Medium	log K_c	log K	Source/ Comment
18 °C, solubility $2.5 \cdot 10^{-5}$ mol/l 3d		-26.9	PLEIßNER (1907) Solubility re-evaluated by speciation calculation Complex formation constants from this work
17 °C		**-27,49 (recommended)**	CHARRETON (1956a,b,c) solubility and potentiometric (Cl). Corrected by reference to solubility constant for anglesite (HAGEMANN, 1999).

Tab. 11.15 Solubility constant for $3PbO \cdot PbSO_4 \cdot H_2O$ (reaction $3PbO \cdot PbSO_4 \cdot H_2O + 2H_2O \rightleftharpoons 4Pb^{2+} + 6OH^- + SO_4^{2-}$)

Medium	log K_c	log K	Source/ Comment
18 °C, solubility $2.5 \cdot 10^{-5}$ mol/l 3d		-58.6	PLEIßNER (1907) Solubility re-evaluated by speciation calculation Complex formation constants from this work
17 °C		**-63.65 (recommended)**	CHARRETON (1956a, b, c) Solubility . Corrected by reference to solubility constant for anglesite (HAGEMANN, 1999).

11.4.3 Chlorosulphates

A few years ago, three more complex basic lead chlorides were discovered, which also contain sulphate: symesite, sundiusite and an as yet unnamed mineral. They are listed in Tab. 11.10. Nothing is known about the synthesis pathways or thermodynamic data.

11.5 Lead carbonate and lead carbonato complexes

11.5.1 Carbonato and carbonatohydroxo complexes

According to consistent studies by several authors, lead forms two complexes with carbonate in aqueous solutions: $[PbCO_3]^0$ and $[Pb(CO_3)_2]^{2-}$ (e.g., BILINSKI et al. 1976, SIPOS et al. 1977). The finding of FROMAGE and FIORINA (1969) on the formation of a tricarbonato complex $[Pb(CO_3)_3]^{4-}$ above 0.4 mol/l CO_3^{2-} was otherwise not confirmed, although there were some measurements at such high carbonate concentrations, e.g., FERRI et al. (1987b). Based on their potentiometric measurements in a solution with 1 mol/l CO_3^{2-}, they instead postulated the existence of a lead carbonato hydroxo complex, which may constitute the main part of the speciation in non-saline carbonate-containing natural waters (Bruno 1990). The complex formation was mainly investigated polarographically and potentiometrically. For the evaluation of the solubility measurements, the solubility constant of lead carbonate (cerussite) is needed. Here we refer back to the measurements of Bilinski and Schindler (1982). They investigated the solubility of cerussite in acidic solutions of constant ionic strength (0.3 M $NaClO_4$) and under different CO_2 pressures. Under these conditions, lead is present exclusively as a free cation. The ion activity coefficients were determined using the SIT model and the interaction coefficients from Ciavatta (1980). The calculation procedure is summarised in Tab. 11.16. It led to a solubility constant for cerussite of

$$\log K\,(PbCO_3) = -13.60.$$

Tab. 11.16 Derivation of the solubility constant of $PbCO_3$ (cerussite) from the work of Bilinski and Schindler (1982)

Reaction	value (log K)	Source
$PbCO_{3(s)} + 2\,H^+ \rightleftharpoons Pb^{2+} + CO_{2(g)} + H_2O$	5.20 (molar, 0.3 M $NaClO_4$)	Bilinski and Schindler (1982)
$CO_{2(g)} + H_2O \rightleftharpoons H^+ + HCO_3^-$	-7.53 (molar, 0.3 M $NaClO_4$)	Bilinski and Schindler (1982)
$PbCO_{3(s)} + H^+ \rightleftharpoons Pb^{2+} + HCO_3^-$	-2.33 (molar, 0.3 M $NaClO_4$)	This work. Basis: Bilinski and Schindler (1982)
$PbCO_{3(s)} + H^+ \rightleftharpoons Pb^{2+} + HCO_3^-$	-3.26 (molal, I=0)	This work. Basis: Bilinski and Schindler (1982)
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	-10.3392 (molal, I=0)	Harvie et al. (1984)
$PbCO_{3\,(s)} \rightleftharpoons Pb^{2+} + CO_3^{2-}$	**-13.60** (molal, I=0)	This work. Basis: Bilinski and Schindler (1982)

For the determination of the complex formation constants, the measurements of Byrne (1981) in untreated seawater were not taken into account, as the exact composition of the seawater was not given. The complex formation constant for $[PbCO_3]^0$ by Bilinski and Schindler (1982) deviates strongly from the other literature values. It is essentially based on a single solubility experiment and is not included in the averaging.

Also not considered were the many "recommended" values included in compilations, which themselves are often not derived from measurement data, but are merely averages of other compilations. One such example is the much-used values from Whitfield and Turner (1980), each of which is an average of the compilations of Zirino and Yamamoto (1972), Lu and Chen (1977), Stumm and Brauner (1975), Schindler (1975), Dyrssen and Wedborg (1974) and the measured value of Sipos et al. (1977).

Under these circumstances, the mean value of the measurements in Tab. 11.18 the following complex formation constants:

$\log \beta_1 = 7.12$ $(Pb^{2+} + CO_3^{2-} \rightleftharpoons [PbCO_3]^0)$

$\log \beta_2 = 10.21$ $(Pb^{2+} + 2CO_3^{2-} \rightleftharpoons [Pb(CO_3)_2]^{2-})$

For the hydroxocarbonato complex $[PbCO_3(OH)]^-$, based on the work of FERRI et al. (1987b), we obtained

$\log \beta_{1.1} = 12.9$ $(Pb^{2+} + CO_3^{2-} + OH- \rightleftharpoons [PbCO_3(OH)]^-)$

This value would make the complex so stable that it would have interfered with numerous earlier determinations of the complexation of lead carbonato complexes. In particular, the determination of β_2 for $[Pb(CO_3)_2]^{2-\ -}$ would be subject to great doubt.

Also, the introduction of $[PbCO_3(OH)]^-$ leads to considerable inconsistencies. For example, the cerussite solubilities of BILINSKI and MARKOVIĆ (1977) and BILINSKI and SCHINDLER (1982) in KNO_3 and $NaClO_4$ solutions, respectively, cannot be explained at carbonate concentrations between 10^{-7} and 10^{-1} mol/l. If this complex is taken into account in model calculations, excessive lead concentrations are obtained (about two to three times too high). The best fit is obtained by excluding the complex $[PbCO_3(OH)]^-$.

The existence of the complex $[PbCO_3(OH)]^-$ and its stability should be made subject to a more detailed examination.

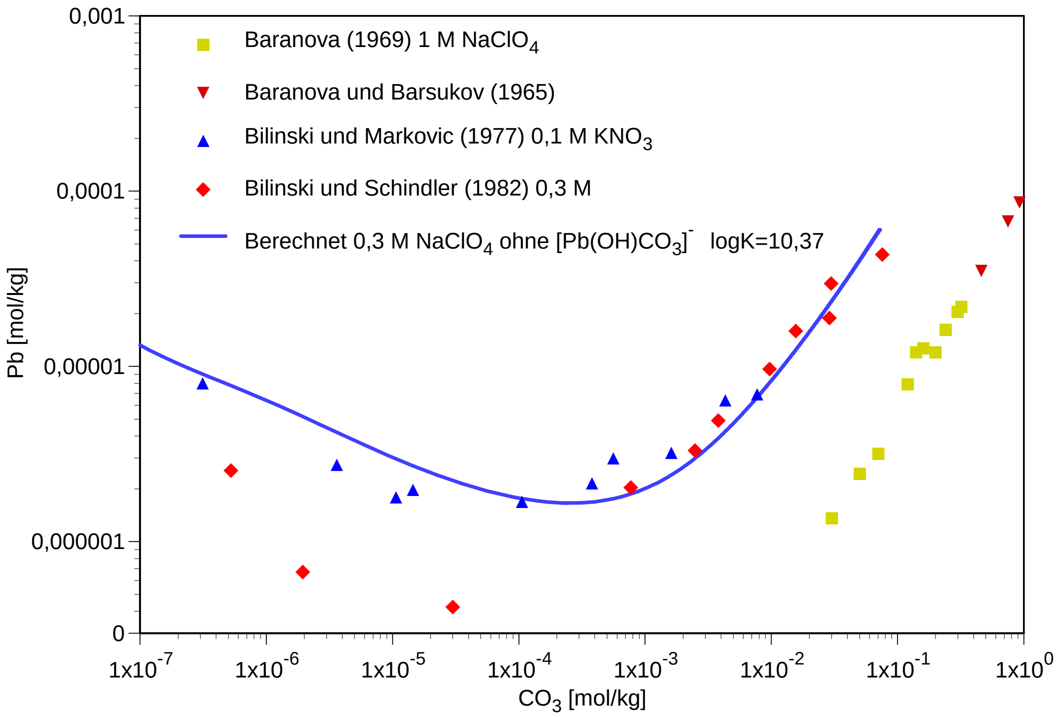


Fig. 11.4 Solubility of cerussite in carbonate-containing solutions

It was not possible to derive interaction coefficients for the ion pair Na^+, $[Pb(CO_3)_2]^{2-}$ analogous to the sodium carbonate-cadmium carbonate system. In principle, solubility experiments of $PbCO_3$ in Na_2CO_3 solutions would be suitable for evaluation. However, as AUERBACH and PICK (1913) were able to show, cerussite is transformed into hydrocerussite $2PbCO_3{\cdot}Pb(OH)_2$ or basic sodium lead carbonate by the action of sodium carbonate. Ion interaction coefficients could also be derived from the solubilities of this basic salt in sodium carbonate solutions. In the available studies with sufficiently high sodium or also potassium carbonate concentrations (BARANOVA and BARSUKOV 1965; BARANOVA, 1968; PATTERSON et al. 1977), $PbCO_3$ was given as the solid phase, which is thermodynamically unstable under the selected boundary conditions. An evaluation therefore had to be omitted. In addition, it is noticeable that the solubility data of BARANOVA and BARSUKOV, 1965 and BARANOVA 1968 cannot be brought into agreement with the solubility measurements of BILINSKI and MARKOVIĆ (1977) and BILINSKI and SCHINDLER (1982). The measured data are an order of magnitude too low.

11.5.2 Hydrogen carbonato complexes

BARANOVA and co-workers (1965, 19681967,) as well as FROMAGE and FIORINA (1969) postulated hydrogen carbonato complexes $[Pb(HCO_3)_n]^{2-n}$ with n = 1...4 based on potentiometric measurements. BILINSKI et al. (1976), however, were able to show that BARANOVA's measurement data can also be interpreted with the help of carbonato complexes. SHIRAI (1961) reported the occurrence of a complex $[Pb(OH)_2(HCO_3)_2]^{2-}$, the sum formula of which is probably to be understood as $[Pb(CO_3)_2]^{2-}$(aq).

Later, NÉHER-NEUMANN (1992) renewed the claim to have found a weak hydrogen carbonato complex at least in lead-rich acidic solutions. However, doubts remain: the measurements were made in solutions with relatively high lead concentrations (0.2 to 0.7 M). The derived complex formation constant shows a linear dependence on the lead concentration. This relationship can also be described as a mere concentration-dependent ion interaction without the formation of a covalent complex bond. The fact that in solutions with a low lead concentration there is so far no clear evidence of hydrogen carbonato complexes also casts doubt on the conclusions of NÉHER-NEUMANN (1992). Based on the literature data so far, BYRNE (1981), SIPOS et al. (1977) and BILINSKI and SCHINDLER (1982) also exclude the formation of significant amounts of a hydrogen carbonato complex. For these reasons, we refrain from deriving a complex formation constant and exclude hydrogen carbonato complexes from our model for the time being.

Tab. 11.17 Previously determined molar formation constants (log $K_{m,n}$) of lead carbonate and lead carbonate hydroxo complexes (formation reaction $m\ Pb^{2+} + n\ CO_3^{2-} + p\ OH^- \rightleftharpoons [Pb_m(CO_3)_n(OH)_p]^{2m-2n-p}$)

Medium	$[PbCO_3]^0$ log K_1	$[Pb(CO_3)_2]^{2-}$ log K_2	$[PbHCO_3]^+$ log K_1	$[PbCO_3(OH)]^-$ log $K_{1.1}$	Method	Source
1.7 M KNO_3		8.2			pol	FAUCHERRE and BONNAIRE (1959) 18 °C
1.0 M $NaNO_3$		8.2			pol	BARANOVA and BARSUKOVA (1965) re-evaluated by BILINSKI et al. (1976)
1.8 M KNO_3		7.9			pol	FROMAGE and FIORINA (1969)
0.1 M KNO_3	6.2				pol	ERNST et al. (1975) DPP
0.1 M KNO_3	6.3				pol	ERNST et al. (1975) DPASV
0.1 M KNO_3	6.4	9.8			pol	BILINSKI et al. (1976) ASV
0.1 M KNO_3	6.1	9.1			pol	BILINSKI et al. (1976) DPP
0.7 M $NaClO_4$	5.7	8.9			pol	SIPOS et al. (1977)
0.1 M KNO_3	6.1				pol	BROWN and KOWALSKI (1979)
0.3 M $NaClO_4$	5.4	8.86			sol.	BILINSKI and SCHINDLER (1982)
3 M $NaClO_4$		8.9		10.9	pot	FERRI et al. (1987b),
3.0 M $NaClO_4$			1.79		pot	NÉHER-NEUMANN (1992)

Tab. 11.18 Previously determined molal formation constants (log $\beta^{\dagger}_{m,n}$) of lead carbonate and lead carbonate hydroxo complexes (formation reaction m Pb^{2+} +n CO_3^{2-} + p $OH^- \rightleftharpoons [Pb_m(CO_3)_n(OH)_p]^{2m-2n-p}$)

Medium	**$[PbCO_3]^0$ log β_1**	**$[Pb(CO_3)_2]^{2-}$ log β_2**	**$[PbHCO_3]^+$ log β_1**	**$[PbCO_3(OH)]^-$ log $\beta_{1.1}$**	**Method**	**Source**
1.7 M KNO_3		10.33			pol	Faucherre and Bonnaire (1959) 18 °C
1.0 M $NaNO_3$		10.08			pol	Baranova and Barsukova (1965) re-evaluated by Bilinski et al. (1976)
1 M $NaClO_4$		9.46			sol.	Baranova (1969) recalc. with log K(cerussite) from Bilinski and Schindler (1982)
1.8 M KNO_3		10.06			pol	Fromage and Fiorina (1969)
0.1 M KNO_3	7.09				pol	Ernst et al. (1975) DPP
0.1 M KNO_3	7.19				pol	Ernst et al. (1975) DPASV
0.1 M KNO_3	7.29	10.70			pol	Bilinski et al. (1976) ASV
0.1 M KNO_3	6.99	10.00			pol	Bilinski et al. (1976) DPP
0.7 M $NaClO_4$	7.14	10.39			pol	Sipos et al. (1977)
0.1 M KNO_3	6.99				pol	Brown and Kowalski (1979)
0.3 M $NaClO_4$	*6.62*	10.08			sol.	Bilinski and Schindler (1982)
3.0 M $NaClO_4$		10.80		12.9	pot	Ferri et al. (1987b),
3.0 M $NaClO_4$			2.38		pot	Néher-Neumann (1992)
I = 0	**7.12**	**10.21**		**12.9**		**Recommended values** (mean value without *italic* data)

11.5.3 Other neutral lead carbonates

Cerussite forms solid solutions with the likewise orthorhombic aragonite ($CaCO_3$). Corresponding compounds are known under the name tarnowitzite. According to Siegl (1936), isomorphous mixtures have a maximum lead carbonate content of 3%. Furthermore, a microcrystalline intergrowth of aragonite and cerussite seems to occur. This would explain that many mineral samples otherwise designated as tarnowitzite are actually a mixture of cerussite and aragonite. Probably because of the different crystal structure, solid solutions with the trigonal minerals calcite ($CaCO_3$) or magnesite ($MgCO_3$) have not yet been encountered. Samples called plumbocalcite are merely intergrowths of calcite and cerussite. Siegl (1936) also reports a sample described as "plumbodolomite", but we found no further indications in the literature as to what properties it has.

With magnesium carbonate, a double carbonate $PbMg(CO_3)_2$ forms at 60°C (BÖTTCHER 1993). It has also been observed in the corrosion of lead pigments with solutions containing Mg^{2+} and CO_3^{2-} (KOTULANOVÁ et al. 2009).

11.5.4 Basic carbonates: overview

Under normal temperatures and pressures, three basic carbonates occur according to largely consistent findings: hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, plumbonacrite, $Pb_{10}(CO_3)_6O_2(OH)_4$ and somersetite, $PbO_8(OH)_4(CO_3)_5$. During thermal decomposition, further anhydrous compounds can occur that are unstable at room temperature and in the presence of water (cf. OLBY 1966; TAYLOR and LOPATA 1984). So far, two further anhydrous compounds have been found in nature, which are probably to be addressed as decomposition products of cerussite or hydrocerussite: $PbCO_3{\cdot}PbO$ (shannonite), $PbCO_3{\cdot}2PbO$ (ROBERTS et al. 1995) and grootfonteinite $2PbCO_3{\cdot}PbO$ (SIIDRA et al. 2018d). Other basic lead carbonates have been described in the literature, but no information is available on their stability (Tab. 11.19 f.)

The formation of basic sodium and potassium lead carbonates such as abellaite, $NaPb_2(CO_3)_2OH$ (IBÁÑEZ-INSA et al. 2017) has been clearly proven. Chlorocarbonates and sulphatocarbonates also exist.

Tab. 11.19 Basic lead carbonates

Solid phase	Alternative formula	Mineral name	Source/ Comment
$Pb_3O_2(CO_3)$	$PbCO_3{\cdot}2PbO$	untitled	First description: ROBERTS et al. (1995) as companion of cerussite, structure: KRIVOVICHEV and BURNS (2000c). Also as an intermediate product in the thermal decomposition of cerussite.
$PbCO_3{\cdot}Pb(OH)_2$	$PbCO_3{\cdot}PbO{\cdot}H_2O$		EUSTON (1914a, b). Little reliable description, as the focus of the work was on the production of white pigments.
$PbCO_3{\cdot}Pb(OH)_2{\cdot}H_2O$	$PbCO_3{\cdot}PbO{\cdot}2H_2O$		VORONOVA and VAJNČTEJN (1964) on leaving an aqueous suspension of red PbO in air. Mixed with hydrocerussite

Tab. 11.19 [cont.] Basic lead carbonates

Solid phase	**Alternative formula**	**Mineral name**	**Source/ Comment**
$Pb_2[O\|CO_3]$	$PbCO_3\cdot PbO$	Shannonite	First description: Roberts et al. (1995) cited in Krivovichev and Burns (2000a). Structure: Krivovichev and Burns (2000a) Thermal decomposition product of plumbonacrite and hydrocerussite (Flemming et al. 1984)
$3PbO\cdot 4PbCO_3\cdot 2H_2O$			Strömholm (1904) quoted after Pleißner (1907): probably only a mixture of hydrocerussite and lead oxide or incomplete reaction.
$3PbCO_3\cdot 2Pb(OH)_2$	$3PbCO_3\cdot 2PbO\cdot 2H_2O$		Mauch and Brunold (1957) by introducing air into a lead-containing 2 M NaOH solution. According to Bilinski and Schindler (1982), it converts rapidly to cerussite in slightly acidic solution. Possibly identical with plumbonacrite
$Pb_8O(OH)_4(CO_3)_5$	$5PbCO_3\cdot 3PbO\cdot 2H_2O$	Somersetite	Siidra et al. (2008c)
$Pb_5(CO_3)_3O(OH)_2$ **previous formula: $Pb_{10}(CO_3)_6O(OH)_6$** (Haake and Williams, 1981)	**$3PbCO_3\cdot 2PbO\cdot H_2O$**	**Plumbonacrite**	First description: Heddle (1889) cited in Krivovichev and Burns (2000b). Olby (1966) Structure: Krivivochev and Burns (2000b)
$2PbCO_3\cdot Pb(OH)_2$	**$2PbCO_3\cdot PbO\cdot H_2O$**	**Hydrocerussite, "lead white**	
$Pb_3O(CO_3)_2$	**$2PbCO_3\cdot PbO$**	**Grootfonteinite**	Siidra et al. (2018d)
$5PbCO_3\cdot 2Pb(OH)_2$	$5PbCO_3\cdot 2PbO\cdot 2H_2O$	"Russian Lead White"	Falk (1910) stable only at ‘low temperatures’. Compound or mixture?
$NaPb_2(CO_3)_2OH$	$2PbCO_3\cdot NaOH$	Abellaite	Auerbach and Pick (1913), Bulakhova et al. (1972) in the reaction of hydrocerussite, Structure: Brooker et al. (1983), Krivovichev and Burns (2000c), Ibáñez-Insa et al. (2007) or in the corrosion of lead in Na_2CO_3 solutions (Fischer et al. 2013).

Tab. 11.19 [cont.] Basic lead carbonates

Solid phase	Alternative formula	Mineral name	Source/ Comment
$NaPb_5(CO_3)_4(OH)_3$			Siidra et al. (2018a)
$KPb_2(CO3)_2OH$			Brooker et al. (1983)
$PbCl_2{\cdot}PbCO_3$	$PbCl_2{\cdot}PbCO_3$	Phosgenite	
$Pb_4Cl_6(CO_3){\cdot}H_2O$	$3\,PbCl_2{\cdot}PbCO_3{\cdot}H_2O$	Barstowite	Mel'nikova (1972), Kutzke et al. (2000)
$Pb_4(SO_4)(CO_3)_2(OH)_2$	$PbSO_4{\cdot}2\,PbCO_3{\cdot}PbO{\cdot}H_2O$	Susannite	
$Pb_4(SO_4)(CO_3)_2(OH)_2$		Leadhillite	
$Pb_4(SO_4)(CO_3)_2(OH)_2$		Macphersonite	Steele et al. (1998)

* **Bold print** means stable phases at 25 °C

11.5.5 Hydrocerussite

Auerbach and Pick (1913) determined at 18 °C the ratio of sodium hydrogen carbonate and sodium carbonate that result when both hydrocerussite and cerussite are present in the system.

If the two compounds are in equilibrium, the following formula apply:

$$K_C = a_{Pb^{2+}}\ a_{CO_3^{2-}} \qquad (11.13)$$

$$K_{HC} = a^3_{Pb^{2+}}\ a^2_{CO_3^{2-}}\ a^2_{OH^-} \qquad (11.14)$$

Putting the equation for cerussite to the power of 3 and dividing it by the equation for hydrocerussite leads to

$$\frac{K_C^3}{K_{HC}} = \frac{a^3_{Pb^{2+}}\ a^3_{CO_3^{2-}}}{a^3_{Pb^{2+}}\ a^2_{CO_3^{2-}}\ a^2_{OH^-}} = \frac{a_{CO_3^{2-}}}{a^2_{OH^-}} \qquad (11.15)$$

If one now additionally takes into account the equilibrium between the carbonate and hydrogen carbonate

$$K_2 = \frac{a_{H^+}\ a_{CO_3^{2-}}}{a_{HCO_3^-}} \qquad (11.16)$$

and the autoprotolysis constant of water

$$K_W = a_{H+}a_{OH-} \qquad (11.17)$$

then the quotient above can be converted to

$$\frac{K_C^3}{K_{HC}} = \frac{a_{CO_3^{2-}}}{a_{OH^-}^2} = \frac{K_2^2\ a_{HCO_3^-}}{K_W^2\ a_{CO_3^{2-}}} \qquad (11.18)$$

The activity coefficients were calculated with the model of HARVIE et al. (1984). The evaluation of the measured values presented in AUERBACH and PICK (1913) then results in the solubility constant for hydrocerussite:

$$\log K = -46.75 \pm 0.03$$

RANDALL and SPENCER (1928) investigated the solubility of hydrocerussite in KOH solutions and extrapolated their calculated solubility constant for the reaction

$$3\,[Pb(OH)_3]^- + 2\,CO_3^{2-} \rightleftharpoons 2PbCO_3 \cdot Pb(OH)_2 + 7\,OH^-$$

to the ionic strength 0. They obtained log K_3= -5.1. Conversion to the reaction

$$3\,Pb^{2+} + 2\,CO_3^- + 2\,OH^- \rightleftharpoons 2\,PbCO_3 \cdot Pb(OH)_2$$

results in log K = -46.5, which is in good agreement with the value calculated above.

BILINSKI and SCHINDLER (1982) investigated the solubility of hydrocerussite in weakly acidic to alkaline solutions at constant ionic strength and defined CO_2 pressure. The data was re-evaluated using the complex formation constant for $[PbCO_3]^0$ derived above. Ultimately, only the measurements in which the hydrocerussite had not partially transformed into cerussite and whose -log c_H value was so small that the hydroxo complex formation can be considered negligible (< -log c_H 7) were evaluable. Ion activity coefficients were calculated using the Pitzer model. For the reaction

$$3\,Pb^{2+} + 2\,CO_3^- + 2\,OH^- \rightleftharpoons 2PbCO_3 \cdot Pb(OH)_2$$

the solubility constant log K = -46.3 was obtained.

TAYLOR and LOPATA (1984) determined the pH and the carbonate content at 22 ± 2 °C in solutions saturated with both hydrocerussite (HC) and cerussite (C). They expressed the carbonate content in terms of a hypothetical CO_2 partial pressure.

For equilibria of the two compounds the following applies

$$K_C = a_{Pb^{2+}}\ a_{CO_3^{2-}} \tag{11.19}$$

$$K_{HC} = a^3_{Pb^{2+}}\ a^2_{CO_3^{2-}}\ a^2_{OH^-} \tag{11.20}$$

Putting the equilibrium constant for cerussite K_C to the power of 3 and forming a quotient with K_{HC}, one obtains

$$\frac{K_C^3}{K_{HC}} = \frac{a^3_{Pb^{2+}}\ a^3_{CO_3^{2-}}}{a^3_{Pb^{2+}}\ a^2_{CO_3^{2-}}\ a^2_{OH^-}} = \frac{a_{CO_3^{2-}}}{a^2_{OH^-}} \tag{11.21}$$

If one now additionally takes into account the equilibrium between the CO_2 partial pressure p_{CO2} and the CO_3^{2-} concentration

$$K_2^g = \frac{a^2_{H^+}\ a_{CO_3^{2-}}}{p_{CO_2}\ a_W} \tag{11.22}$$

and the autoprotolysis constant of water

$$K_W = a_{H^+} a_{OH^-} \tag{11.23}$$

the equilibrium between cerussite and hydrocerussite can be expressed as

$$\frac{K_C^3}{K_{HC}} = \frac{a_{CO_3^{2-}}}{a^2_{OH^-}} = \frac{K_2^g\ p_{CO_2}\ a_W}{K_W^2} \tag{11.24}$$

TAYLOR and LOPATA (1984) determined the CO_2 equilibrium partial pressure to be 8 to 15 Pa. This leads to a solubility constant for hydrocerussite K_{HC} of

$\log K_{HC} = -46.77$

According to their statements, nothing significant changes in the position of this equilibrium up to 100 °C. Therefore, both their data and those of AUERBACH and PICK (1913) at 18 °C can be used without further corrections.

The potentiometric measurements of MERCY et al. (1998) with a measuring cell

$$\text{Pb(Hg, 2-Phasen)} \mid Pb(OH)_2 \cdot 2\,PbCO_3 \mid KOH, K_2CO_3\ (aq) \mid HgO \mid Hg$$

provided a free standard enthalpy of formation for hydrocerussite at heights of

$\Delta G_f^0 = -1699.80 \pm 1.6$ kJ/mol

After applying the free standard enthalpies of formation for the ions involved (GRENTHE et al. 1992), this corresponds to a solubility constant of

$$\log K_{HC} = -45.0 \pm 0.3$$

This value is more than one log K unit below the experimental measured values of the other authors. Deviations of this kind are often observed when using amalgam electrodes in strongly basic solutions (see also the potentiometric measurement of the solubility constant of $CdCO_3$ by SAEGUSA, 1950). Preference is given to the solubility measurements which agree very well with each other.

The determination of the solubility of hydrocerussite in "CO_2-saturated" water by RUCHHOFT and KACHMAR (1942) cannot be used, as it is not clear from the article under which CO_2 pressure this saturation was carried out.

The obtained mean value from the four solubility tests is:

$$\log K_{HC} = -46.6$$

Noteworthy are the investigations of SIIDRA et al. (2017), who tried in vain to find a single crystal for the structural chemical investigation of hydrocerussite. Natural samples from different localities previously described as "hydrocerussite", $2PbCO_3 \cdot PbO \cdot H_2O$, showed instead (partly in mixture) plumbonacrite / $3PbCO_3 \cdot 2PbO \cdot H_2O$, grootfonteinite / $2PbCO_3 \cdot PbO$, somersetite / $5\,PbCO_3 \cdot 3\,PbO \cdot H_2O$ or abellaite, $2PbCO_3 \cdot NaOH$.

Tab. 11.20 Solubility constant for hydrocerussite (reaction $2\,PbCO_3{\cdot}Pb(OH)_2 \rightleftharpoons 3\,Pb^{2+} + 2\,CO_3^{2-} + 2\,OH^-$)

Medium	**log K_c**	**log K**	**Source/ Comment**
variable 18°C		-46.75	Auerbach and Pick (1913), Solubility in Na_2CO_3/$NaHCO_3$
variable, extrapolated to I = 0		-46.5	Randall and Spencer (1928)
0.3 M $NaClO_4$	-42.00	-46.3	Bilinski and Schindler (1982) newly corrected with log β_1 from this work
variable 22 ±2 °C		-46.77	Taylor and Lopata (1984), converted to nominal reaction with β_3 for $[Pb(OH)_3]^-$ from this work
		-45.02	Mercy et al. (1998) potentiometric
		-46.6	This work: mean value from above works without Mercy et al. (1998)

11.5.6 Plumbonacrite and $3PbCO_3{\cdot}2Pb(OH)_2$

Although first described in 1899 (Heddle 1889), it took almost 80 years until a second locality of this extraordinarily rare mineral became known (cf. Haacke and Williams 1981). For a long time, the formula was considered to be $Pb_{10}(CO_3)_6O(OH)_6$, before Krivovichev and Burns (2000b) were able to determine it more precisely as $Pb_5(CO_3)_3O(OH)_2 = ½\,Pb_{10}(CO_3)_6O_2(OH)_4 = 3\,PbCO_3{\cdot}2\,PbO{\cdot}H_2O$ on the basis of new X-ray structural investigations.

According to Olby (1966) as well as Haacke and Williams (1980), plumbonacrite is only a metastable intermediate product that decomposes into hydrocerussite and cerussite (Olby 1966) or hydrocerussite and lithargite, depending on the environmental conditions. This is contradicted by Taylor and Lopata (1984), who also observed the transformation of hydrocerussite into plumbonacrite in a narrow KOH concentration range (0.05 - 0.08 mol/l KOH). At higher concentrations, the transformation into massicot is observed, at lower concentrations into hydrocerussite. From the statements it can be concluded that plumbonacrite is only stable under certain, narrowly defined conditions.

The compound is formed, among other things, when a CO_2 stream is introduced into a PbO suspension: first plumbonacrite (= 7.07) is found at pH 7- 8, and the more carbonate-rich hydrocerussite is found upon further introduction at pH 4- 5 (Olby, 1966).

It can be assumed that the compound $3PbCO_3{\cdot}2Pb(OH)_2 = PbCO_3{\cdot}2PbO{\cdot}2H_2O$ (Mauch and Brunhold 1967; Bilinski and Schindler 1982), which has been described several times, is either identical or very closely related to plumbonacrite, especially since the synthesis conditions (KRIVOVICHEV and BURNS 2000a, MAUCH and BRUNHOLD 1967) differ only slightly.

The solubility measurements of HAACKE and WILLIAMS (1980) are only incompletely documented. They investigated the solubility of plumbonacrite (PN) in 0.01 M NaOH. A control of the CO_2 partial pressure did not take place, so that it cannot be excluded that the presented derivations are erroneous. As the result of their investigations, the authors presented the free standard enthalpy of reaction for the following reaction:

$$Pb_{10}(CO_3)_6O(OH)_6 + 8\,H^+ \rightleftharpoons 10\,Pb^{2+} + 6\,CO_3^{2-} + 7\,H_2O \qquad (11.25)$$

$$\Delta G_r^0(PN) = -50.0 \pm 0.5\ \mathrm{kJ\ mol^{-1}} \qquad (11.26)$$

$$\log K_{PN}^* = -9.0$$

The solubility constant is also valid for the formula found by KRIVOVICHEV and BURNS (2000b)

$$Pb_{10}(CO_3)_6O_2(OH)_4 + 8\,H^+ \rightleftharpoons 10\,Pb^{2+} + 6\,CO_3^{2-} + 6\,H_2O \qquad (11.27)$$

For the reaction

$$Pb_{10}(CO_3)_6O(OH)_6 \rightleftharpoons 10\,Pb^{2+} + 6\,CO_3^{2-} + 8OH^- + 6\,H_2O \qquad (11.28)$$

it follows

$$\log K_{PN}^{**} = -121.0$$

or $\log K_{PN} = -60.5$ for $Pb_5(CO_3)_3O(OH)_2$

TAYLOR and LOPATA (1984) determined the equilibrium constant for the reaction between PbO (used as a lithargite/massicot mixture) and plumbonacrite. It should be noted, however, that they never reached true equilibria. Because of the slow rates of transformation they could only characterise the concentration limits at which a transformation PbO → plumbonacrite or vice versa began. Their concentration limits determined in this way have great uncertainties.

$$10\,PbO + 6\,CO_3^{2-} + 9\,H_2O \rightleftharpoons Pb_{10}(CO_3)_6O(OH)_6 + 12\,OH^- \qquad (11.29)$$

For the evaluation, the question of the water content of plumbonacrite is initially irrelevant, as measurements were only made in sufficiently diluted solutions. The following quotient of the solubility constants for lithargite PbO (the more soluble component of the PbO mixture used) and plumbonacrite applies:

$$\frac{K_L^{20}}{K_{PN}} = \frac{a_{Pb^{2+}}^{10} a_{OH^-}^{20}}{a_{Pb^{2+}}^{10} a_{CO_3^{2-}}^{6} a_{OH^-}^{8} a_W^{7}} = \frac{a_{OH^-}^{12}}{a_{CO_3^{2-}}^{6} a_W^{7}} \qquad (11.30)$$

For the quotient

$$\frac{a_{OH^-}^2}{a_{CO_3^{2-}}} \qquad (11.31)$$

the authors determined the following value

$\log K_{PbO/PN} = 0.1 \pm 0.6$

From this ratio, the solubility constant of plumbonacrite can be derived:

$\log K_{PN}{}^{**} = -150 \pm 4$ for $Pb_{10}(CO_3)_6O(OH)_6$

or half this value $\log K_{PN} = -75 \pm 2$ for $Pb_5(CO_3)_3O(OH)_2$

If one applies this solubility constant or the one that results from converting the free standard enthalpy of formation given by the authors (-5310 ± 31 kJ/mol), there are no solution conditions under which plumbonacrite would be stable. Therefore, the documented measurement data from TAYLOR and LOPATA (1984) was re-evaluated. In summary: At a (potassium?) carbonate concentration of 0.05 mol/l, hydrocerussite transforms into plumbonacrite. The reverse reaction is observed at ≤ 0.01 M KOH. The transformation point between plumbonacrite and hydrocerussite must therefore be between 0.01 and 0.05 mol/l KOH. Similarly, it can be deduced that the transformation point between plumbonacrite and massicot is between 0.1 and 0.5 mol/l KOH. These conditions are only fulfilled with

$\log K_{PN} = -78.2 \pm 0.2$

The numerical value is subject to some doubt because of the ambiguity of the data in the article by TAYLOR and LOPATA (1984), but in contrast to the data by HAACKE and WILLIAMS (1980), it should be fairly close to reality.

Tab. 11.21 Solubility constant for plumbonacrite (reaction $Pb_5(CO_3)3O(OH)_2 + H_2O \rightleftharpoons 5\,Pb^{2+} + 3\,CO_3^{2-} + 4\,OH^-$)

Medium	log K_c	log K	Source/ Comment
unknown		-60.4	HAACKE and WILLIAMS (1980)
variable 22±°C 2		-75± 2	TAYLOR and LOPATA (1984), converted with new solubility constant for cerussite
I = 0		**-78.2 ± 0.2**	This work based on the transformation conditions in TAYLOR and LOPATA (1984),

11.5.7 Other basic lead carbonates

EUSTON (1914a, b) reported that when lead carbonate is allowed to react with a lead-containing basic solution (e.g., lead acetate), the solid phase transforms to $PbCO_3 \cdot Pb(OH)_2$. This effect can also be observed with other minerals. For example, basic zinc carbonate transforms into $ZnCO_3 \cdot Zn(OH)_2 \cdot 3Pb(OH)_2$, $CaCO_3$ becomes $2CaCO_3 \cdot Pb(OH)_2$, $BaSO_4$ becomes $3BaSO_4 \cdot Pb(OH)_2$, $BaCO_3$ becomes $3BaCO_3 \cdot Pb(OH)_2$. Whether these are really compounds or just mixtures, is unclear. The accuracy of the analyses may be doubted, as the author was primarily concerned with the suitability of the white pigments obtained for painting purposes.

$Pb_3O_2(CO_3) = 2\,PbO \cdot PbCO_3$ as well as shannonite $PbO \cdot PbCO_3$ were first described by ROBERTS et al. (1995) on natural cerussite samples. They are also formed during the thermal decomposition of cerussite or hydrocerussite or plumbonacrite (cf. FLEMMING et al. 1984) and can be obtained at 230°C by reacting PbO in a K_2CO_3 solution (KRIVOVICHEV and BURNS 2000a). It is not clear whether these compounds are also stable at 25°C in natural aqueous systems. They have not been observed in solubility experiments under similar concentration conditions (cf. BARANOVA 1967; BILINSKI and SCHINDLER 1982).

The $3PbO \cdot 4PbCO_3 \cdot 2H_2O$ described by STRÖMHOLM (1904, cited by PLEIßNER1907) is probably only a mixture of hydrocerussite and lead oxide.

$NaPb_2(CO_3)_2OH$ is formed by the action of Na_2CO_3 solutions on cerussite. AUERBACH and PICK (1913), as well as BULACHOVA et al (1970b) and BULAKHOVA ET AL (1972) and later BROOKER et al (1983) obtained the same compound by the action of $NaCO_3$/$NaHCO_3$ on hydrocerussite or cerussite at room temperature. KRIVOVICHEV and BURNS (2000c) obtained the compound by boiling a mixture of PbO, $PbCl_2$ and $PbCO_3$ in NaOH solution under pressure at 230°C . A corresponding potassium salt $KPb_2(CO_3)_2OH$, which BULACHOVA and BEN'JAŠ (1970b) could not obtain at room temperature, was found after boiling cerussite with a concentrated potassium carbonate solution (BROOKER et al. 1983).

Thermodynamically evaluable are the results of AUERBACH and PICK (1913). They investigated the equilibrium between $NaPb_2(CO_3)_2OH$ and $PbCO_3$ in sodium carbonate / sodium hydrogen carbonate solutions. If both compounds are present at the same time, their solubility constants can be related as follows:

$$\frac{K_C^2}{K_{NaC}} = \frac{a_{Pb^{2+}}^2 \ a_{CO_3^{2-}}^2}{a_{Na^+} \ a_{Pb^{2+}}^2 \ a_{CO_3^{2-}}^2 \ a_{OH^-}} = \frac{1}{a_{Na^+} \ a_{OH^-}} \qquad (11.32)$$

Considering the equilibrium between carbonate and hydrogen carbonate

$$K_2 = \frac{a_{H^+} \ a_{CO_3^{2-}}}{a_{HCO_3^-}} \qquad (11.33)$$

then results:

$$\frac{K_C^2}{K_{NaC}} = \frac{1}{a_{Na^+} \ a_{OH^-}} = \frac{K_2 \ a_{HCO_3^-}}{a_{Na^+} \ K_W \ a_{CO_3^-}} \qquad (11.34)$$

As solubility constant for $NaPb_2(CO_3)_2OH$ the following value was obtained:

$\log K_{NaC} = -32.32 \pm 0.04$.

For the other compounds mentioned, no thermodynamically evaluable information is currently available.

11.5.8 Chloro carbonate

Two minerals containing both chloride and carbonate have been described so far: the rare barstowite $Pb_4Cl_6(CO_3)\cdot H_2O = 3PbCl_2\cdot PbCO_3\cdot H_2O$ and the more common phosgenite $PbCl_2\cdot PbCO_3$. The former was first found in the 1970s (MEL'NIKOVA, 1972) and described in more detail in the 1990s. It was found on ancient ore slags near the sea (FRANZINI et al. 1992a, b; PERCHIAZZI and REWITZER 1995) and in archaeological underwater finds on lead bars and lead anchors (ancient shipwrecks in the Mediterranean, e.g., Mahdia; KUTZKE et al. 1996, 1998, 2000). There it is found as a corrosion product of metallic lead. It is interesting that other lead minerals were also found as corrosion products: Penfieldite, Anglesite, Galenite, Phosgenite, Cotunnite. Barstowite has also been found in places where lead veins are in direct contact with seawater and air. It is likely that it has been confused in the past with the structurally similar cerussite $PbCO_3$ and cotunnite $PbCl_2$ (CERUTTI and PREITE 1995; KUTZKE and EGGERT 1998). So far, no work is available in which a synthetic pathway could be demonstrated. Solubility measurements are therefore lacking.

The solubility constant of phosgenite was determined by NÄSÄNEN et al. (1962, 1963). In two series of experiments, the equilibrium conditions for the reaction between phosgenite and cotunnite were determined.

$$2\,PbCl_2 + CO_{2(g)} + H_2O \rightleftharpoons PbCl_2\cdot PbCO_3 + H^+ + Cl^- \qquad (11.35)$$

and between phosgenite (P) and cerussite (C):

$$PbCl_2\cdot PbCO_3 + CO_{2(g)} + H_2O \rightleftharpoons PbCO_3 + H^+ + Cl^- \qquad (11.36)$$

If phosgenite and cerussite are present next to each other, the equilibrium is expressed by the ratio of the chloride and carbonate concentrations:

$$\frac{K_P}{K_C^2} = \frac{a_{Pb^{2+}}^2\ a_{Cl^-}^2\ a_{CO_3^{2-}}}{a_{Pb^{2+}}^2\ a_{CO_3^{2-}}^2} = \frac{a_{Cl^-}^2}{a_{CO_3^{2-}}} \qquad (11.37)$$

This formula can be evaluated after taking into account the carbonic acid equilibrium

$$K_2^g = \frac{a_{H^+}^2\ a_{CO_3^{2-}}}{p_{CO_2}\ a_{H_2O}} \qquad (11.38)$$

which converts to

$$K_P = \frac{a_{Cl^-}^2 \; a_{H^+}^2 \; K_C^2}{K_{2g}^g \; p_{CO_2} \; a_{H_2O}} \qquad (11.39)$$

The second series of experiments is more suitable for evaluation, as only very little chloride is bound in lead chloro complexes due to the lower lead concentration. Thus, the free chloride concentration can also be derived without iteration. The evaluation of the experimental data, after calculating the ion activity coefficients with the data set of Harvie et al. (1984), gives a solubility constant for the oceanic salt system of:

log K (phosgenite) = -20.64

The difference to the value derived by NÄSÄNEN et al. (-19.94) is largely due to the higher assumed solubility of cerussite used by the authors (log K = -13.13 instead of -13.6).

A short time later, NÄSÄNEN et al. (1963) published another paper in which solubility measurements of phosgenite were made in NaOH solutions of different concentrations. The evaluation of these data proved to be difficult since the activity of the free lead ion is now no longer determined by a second lead-containing phase. In the experimental pH range around 10, a wide variety of simple and probably also mixed lead complexes with hydroxide, chloride and carbonate occur, the quantification of which is not easy. No evaluation was done at this point.

11.5.9 Sulphato carbonate

So far, only one compound has been described that contains both carbonate and sulphate, the mineral group with the formula $Pb_4(SO_4)(CO_3)_2(OH)_2$. It exists in three modifications: susannite, leadhillite and macphersonite. All compounds are weathering products of primary lead minerals. It is found, for example, in Baratti (Italy) as a secondary mineral on ancient lead-bearing slags (FRANZINI et al. 1992a, b). The crystal structure of macphersonite, like that of leadhillite, has a layered structure consisting of a succession of Pb/OH, $PbCO_3$ and SO_4 structures. The minerals differ only in the different arrangement of the layers in relation to each other and in the orientation of the SO_4 octahedra (STEELE et al. 1998, 1999).

The solubility of a natural leadhillite was studied by ABDUL-SAMAD et al. (1982). According to the authors, the mineral dissolves congruently and reaches a solubility of $1.08 \cdot 10^{-5}$ mol/l at pH 6.62. Taking into account the previously derived complex formation constants for the lead hydroxo complexes, this leads to the following reaction

$$Pb_4(SO_4)(CO_3)_2(OH)_2 \rightleftharpoons 4\,Pb^{2+} + SO_4^{2-} + 2\,CO_3^{2-} + 2\,OH^- \qquad (11.40)$$

with a solubility constant of

$\log K$ (leadhillite) = -54.9

Leadhillite is thus stable against decomposition into cerussite and lanarkite:

$$Pb_4(SO_4)(CO_3)_2(OH)_2 \rightarrow 2\,PbCO_3 + Pb_2OSO_4 + H_2O \qquad (11.41)$$

$\log K = -54{,}9 - 2 \cdot 13{,}6 - 27{,}49 = 0{,}24$

11.6 Result overview

The following tables contain an overview of the thermodynamic quantities obtained in this work.

Tab. 11.22 Complex formation constants in the system Pb^{2+} - CO_3^{2-} – OH^- – H_2O

Reaction	Value (log β)	Source
$Pb^{2+} + OH^- \rightleftharpoons [PbOH]^+$	6.77	This work
$Pb^{2+} + 2\,OH^- \rightleftharpoons [Pb(OH)_2]^0$	11.08	This work
$Pb^{2+} + 3\,OH^- \rightleftharpoons [Pb(OH)_4]^{2-}$	13.8	This work
$3\,Pb^{2+} + 4\,OH^- \rightleftharpoons [Pb_3(OH)_4]^{2-}$	32.81	This work
$4\,Pb^{2+} + 4\,OH^- \rightleftharpoons [Pb_4(OH)_4]^{2-}$	34.78	This work
$6\,Pb^{2+} + 8\,OH^- \rightleftharpoons [Pb_6(OH)_8]^{2-}$	67.51	This work
$Pb^{2+} + CO_3^- \rightleftharpoons [PbCO_3]^0$	7.12	This work
$Pb^{2+} + 2CO_3^- \rightleftharpoons [Pb(CO_3)_2]^{2-}$	10.16	This work

Tab. 11.23 Binary ion interaction coefficients for lead species

Ion pair	$\beta^{(0)}$	$\alpha^{(1)}$	$\beta^{(1)}$	C^{γ}	Source
$[Pb(OH)_3]^-$ - Na^+	0.20538	2	0	-0.00663	This work
$[Pb(OH)_3]^-$ - K^+	0.25725	2	0	0.00214	This work

Tab. 11.24 Solubility constants of basic lead-containing compounds

Connection	Reaction	log K	Source
PbO (red) (lithargite)	PbO (red) + $H_2O \rightleftharpoons Pb^{2+} + 2\,OH^-$	-15.09	This work
PbO (yellow) (massicot)	PbO (yellow) +$H_2O \rightleftharpoons Pb^{2+}$ + $2\,OH^-$	-14.93_5	This work
$PbO\cdot Pb(OH)_2$	½ $(PbO\cdot Pb(OH)_2$ +½ $H_2O \rightleftharpoons Pb^{2+}$ + $2\,OH^-$	-14.93_2	This work
Pb(OH)Cl	$Pb(OH)Cl \rightleftharpoons Pb^{2+} + OH^- + Cl^-$	-13.7	This work
$3\,PbO\cdot PbCl_2\cdot H_2O$ (blixite)	$3\,PbO\cdot PbCl_2\cdot H_2O + 2H_2O \rightleftharpoons$ $4\,Pb^{2+} + 6\,OH^- + 2\,Cl^-$	-61.8	Näsänen and Lindell (1978)
$6\,PbO\cdot PbCl_2\cdot 2H_2O$	$6PbO\cdot PbCl_2\cdot 2H_2O + 4H_2O \rightleftharpoons$ $7\,Pb^{2+} + 12\,OH^- + 2\,Cl^-$	-108.7	Edwards et al. (1992)
$PbO\cdot PbSO_4$ (lanarkite)	$PbO\cdot PbSO_4 + H_2O \rightleftharpoons 2\,Pb^{2+}$ + $2\,OH^- + SO_4^{2-}$	-27.49	This work based on Charreton (1956a,b,c)
$3\,PbO\cdot PbSO_4\cdot H_2O$	$3\,PbO\cdot PbSO_4\cdot H_2O + 2\,H_2O \rightleftharpoons$ $4\,Pb^{2+} + 6\,OH^- + SO_4^{2-}$	-63.65	This work based on Charreton (1956a,b,c)
$2\,PbCO_3\cdot PbO\cdot H_2O$ (hydrocerussite)	$2\,PbCO_3\cdot Pb(OH)_2$ $\rightleftharpoons 3\,Pb^{2+} + 2\,CO_3^{2-} + 2\,OH^-$	-46.6	This work
$PbCO_3$ (cerussite)	$PbCO_3 \rightleftharpoons Pb^{2+} + CO_3^{2-}$	-13.60	This work based on Bilinski and Schindler (1982)
$3\,PbCO_3\cdot 2\,PbO\cdot H_2O$ $_2$ (plumbonacrite)	$3PbCO_3\cdot 2PbO\cdot H_2O + H_2O$ $\rightleftharpoons 5\,Pb^{2+} + 3\,CO_3^{2-} + 4\,OH^-$	-78.2	This work based on Taylor and Lopata (1984)
$NaPb_2(CO_3)_2OH$	$NaPb_2(CO_3)_2OH \rightleftharpoons 2\,Pb^{2+} + Na^+$ + $2\,CO_3^{2-} + OH^-$	-32.32	This work based on Auerbach and Pick (1913)
$PbCl_2\cdot PbCO_3$ (phosgenite)	$PbCl_2\cdot PbCO_3 \rightleftharpoons 2\,Pb^{2+} + CO_3^{2-}$ $+ 2\,Cl^-$	-20.64	This work based on Näsänen et al. (1962, 1963)
$Pb_4(SO_4)(CO_3)_2(OH)_2$ (leadhillite)	$Pb_4(SO_4)(CO_3)_2(OH)_2$ $\rightleftharpoons 4\,Pb^{2+} + SO_4^{2-} + 2\,CO_3^{2-}$ + $2\,OH^-$	-54.9	This work based on Abdul-Samad et al. (1982)

12 Auxiliary data

12.1 SIT parameters

The Specific Ion Interaction Theory (SIT) was used to correct experimental equilibrium constants to zero ionic strength. For measurements carried out at constant ionic strength, or more precisely, at constant solution medium, the application of SIT leads to more reliable derivations than the application of the Pitzer formalism. In these measurements, there is usually a high background salt concentration (e.g., $NaClO_4$) that does not change or changes only insignificantly during a series of measurements, while the metal ions or metal complexes of interest occur only in traces. In such solutions, the interactions between the media ions and the dissolved trace compounds can be expressed solely by binary interaction coefficients (BIEDERMANN, 1975; CIAVATTA, 1980):

$$\log\gamma_i = -z_i^2 \frac{A\sqrt{I}}{1+1{,}5\sqrt{I}} + \sum_k \varepsilon(i,k)m_k \qquad (12.1)$$

These are available in large numbers for most relevant cation/anion pairs (CIAVATTA 1980; CIAVATTA 1990, BRETTI et al. 2006). For complexes, they can be derived from the interaction coefficients of the metal core and the ligands. Thus, the interaction coefficient for $[Cd(OH)]^+$ with the media ions Na^+ and ClO_4^-, ($[Cd(OH)]^+$, $NaClO_4$) is obtained from a mathematical relationship of the coefficients (Cd^{2+}, ClO_4^-) and (Na^+, OH^-). Here it is assumed that a 1:1 complex ML interacts with the media ions X and Y in a similar way as the free components of the complex M and L interact with the media ions X and Y:

$$\varepsilon(ML, XY) = \tfrac{1}{2}\left[\varepsilon(M, Y) + \varepsilon(L, X)\right] \qquad (12.2)$$

A similar relationship applies to 1:2 complexes:

$$\varepsilon(ML_2, XY) = \tfrac{1}{3}\left[\varepsilon(M, Y) + 2\,\varepsilon(L, X)\right] \qquad (12.3)$$

For more information, see CIAVATTA (1980, 1990).

For mixed complexes with two different ligands *La* and *Lb* such as $[Pb(CO_3)(OH)]^-$, analogous deductions could be made:

$$\varepsilon(\mathrm{MLaLb},\mathrm{XY}) = \tfrac{1}{3}\left[\varepsilon(\mathrm{M},\mathrm{Y}) + \varepsilon(\mathrm{La},\mathrm{X}) + \varepsilon(\mathrm{Lb},\mathrm{X})\right] \tag{12.4}$$

Analogous derivations are currently not possible for the Pitzer coefficients of complexes. Moreover, experience shows that the properties of trace components in concentrated salt solutions can only be described correctly with the Pitzer approach if the ternary interaction coefficients are known in addition to the binary ones. These are not only missing for the complexes, but also for many important simple ion triples such as Cd^{2+}-Na^{+}-ClO_4^{-} or Cd^{2+}-K^{+}-NO_3^{-}.

The following tables list the SIT parameters used in this work. Most of them are taken from Ciavatta (1980), some were newly determined on the basis of experimental data or, in the case of interactions of complex ions, derived according to Ciavatta (1990).

Tab. 12.1 SIT parameters: Anions in the medium (all data from Ciavatta (1980), unless otherwise indicated)

Cation	**Li^{+}**	**Na^{+}**	**K^{+}**
Cl^{-}		0.03 ± 0.01	
ClO_4^{-}	0.15 ± 0.01	0.01 ± 0.01	
CO_3^{2-}		-0.08± 0.03	0.02 ± 0.01
HCO_3^{-}		0.00 ± 0.03	
NO_3^{-}		-0.04± 0.03	-0.11± 0.04
OH^{-}	-0.04± 0.01	0.04 ± 0.01	0.09 ± 0.01
SO_4^{2-}		-0.18	

Tab. 12.2 SIT parameters: Cations in the medium (all data from Ciavatta (1980), unless otherwise indicated)

Cation	**ClO_4^{-}**	**NO_3^{-}**	**Cl^{-}**	**Source**
Cd^{2+}	0.28 ±* 0.03	0.09**		* This work; data source: Pan and Ni (1968). ** This work; basis: Robinson et al. (1942), Motornaja et al. (1969), Motornaya and Ben'yash (1973)
Pb^{2+}	0.15	-0.34		
Zn^{2+}	0.33	0.16	0.15***	*** This work; mean value from the respective very similar data for Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} (Ciavatta, 1980).

Tab. 12.3 SIT parameters for complexes derived in this work according to CIAVATTA (1990).

Cation	**$NaClO_4$**	**$LiClO_4$**	**KNO_3**	**$NaNO_3$**	**NaCl**
$[CdOH]^+$	0.16	0.12	0.09	0.065	
$[Cd(OH)_2]^0$	0.12				
$[Cd(OH)_4]^{2-}$	0.04				
$[CdCO]_3^0$			0.055		
$[CdHCO]_3^0$	0.14		0.075		
$[ZnOH]^+$	0.185	0.145	0.220	0.195	0.095
$[Zn(OH)_2]^0$	0.137		0.177	0.143	
$[ZnHCO]_3^+$	0.165				0.075
$[Zn(CO_3)_2]^{2-}$	0.057				-0.003
$[PbOH]^+$	0.095		-0.125	-0.15	
$[Pb(OH)_2^0$	0.08	0.055	-0.05		
$[Pb(OH)_3^-$	0.03*				
$[PbCO_3]^0$	0.035		-0.016	-0.210	
$[Pb(CO_3)_2^{2-}$	-0.003		-0.1	-0.17	
$[PbCO_3(OH)]$	0.037				

* Ciavatta (1990)

12.2 Carbonic acid equilibrium and autoprotolysis constant of carbonic acid and water in different media

The equilibrium constants for the carbonic acid equilibrium were taken from WAGMAN et al. (1982) (Tab. 12.4). In addition, some equilibrium constants for electrolyte solutions are used (Tab. 12.5). Tab. 12.6 also contains the autoprotolysis constants for water measured in various media.

Tab. 12.4 Constants used in this work to describe the carbonic acid equilibrium (WAGMAN et al. 1982)

Constant	Reaction	log K^0 I = 0
K_H	$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$	-1.468
K_1	$CO_{2(aq)} + H_2O \rightleftharpoons H^+ + HCO_3^-$	-6.366
K_2	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	-10.330
K_HK_1	$CO_{2(g)} + H_2O \rightleftharpoons H^+ + HCO_3^-$	-7.834

Tab. 12.5 The constant K_HK_1 of the carbonic acid equilibrium in different media

Medium	Concentration [mol/kg]	Value	
I = 0	0	-7.834	WAGMAN et al., 1982
$NaClO_4$	0.3 M	-7.53	BILINSKI and SCHINDLER (1982)
$NaClO_4$	1	-7.55 ± 0.01	CIAVATTA et al. (1981) FERRI et al. (1983) and GRENTHE et al. (1984) (log K = -7.86)
$NaClO_4$	3	-7.80	GIANTS (1969)
$NaClO_4$	3.50 (= 3 M)	-7.88 ± 0.01	NILSSON et al. (1958), FRYDMAN et al. (1958)

Tab. 12.6 Autoprotolysis constant of water in different media

Solution	Concentration [mol/l]	-log Kw (molar)	Source
KNO_3	0.2	13.70 ± 0.02	SCHINDLER et al. (1964)
$LiClO_4$	3	13.87 ± 0.01	KAWAI et al. (1980)
$NaClO_4$	0.1	13.79 ± 0.03	FANGHÄNEL et al. (1996)
$NaClO_4$	0.2	13.70 ± 0.02	SCHINDLER et al. (1964)
$NaClO_4$	1	13.81 ± 0.04	FANGHÄNEL et al. (1996)
$NaClO_4$	2	13.88	FISCHER and BYÉ (1964)
$NaClO_4$	3	14.22	INGRI et al. (1957)
$NaClO_4$	5	14.90 ± 0.06	FANGHÄNEL et al. (1996)

12.3 Determination of the density of salt solutions

From some sources, solution concentrations were only available as molarities. These can be converted into molarities, at least in solutions in which one salt is very predominant and the other solution components are present only in negligible amounts, if suitable conversion functions are available. These were redetermined for a number of salts. In all cases, linear or quadratic functions were sufficient at 25 °C to describe the relationship between molarities c and density (12.5).

$$\rho_{MX}[kg/l] = 0{,}997047 + b_1 c + b_2 c^2 \qquad (12.5)$$

Tab. 12.7 Functions for calculating the density of binary solutions at 25 °C

Solution	b_1	b_2	R	Data source
$NaClO_4$	0.0762	-	0.9983	LOBO (1984)
$LiClO_4$	0.0618	-	0.9999	LOBO (1984)
NaOH	0.0396	-0.006	0.9995	D'ANS and LAX (1967)
KOH	0.0467	-0.007	0.9998	D'ANS and LAX (1967)
KNO_3	0.0597	-	0.9996	LOBO (1984)
Na_2CO_3	0.1084	-0.0097	1.0	HERSHEY et al. (1983)
$NaNO_3$	0.0559	-0.0009	1.0	ISONO (1984)
NaOH	0.0396	-0.0006	0.9995	D'ANS and LAX (1967)
K_2CO_3	0.115	-0.0034	0.9999	MILLERO et al. (1977) GONÇALVES and KESTIN (1981)
$ZnSO_4$	0.1593	-	0.9991	LO SURDO and MILLERO (1980), PUCHALSKA ET AL. (1993)
$ZnSO_4$	0.1589	-0.0030	0.9977	This work for $CaSO_4$ saturated$_4$ $ZnSO_4$ solutions

12.4 Correction terms for converting measured pH to -log c_H at different background salt concentrations [mol/kg].

The literature often contains pH measurements of solutions whose ionic strengths were considerably higher than those of the calibration solutions. The resulting measured pH values deviate more and more from the ‘true pH’ due to the variable transition potential between the internal electrolyte of the reference electrode and the measuring solution. In these cases, it makes more sense to relate the measurement to the concentration of H^+ rather than to the theoretical construct of the single ion activity for H.$^+$ In this case, a concentration value can be calculated. In this case, a concentration-dependent relationship can be established between the measurand ‘pH’ and the H^+ concentration:

$$-\log c_H = pH_{mess} + \Delta_{korr} pH + b_1\, m_S + b_2\, m_S^2 \qquad (12.6)$$

This relationship was investigated by measuring the ‘pH’ in solutions of increasing NaCl concentration but known H^+ concentration. The following table shows the derived parameters.

Tab. 12.8 Correction terms for converting measured pH to -log c_H in NaCl solutions

Solution	**b_1**	**b_2**	**Δ_{korr}pH**	**R**	**Validity range [mol/kg]**	**Data source**
NaCl	0.1539	0.0037	-0.0939	0.9995	0.5 - 5.7	This work

13 Summary

The aim of the project was to develop a consistent thermodynamic database for the pollutants zinc, lead and cadmium, which are particularly strongly represented in industrial chemical-toxic wastes. It should allow modelling in all chemical environments relevant for underground disposal sites. Previous studies had shown that the data found in the literature was in many cases insufficient to produce a complete data set. Furthermore, it had been shown that Zn, Pb and Cd in saline equilibrium solutions no longer occur as free cations, but in the form of chloro complexes. Therefore, the modelling of saturated solution systems containing zinc and cadmium was only possible to a very limited extent or not at all. The aim of the present study was to achieve this goal in two ways: On the one hand, to better describe the complexation of lead, cadmium and zinc with naturally occurring ligands (chloride, sulphate, hydroxide, carbonate), and on the other hand, to establish a consistent data set for the stability of poorly soluble phases, especially oxides, hydroxides and carbonate.

For lead, a thermodynamic model was developed in an earlier work by adding spectroscopic data, in which complex formation was explicitly taken into account. This significantly improved the ability to model the solubility of lead in complex saline solutions. The aim was to also obtain corresponding spectroscopic data for zinc and cadmium as a basis for quantifying complex formation. While the investigation of chloro complex formation of lead succeeded with the help of UV measurements, another method had to be used for the non-UV-active zinc and cadmium species: Raman spectroscopy. It was known from the literature that both the free metal ions and compounds with chloride are Raman-active. With the help of systematic investigations, it had to be clarified how many different chloro complexes are formed and in which ratios they occur depending on the chloride concentration. A new calculation code was developed for this purpose. It contains as an essential element an algorithm for carrying out an *Evolving Factor Analysis* (EFA). This is a procedure to convert complex and strongly superimposed solution spectra into single species spectra without a model and to determine the species concentrations at the same time.

Using EFA, the zinc and cadmium speciation in aqueous solutions of NaCl, KCl, $CaCl_2$, $MgCl_2$ and LiCl were thus quantified. For both cadmium and zinc, only two chloro complexes $[MCl_2]^0$ and $[MCl_4]^{2-}$ could be identified. The compounds $[MCl]^+$ and $[MCl_3]^-$ do not appear to play a significant role, in agreement with independently obtained findings. Based on the speciation data, it was possible to set up a thermodynamic model for both metals that quantitatively describes the chloro complex formation in the solutions of the above-mentioned chlorides. However, difficulties arose in bringing the data determined in this way into agreement with independently obtained investigation results, e.g., potentiometric measurements of activity coefficients. The necessary presence of perchlorate in the solutions of the Raman measurements can be assumed as the cause. Perchlorate serves as an internal standard and is present in concentrations of about 1 - 2 mol/kg. Future work will therefore have to be directed towards taking into account the specific influence of perchlorate. To avoid inconsistencies with other physico-chemical measurement data, a parameter set was therefore developed that can satisfactorily describe the thermodynamic activity of zinc and cadmium in chloride-containing solutions but does not explicitly consider chloro complexation. This was achieved by limiting the applicability to solutions containing less than 2 mol/kg cadmium or zinc. This applies to all known waste solution systems except for a few extreme cases.

Although initially no satisfactory solution could be found to describe the chloro complex formation of zinc and cadmium in perchlorate-free solutions, new solubility measurements and isopiestic investigations contributed considerably to the completion of the experimental data pool. Now sufficient data are available for all relevant ternary systems of the types $(Zn,Cd)Cl_2$-MCl_2 and $(Zn,Cd)SO_4$-MSO_4 (M = Na,K,Mg,Ca,Zn,Cd). In addition, some quaternary systems were also investigated in order to test the applicability of the database to be developed later also in more complex mixed systems. Based on these results and critical evaluated literature data, a consistent thermodynamic data set for zinc and cadmium was developed to describe activity coefficients and solubilities in the system (Na,K,Mg,Ca)-(Zn,Cd)-Cl,SO_4-H_2O for 298.15 K. The agreement of the measured data with modelled values is very good in sulphatic systems.

With the help of EFA, the solution spectra of solutions containing lead chloride determined earlier were re-analysed. This showed that the previous model with five lead species involved (Pb^{2+} and four chloro complexes) is not sufficient to satisfactorily explain the observed solution spectra. A possible interpretation is the formation of a further, fifth complex at very high chloride concentrations (> 6 mol/kg). At least from solid phase investigations, two further complexes are known. Their formation in solution can at least not be excluded. A new parameter set was not created, as it did not represent any significant improvements over previously published ones.

Another focus of the work was on determining stability data for the complexes and poorly soluble compounds of lead, zinc and cadmium that occur particularly in neutral and basic solutions. On the basis of the available literature, a chemical model was first developed that only took into account the complexes and solid phases that were clearly detectable by experiments or without which the experiments cannot be explained otherwise. Thus, zinc and cadmium clearly form only four hydroxo complexes with one to four hydroxide ions per metal cation $[M(OH)_n]^{2-n}$. In the case of lead, there are a maximum of three hydroxide ions. All three metals form two carbonato complexes $[M(CO)_n]^{2-2n}$. Mixed complexes of carbonate and hydroxide or chloride and hydroxide are to be expected but are only really detectable in a few cases and even more rarely necessary to explain the ratios in relevant systems. For some anionic hydroxo and carbonato complexes, ion interaction coefficients could be derived based on solubility measurements. For cationic complexes and most neutral complexes this was not possible due to insufficient data. Additional investigations would be necessary here, especially for neutral and weakly basic but chloride-containing solutions.

In the case of solid phases, it was possible to extract those phases from the very large number of compounds postulated in the literature that can be classified as stable or at least metastable. Particularly in hydroxide-containing systems, solid phases occur in precipitation experiments which, on closer inspection, are either contaminated pure phases of a different composition or mixtures of various stable and metastable phases. For zinc, lead and cadmium, the stable and metastable phases could be identified for hydroxides, carbonates as well as for basic chlorides, sulphates and carbonates and provided with solubility constants.

In its present form, the database derived in this way allows the determination of the activity coefficients and solubility of zinc, lead and cadmium in strongly mineralised acidic to neutral solutions and the modelling of the activity, complex formation and solubility in weakly mineralised solutions in acidic, neutral and basic solutions at 25 °C.

Literature

Editorial remark: The following references are listed as in the original (German) GRS report 219. Russian and Bulgarian names and titles from original Russian or Bulgarian publications were converted to Roman script by using the scientific (linguistic) transliteration system, not one of the more commonly used British or American transliteration systems.

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A Appendix: Additional tables

A.1 Experimentally derived lead speciation (6-species model)

Tab. 13.1 Lead speciation in $CaCl_2$ solutions (6-species model)

No.	Pb [mol/kg]	Ca [mol/kg]	Cl [mol/kg]	Species 1	2	3	4	5	6
				Share [%]					
1	0.0001005	0.00152	0.00349	88.3	11.7				
2	0.0001005	0.0051	0.0106	73.9	26.1				
3	0.0001005	0.0152	0.0316	51.3	48.7				
4	0.0001006	0.0480	0.0972	22.6	68.9	8.5			
5	0.0001007	0.0973	0.1959	8.2	68.1	23.7			
6	0.0001008	0.1408	0.2828	2.5	61.3	35.9	0.3		
7	0.0001010	0.2426	0.4863		42.3	52.6	5.1		
8	0.0001012	0.3376	0.6765		27.9	60.4	11.7		
9	0.0001016	0.4857	0.9726		13.4	62.7	23.9		
10	0.0001018	0.5816	1.1644		7.8	59.7	32.3	0.2	
11	0.0001021	0.6809	1.3629		3.9	55.3	39.5	1.3	
12	0.0001023	0.7828	1.5669			50.7	46.2	3.2	
13	0.0001026	0.8837	1.7686			43.9	50.5	5.5	
14	0.0001029	0.9855	1.9723			37.7	54.0	8.3	
15	0.0001033	1.1436	2.2884			29.3	57.4	13.3	
16	0.0001037	1.2977	2.5966			22.3	57.3	20.4	
17	0.0000781	1.4437	2.8885			16.7	56.7	26.6	
18	0.0000784	1.5984	3.1981			11.8	55.2	33.0	
19	0.0000787	1.7464	3.4939			7.8	52.9	38.6	0.7
20	0.0000791	1.8996	3.8003			4.9	49.4	44.0	1.7
21	0.0000808	2.2553	4.5119			0.4	40.8	53.4	5.3
22	0.0000801	2.3603	4.7218				37.0	55.9	7.1
23	0.0000802	2.3825	4.7663				36.5	56.2	7.3
24	0.0000814	2.8849	5.7710				23.7	60.1	16.2
25	0.0000821	3.1574	6.3161				18.4	59.7	22.0
26	0.0000552	3.3955	6.7921				14.4	58.4	27.2
27	0.0000557	3.7222	7.4456				7.7	58.5	33.8
28	0.0000563	4.0242	8.0496				4.9	55.4	39.7
29	0.0000568	4.3436	8.6885				3.0	50.5	46.6
30	0.0000574	4.6594	9.3201				1.2	47.7	51.1
31	0.0000581	4.9997	10.0006					44.3	55.7
32	0.0000587	5.3101	10.6215					40.6	59.4
33	0.0000601	5.9962	11.9938					37.1	62.9
34	0.0000597	5.8269	11.6551					37.8	62.2
35	0.0000609	6.3403	12.6819					36.1	63.9

Tab. 13.2 Lead speciation in KCl solutions (6-species model)

No.	Pb [mol/kg]	K [mol/kg]	Cl [mol/kg]	Species 1	2	3	4	5	6
				Share [%]					
2	0.0001005	0.00101	0.00141	94.8	5.2				
4	0.0001005	0.00302	0.00343	89.0	11.0				
5	0.0001005	0.0101	0.0105	72.7	27.3				
6	0.0001006	0.0303	0.0315	48.8	51.2				
7	0.0001008	0.1045	0.1057	17.8	70.9	11.3			
8	0.0001012	0.2593	0.2605	2.0	61.2	36.5	0.3		
9	0.0001015	0.3590	0.3602		50.4	47.1	2.5		
10	0.0001020	0.5154	0.5166		34.5	58.1	7.4		
11	0.0001025	0.6747	0.6759		22.5	63.5	14.1		
12	0.0001031	0.8957	0.8969		11.7	63.9	24.4		
13	0.0001036	1.0491	1.0503		7.0	61.0	32.0		
14	0.0001043	1.2700	1.2713		2.6	55.6	40.7	1.2	
15	0.0001050	1.4958	1.4971			48.7	47.9	3.4	
16	0.0001056	1.6750	1.6763			42.6	51.6	5.8	
17	0.0001064	1.9366	1.9379			34.2	55.9	9.9	
18	0.0001071	2.1601	2.1613			28.4	57.4	14.2	
19	0.0001079	2.4076	2.4089			23.0	57.8	19.2	
20	0.0001087	2.6425	2.6441			17.9	58.5	23.6	
21	0.0001093	2.8538	2.8554			14.5	57.9	27.6	
22	0.0001102	3.1096	3.1112			10.6	56.7	32.8	

Tab. 13.3 Lead speciation in $MgCl_2$ solutions (6-species model)

No.	Pb [mol/kg]	Mg [mol/kg]	Cl [mol/kg]	Species 1	2	3	4	5	6
				Share [%]					
1	0.0001005	0.000505	0.00146	93.0	7.0				
2	0.0001005	0.00151	0.00348	88.6	11.4				
3	0.0001005	0.00505	0.0105	73.9	26.1				
4	0.0001005	0.0151	0.0315	51.1	48.9				
5	0.0001007	0.0506	0.1023	21.0	69.7	9.4			
6	0.0001006	0.0940	0.1892	9.6	66.9	23.5			
7	0.0001007	0.1410	0.2832	2.2	61.3	36.1	0.5		
8	0.0001009	0.2344	0.4701		43.3	52.0	4.7		
9	0.0001011	0.3283	0.6579		28.8	60.1	11.1		
10	0.0001014	0.4748	0.9507		13.6	63.1	23.3		
11	0.0001016	0.5695	1.1403		8.3	60.0	31.7	0.0	
12	0.0001018	0.6664	1.3340		3.9	55.9	39.2	1.0	
13	0.0001020	0.7613	1.5239			51.5	45.9	2.6	
14	0.0001022	0.8581	1.7174			44.9	50.4	4.7	
15	0.0001024	0.9538	1.9089			38.5	54.2	7.3	
16	0.0001029	1.0994	2.2001			22.5	59.8	17.7	
17	0.0001031	1.2486	2.4985			22.5	59.8	17.7	
18	0.0000776	1.3964	2.7940			16.9	57.5	25.6	
19	0.0000778	1.5474	3.0959			11.2	56.3	32.4	
20	0.0000781	1.7052	3.4115			7.7	53.3	39.1	
21	0.0000784	1.8449	3.6910			4.5	50.0	44.9	0.7
22	0.0000786	1.9500	3.9013			2.8	47.0	48.7	1.5
23	0.0000790	2.1479	4.2969			0.7	40.6	55.1	3.6
24	0.0000795	2.3769	4.7550				33.5	60.1	6.4
25	0.0000799	2.5961	5.1934				26.9	63.2	9.9
26	0.0000542	2.8233	5.6478				21.3	65.1	13.6
27	0.0000539	3.0039	6.0089				16.1	66.0	17.9
28	0.0000543	3.2802	6.5616				10.6	65.4	24.0
29	0.0000548	3.6043	7.2099				5.0	63.6	31.4
30	0.0000552	3.8670	7.7352				4.2	58.2	37.6
31	0.0000556	4.1330	8.2671				2.2	54.6	43.2
32	0.0000561	4.4340	8.8693				1.0	49.9	49.2
33	0.0000565	4.7154	9.4321					46.7	53.3
34	0.0000570	5.0244	10.0500					42.9	57.1

Tab. 13.4 Lead speciation in NaCl solutions (6-species model)

No.	Pb	Na	Cl	Species 1	2	3	4	5	6
	[mol/kg]	[mol/kg]	[mol/kg]	Share [%]					
1	0.0000352		0.0003	100.0					
2	0.0001005		0.0004	98.4	1.6				
3	0.0003014		0.0008	96.8	3.2				
4	0.0000352	0.00100	0.00127	95.2	4.8				
5	0.0001005	0.00100	0.00140	94.4	5.6				
6	0.0003014	0.00100	0.00180	93.2	6.8				
7	0.0001005	0.00299	0.0034	88.5	11.5				
8	0.0001005	0.0100	0.0104	72.7	27.3				
9	0.0001006	0.0299	0.0311	49.3	50.7				
10	0.0001007	0.1006	0.1018	16.5	72.6	10.9			
11	0.0001009	0.2007	0.2019	5.0	67.3	27.7			
12	0.0001014	0.5080	0.5092		36.7	57.0	6.4		
13	0.0001018	0.7135	0.7148		22.1	63.8	14.1		
14	0.0001024	1.0219	1.0231		9.2	63.0	27.9		
15	0.0001031	1.3394	1.3406		2.1	56.8	40.1	1.0	
16	0.0001037	1.6579	1.6592			47.3	48.8	3.8	
17	0.0001045	2.0839	2.0851			34.7	55.9	9.5	
18	0.0001053	2.4349	2.4361			26.2	58.5	15.3	
19	0.0001060	2.7648	2.7660			19.5	58.0	22.4	
20	0.0001070	3.1961	3.1973			12.7	56.4	30.9	
21	0.0001077	3.5267	3.5279			8.6	53.9	36.7	0.8
22	0.0001085	3.8915	3.8928			5.2	49.9	43.0	1.9
23	0.0001095	4.3486	4.3499			2.2	44.4	49.2	4.2
24	0.0001104	4.7246	4.7259			0.5	39.7	53.2	6.6
25	0.0001112	5.0814	5.0827				34.8	56.1	9.1

A.2 Composition of the solutions examined by Raman spectroscopy

Tab. 13.5 Composition of the investigated solutions containing zinc chloride (I)

No.	$Zn(ClO_4)_2$ [mol/l]	LiCl [mol/l]	Density [g/cm^3]	$Zn(ClO_4)_2$ [mol/l]	NaCl [mol/l]	Density [g/cm^3]
1	1.23387	0	1.23987	1.12238	0.3559	1.23343
2	1.23466	0.28521	1.24579	1.12668	0.8077	1.24510
3	1.24208	0.88464	1.26009	1.12507	1.3739	1.26269
4	1.23944	1.51734	1.26440	1.12059	1.8702	1.27253
5	1.23912	2.13966	1.27372	1.11548	2.4351	1.28188
6	1.24188	2.66596	1.28116	1.12638	2.9977	1.29775
7	1.23976	3.33994	1.28670	1.12858	3.6648	1.30977
8	1.24021	3.91342	1.29602	1.11774	4.1634	1.32409
9	1.24300	4.56688	1.30645	1.10279	4.7972	1.33327
10	1.00596	4.13777	1.25680	1.10137	5.4490	1.34591
11	1.00875	4.59896	1.26516	1.10140	6.0889	1.36574
12	1.00798	5.16631	1.27623	1.09679	6.7941	1.37554
13	0.73454	4.15338	1.21105	1.12345	7.9354	1.39874
14	0.75207	4.63010	1.22624			
15	0.76071	5.11866	1.23751			
16	0.74692	5.61949	1.23575			
17	0.68616	5.37700	1.21660			

Tab. 13.6 Composition of the investigated solutions containing zinc chloride (II)

No.	$Zn(NO_3)_2$ [mol/l]	KCl [mol/l]	Density [g/cm^3]	$Zn(ClO_4)_2$ [mol/l]	$MgCl_2$ [mol/l]	Density [g/cm^3]
1	0.97415	0	1.16893	0.25897	3.95705	1.31458
2	0.97362	0.43042	1.18724	0.83894	3.78517	1.40709
3	0.96869	0.87090	1.20265	0.98903	3.63135	1.43515
4	0.97708	1.37724	1.22279	1.13423	3.49765	1.42576
5	0.97496	1.81906	1.23827	1.11098	3.32909	1.40965
6	0.96205	2.29267	1.25227	1.11068	3.15139	1.39807
7	0.96017	2.74375	1.26653	1.11267	3.01608	1.39372
8	0.95554	3.39548	1.28863	1.11978	2.85252	1.38006
9	0.92893	3.85045	1.30149	1.11308	2.63721	1.36138
10				1.12096	2.49090	1.35934
11				1.11484	2.27943	1.34607
12				1.12486	2.12263	1.34077
13				1.11705	1.91688	1.32809
14				1.11593	1.76077	1.31755
15				1.11494	1.58468	1.30767
16				1.11438	1.39993	1.30225
17				1.11723	1.23114	1.28690
18				1.11866	1.04423	1.27878
19				1.11886	0.87299	1.26977
20				1.11949	0.68658	1.26261
21				1.11662	0.49385	1.25177
22				1.11951	0.35163	1.24338
23				1.11876	0.16067	1.23027

Tab. 13.7 Composition of the investigated solutions containing zinc chloride (III)

No.	$Zn(ClO_4)_2$ [mol/l]	$CaCl_2$ [mol/l]	Density [g/cm]^3
1	1.11083	3.94961	1.49647
2	1.10028	3.46166	1.45458
3	1.09418	3.04869	1.42885
4	1.09816	2.55579	1.38925
5	1.09448	2.10167	1.35501
6	1.09599	1.65987	1.32676
7	1.09485	1.18294	1.29629
8	1.09112	0.70324	1.25972
9	1.09228	0.38576	1.24200

Tab. 13.8 Composition of the investigated solutions containing cadmium chloride (I)

No.	$Cd(ClO_4)_2$ [mol/l]	LiCl [mol/l]	Density [g/cm^3]	$Cd(ClO_4)_2$ [mol/l]	NaCl [mol/l]	Density [g/cm^3]
1	0.9985	0.0000	1.2321	1.0544	0.0000	1.2456
2	1.0008	0.3001	1.2356	1.0603	0.3258	1.2566
3	0.9966	0.9441	1.2424	1.0623	0.7477	1.2740
4	1.0011	1.6498	1.2592	1.0586	1.2451	1.2906
5	1.0124	2.3604	1.2864	1.0615	1.6830	1.3047
6	0.9980	3.0864	1.2962	1.0581	2.1722	1.3233
7	0.9927	3.8050	1.3057	1.0590	2.6106	1.3391
8	1.0234	4.5395	1.3240	1.0580	3.0909	1.3531
9	0.7601	3.8689	1.2511	1.0614	3.4531	1.3735
10	0.7566	4.4211	1.2633	1.0464	3.9356	1.3784
11	0.7611	4.9182	1.2728	1.0013	3.9873	1.3670
12	0.8874	5.2385	1.3071	0.2340	2.8308	1.1581
13	0.7526	5.0274	1.2674	0.2309	3.4760	1.1779
14	0.7548	5.4784	1.2798	0.2291	3.9295	1.2010
15	0.7521	6.2748	1.2933	0.2249	4.3547	1.2125

Tab. 13.9 Composition of the investigated solutions containing cadmium chloride (II)

No.	$Cd(ClO_4)_2$ [mol/l]	$MgCl_2$ [mol/l]	Density [g/cm^3]	$Cd(ClO_4)_2$ [mol/l]	$CaCl_2$ [mol/l]	Density [g/cm^3]
1	0.3340	3.7859	1.3312	1.0118	0.2871	1.2550
2	0.8563	3.4607	1.4352	1.0175	0.7395	1.2938
3	0.9527	3.4125	1.4416	1.0115	1.2044	1.3276
4	1.0196	3.3328	1.4476	1.0107	1.6633	1.3636
5	1.0200	3.1677	1.4384	1.0111	2.1277	1.3988
6	1.0194	3.0065	1.4313	1.0107	2.5161	1.4297
7	1.0325	2.8666	1.4249	1.0134	2.9891	1.4645
8	1.0247	2.6407	1.4042	1.0100	3.4516	1.4974
9	1.0438	2.4721	1.3991	1.0073	3.8884	1.5281
10	1.0473	2.2710	1.3873			
11	1.0323	2.1199	1.3736			
12	1.0335	1.9117	1.3637			
13	1.0345	1.7717	1.3545			
14	1.0344	1.6099	1.3445			
15	1.0356	1.4136	1.3332			
16	1.0313	1.2641	1.3229			
17	1.0368	1.0652	1.3131			
18	1.0375	0.8542	1.2994			
19	1.0382	0.6881	1.2850			
20	1.0398	0.5077	1.2728			
21	1.0385	0.3749	1.2656			
22	1.0411	0.1584	1.2545			
23	0.2436	3.8015	1.3106			
24	0.2368	3.0058	1.2575			
25	0.2628	2.3206	1.2124			
26	0	2.2631	1.1599			

Tab. 13.10 Composition of the examined LiCl solutions

No.	LiCl [mol/l]	$NaClO_4$ [mol/l]	Density [g/cm^3]
1	0.98797	0.045234	1.03148
2	2.13305	0.041437	1.05086
3	2.72753	0.041792	1.06315
4	3.94197	0.041617	1.08889
5	5.03633	0.040845	1.12645
6	5.90493	0.041135	1.13209
7	7.16679	0.040805	1.15404
8	7.97783	0.042462	1.17478
9	10.58269	0.041282	1.23560

Tab. 13.11 Zinc speciation in LiCl solutions

No.	$Zn(ClO_4)_2$ [mol/l]	LiCl [mol/l]	Cl^- (free) [mol/l]	Zn^{2+} [%]	$[ZnCl_2]^0$ [%]	$[ZnCl_4]^{2-}$ [%]
1	1.23387	0	0	99.9	0.1	0
2	1.23466	0.28521				
3	1.24208	0.88464	0.781	92.5	7.5	0
4	1.23944	1.51734	1.257	83.0	17.0	0
5	1.23912	2.13966	1.747	74.0	26.0	0
6	1.24188	2.66596	1.756	62.1	27.8	10.1
7	1.23976	3.33994	1.529	42.6	30.4	26.9
8	1.24021	3.91342	1.954	36.9	31.7	31.4
9	1.24300	4.56688	1.522	14.8	26.3	58.8
10	1.00596	4.13777				
11	1.00875	4.59896	1.261	0	22.3	77.7
12	1.00798	5.16631	1.712	0	10.9	89.1
13	0.73454	4.15338	1.719	0.8	14.0	85.1
14	0.75207	4.63010	2.151	0	11.0	89.0
15	0.76071	5.11866	2.559	0	1.4	98.6
16	0.74692	5.61949	3.289	0	0	100
17	0.68616	5.37700	3.261	0	0	100

Tab. 13.12 Zinc speciation in NaCl solutions

No.	$Zn(ClO_4)_2$ [mol/l]	NaCl [mol/l]	Cl^- (free) [mol/l]	Zn^{2+} [%]	$[ZnCl_2]^0$ [%]	$[ZnCl_4]^{2-}$ [%]
1	1.12238	0.3559	0.323	98.6	1.4	0.0
2	1.12668	0.8077	0.665	94.3	5.7	0.0
3	1.12507	1.3739	1.085	88.5	11.5	0.0
4	1.12059	1.8702	1.420	82.3	17.7	0.0
5	1.11548	2.4351	1.829	76.5	23.5	0.0
6	1.12638	2.9977	1.625	60.7	26.7	12.6
7	1.12858	3.6648	1.690	49.0	29.2	21.9
8	1.11774	4.1634	2.091	46.9	29.4	23.6
9	1.10279	4.7972	1.445	23.3	29.8	46.9
10	1.10137	5.4490	1.505	12.5	31.7	55.8
11	1.10140	6.0889	1.274	0	26.8	73.2
12	1.09679	6.7941	1.641	0	17.5	82.5
13	1.12345	7.9354	1.965	0	0	100

Tab. 13.13 Zinc speciation in $CaCl_2$ solutions

No.	$Zn(ClO_4)_2$ [mol/l]	$CaCl_2$ [mol/l]	Cl^- (free) [mol/l]	Zn^{2+} [%]	$[ZnCl_2]^0$ [%]	$[ZnCl_4]^{2-}$ [%]
1	1.11083	3.94961	4.520	0	0	100
2	1.10028	3.46166	3.235	0	0	100
3	1.09418	3.04869	2.186	0	1.42	98.58
4	1.09816	2.55579	1.174	2.44	5.98	91.58
5	1.09448	2.10167	1.102	19.33	11.23	69.44
6	1.09599	1.65987	1.197	41.06	12.99	45.95
7	1.09485	1.18294	1.248	65.23	11.42	23.35
8	1.09112	0.70324	1.076	86.09	7.42	6.48
9	1.09228	0.38576	0.745	96.12	3.51	0.37

Tab. 13.14 Element and species concentration in the test solutions of the systems $Cd(ClO_4)_2$- NaCl - H_2O and $Cd(ClO_4)_2$-LiCl - H_2O

No.	Designation	Density	Cd^{2+}	Na^+	Li^+	ClO_4^-	Cl^-	Cd^{2+}	$[CdCl_2]^0$	$[CdCl_4]^{2-}$
		[g/cm³]	[mol/l]					Share [%]		
1	CdNaCl12	1.24562	1.054	0	0	2.109	0	100.0	0	0
2	CdNaCl1	1.25660	1.060	0.326	0	2.121	0.326	87.9	12.1	0
3	CdNaCl2	1.27404	1.062	0.748	0	2.125	0.748	70.4	29.6	0
4	CdNaCl3	1.29058	1.059	1.245	0	2.117	1.245	51.7	48.0	0.2
5	CdNaCl4	1.30465	1.062	1.683	0	2.123	1.683	38.9	59.4	1.7
6	CdNaCl5	1.32329	1.058	2.172	0	2.116	2.172	27.3	67.6	5.1
7	CdNaCl6	1.33905	1.059	2.611	0	2.118	2.611	19.6	70.8	9.7
8	CdNaCl7	1.35309	1.058	3.091	0	2.116	3.091	14.0	69.0	17.0
9	CdNaCl8	1.37354	1.061	3.453	0	2.123	3.453	10.0	67.1	22.9
10	CdNaCl9	1.37835	1.046	3.936	0	2.093	3.936	0	65.0	35.0
11	CdNaCl10	1.36699	1.001	3.987	0	2.003	3.987	0	61.2	38.8
12	CdNaCl11	1.35040	0.913	4.095	0	1.826	4.095	0	54.1	45.9
13	CdLiCl1	1.23214	0.998	0	0	1.997	0	100.0	0	0
14	CdLiCl2	1.23560	1.008	0	0.301	2.016	0.301	85.3	14.7	0
15	CdLiCl3	1.24244	0.997	0	0.944	1.993	0.944	59.7	40.1	0.2
16	CdLiCl4	1.25922	1.001	0	1.650	2.002	1.650	35.3	62.4	2.3
17	CdLiCl5	1.28638	1.012	0	2.360	2.025	2.360	18.0	73.5	8.5
18	CdLiCl6	1.29620	0.998	0	3.086	1.996	3.086	6.7	70.8	22.5
19	CdLiCl7	1.30570	0.993	0	3.805	1.985	3.805	0	59.0	41.0
20	CdLiCl8	1.32402	1.023	0	4.540	2.047	4.540	0	43.2	56.8
21	CdLiCl9	1.25109	0.760	0	3.869	1.520	3.869	0	45.4	54.6
22	CdLiCl10	1.26329	0.757	0	4.421	1.513	4.421	0	27.9	72.1
23	CdLiCl11	1.27275	0.761	0	4.918	1.522	4.918	0	17.0	83.0
24	CdLiCl12	1.30710	0.887	0	5.238	1.775	5.238	0	17.9	82.1
25	CdLiCl13	1.26736	0.753	0	5.027	1.505	5.027	0	13.2	86.8
26	CdLiCl14	1.27982	0.755	0	5.478	1.510	5.478	0	9.0	91.0
27	CdLiCl15	1.29328	0.752	0	6.275	1.504	6.275	0	4.2	95.8

Tab. 13.15 Experimental solubilities in the system $ZnCl_2$ - NaCl - H_2O (previously unpublished data by POPOV 1989)

$ZnCl_2$ mol/kg	NaCl mol/kg	Phase
0	6.16	NaCl
1.15	6.56	NaCl
2.72	7.37	NaCl
2.93	7.27	NaCl
4.27	8.15	NaCl
5.21	8.85	NaCl
6.08	9.75	NaCl
6.93	10.36	NaCl
6.93	10.36	$ZnCl_2 \cdot 2\,NaCl \cdot 3\,H_2O$
7.47	9.28	$ZnCl_2 \cdot 2\,NaCl \cdot 3\,H_2O$
7.96	8.25	$ZnCl_2 \cdot 2\,NaCl \cdot 3\,H_2O$
8.66	7.06	$ZnCl_2 \cdot 2\,NaCl \cdot 3\,H_2O$
9.35	5.76	$ZnCl_2 \cdot 2\,NaCl \cdot 3\,H_2O$
11.48	4.27	$ZnCl_2 \cdot 2\,NaCl \cdot 3\,H_2O$
15.57	3.23	$ZnCl_2 \cdot 2\,NaCl \cdot 3\,H_2O$
18.06	2.85	$ZnCl_2 \cdot 2\,NaCl \cdot 3\,H_2O$
18.06	2.85	$2\,ZnCl_2 \cdot 3\,H_2O$*
18.25	2.29	$2\,ZnCl_2 \cdot 3\,H_2O$*
18.62	1.54	$2\,ZnCl_2 \cdot 3\,H_2O$*
20.97	0.43	$2\,ZnCl_2 \cdot 3\,H_2O$*
24.25	0.31	$2\,ZnCl_2 \cdot 3\,H_2O$*
29.96	0	$2\,ZnCl_2 \cdot 3\,H_2O$

* According to information from A. V. Rumyantsev, the supervisor of this work, it was not so much $2ZnCl_2 \cdot 3H_2O$, but probably an unidentified double salt, since the solid phases had high proportions of NaCl.

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