

Solubility equilibria in multicomponent oceanic salt systems from $t = 0$ to $200\text{ }^{\circ}\text{C}$. Model parameterization and databases^{*,†}

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Abstract: In this paper the application of Pitzer's equations for modeling of solubility equilibria in the hexary oceanic salt system Na^+ , K^+ , Mg^{2+} , Ca^{2+} // Cl^- , SO_4^{2-} - H_2O and its subsystems over large temperature intervals is discussed. Lack of ternary solution data considerably restricts the use of the equations as an evaluation tool for the quality of solubility data. Models optimized for the available data in two temperature intervals have been derived. Since Pitzer's model gives no guidance for temperature dependence, the number of parameters is dominated by temperature coefficients. Thus, for extended temperature intervals other approaches like the Cohen-Adad formalism can be advantageous in solubility data evaluation.

INTRODUCTION

Major components of sea water comprise the ions Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} forming a hexary aqueous system. Evaporation yields a crystallization sequence of various simple salts, salt hydrates, double salts, and salt phases of higher complexity (see Table 1). Knowledge of the temperature–pressure–composition ranges where the phases can exist or co-exist is essential for technology, geochemistry, and environmental assessment procedures.

Beginning with van't Hoff [1,2], continued by D'Ans [3], Autenrieth [4–6], Braitsch [7], Emons [8–10] and the Russian school of Kurnakov [11–14], Lepeshkov [15–18], Zdanovskii [19] we look back on nearly 100 years of continuous solubility investigations within the hexary oceanic salt system. Thereby, methods for graphical representation of solubility equilibria in multicomponent systems had been developed and used as guidelines for new experiments.

Whereas in the first decades the investigations were focused on improvements in potash recovery, in recent years other fields became important, like waste management, back fill of old salt mines, natural oil recovering and storage, chemistry of salt lakes, etc. Modern process control technology and simulation of solution processes in natural environments require models where phase equilibria can be quantitatively described over the entire range of composition, temperature, and pressure.

The development of the ion interaction equations by Pitzer and coworkers [20,21] provided a practical framework for a thermodynamic treatment of multicomponent electrolyte solutions with high ionic strengths. The latter aspect is especially important for solutions saturated in respect to salts like NaCl , KCl , MgCl_2 , or CaCl_2 , where ionic strengths vary typically between 5 and 30 mol/kg H_2O . Much effort was put into establishing sets of so-called Pitzer coefficients and compatible solubility constants for a variety of electrolyte systems, including oceanic salts [22,23].

*Lecture presented at the 9th IUPAC International Symposium on Solubility Phenomena (9th ISSP), Hammamet, Tunisia, 25–28 July 2000. Other presentations are published in this issue, pp. 761–844.

†Dedicated to Prof. Dr. Dr. h.c. mult. H.-H. Emons on the occasion of his 70th birthday.

Table 1 Important stable crystallizing salts in the hexary oceanic salt system.

Halite	NaCl	Kainite	4KCl·4MgSO ₄ ·11H ₂ O
Sylvite	KCl	Glaserite	3K ₂ SO ₄ ·Na ₂ SO ₄
Bischofite	MgCl ₂ ·6H ₂ O	Bloedite	Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O
Mirabillite	Na ₂ SO ₄ ·10H ₂ O	Loeweite	6Na ₂ SO ₄ ·7MgSO ₄ ·15H ₂ O
Thenardite	Na ₂ SO ₄	Vanthoffite	3Na ₂ SO ₄ ·MgSO ₄
Arcanite	K ₂ SO ₄	Picromerite	K ₂ SO ₄ ·MgSO ₄ ·6H ₂ O
Epsomite	MgSO ₄ ·7H ₂ O	Leonite	K ₂ SO ₄ ·MgSO ₄ ·4H ₂ O
Hexahydrate	MgSO ₄ ·6H ₂ O	Langbeinite	K ₂ SO ₄ ·2MgSO ₄
Kieserite	MgSO ₄ ·H ₂ O	Glauberite	Na ₂ SO ₄ ·CaSO ₄
Gypsum	CaSO ₄ ·2H ₂ O	Syngenite	K ₂ SO ₄ ·CaSO ₄ ·H ₂ O
Anhydrite	CaSO ₄	Pentasalt	K ₂ SO ₄ ·5CaSO ₄ ·H ₂ O
Carnallite	KCl·MgCl ₂ ·6H ₂ O	Polyhalite	K ₂ SO ₄ ·MgSO ₄ ·2CaSO ₄ ·2H ₂ O
D'Ansite	3NaCl·9Na ₂ SO ₄ ·MgSO ₄		

This paper emphasizes the application of the Pitzer approach in interpolation, prediction, and evaluation of solubility data in systems of the major components of oceanic salts at various temperature ranges. An alternative method to model solubilities in multicomponent systems will be discussed in comparison with Pitzer's equations.

PITZER MODELS FOR OCEANIC SALT SYSTEMS

One of the large milestones is the work of Harvie, Weare, and Eugster [24–26], in which all solubility equilibria of the hexary oceanic salt system were calculated and compared with existing data at $t = 25\text{ }^{\circ}\text{C}$. Later the model was expanded to include CO_2 , CO_3^{2-} , H^+ , and OH^- [27]. The parameter set given in [27] is considered as a standard for modeling of evaporitic deposits in geochemistry today. A less satisfactory situation is met at temperatures other than $25\text{ }^{\circ}\text{C}$. Pabalan and Pitzer [28] were the first to have derived a temperature-dependent set of ion interaction parameters from 0 to $250\text{ }^{\circ}\text{C}$. Available activity, enthalpy, and heat capacity data of solutions were exploited to obtain interaction coefficients. Examples in the systems $\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$ and $\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$ showed that with the model's formalism the solubility of simple salts, salt hydrates, and double salts can be described up to high temperatures and concentrations. For NaCl and $\text{MgSO}_4\cdot\text{H}_2\text{O}$ the authors demonstrated that solubility is predicted correctly at high temperatures using only C_p values of the solid, one solubility data point at $25\text{ }^{\circ}\text{C}$ and the temperature functions of the ion interaction coefficients. However, the intention of the authors in [15] was not to derive a complete solubility model of the oceanic salt system, and thus, double salts other than carnallite were not considered and no extensive evaluation of data of multicomponent systems had been performed. Such work was done by Möller [29] and Greenberg, Möller [30] for the systems Na^+ , $\text{Ca}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-}\text{-H}_2\text{O}$, and Na^+ , K^+ , $\text{Ca}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-}\text{-H}_2\text{O}$ from 0 to $250\text{ }^{\circ}\text{C}$. Unlike Pabalan and Pitzer, Möller and Greenberg did not use C_p data of solid phases to fix the temperature dependence of solubility constants. For the representation of the temperature functions of Pitzer parameters and solubility constants up to seven coefficients per parameter had been used, often not covering the entire range of temperature.

Within a more limited range of temperature (mostly $50\text{--}140\text{ }^{\circ}\text{C}$) Ziegenbalg and Petrenko [31,32] derived a Pitzer model for the quinary system Na^+ , K^+ , $\text{Mg}^{2+} // \text{Cl}^-$, $\text{SO}_4^{2-}\text{-H}_2\text{O}$. At $t = 90\text{ }^{\circ}\text{C}$ predicted invariant compositions agreed reasonably with new experimental data cited in their paper.

Low-temperature Pitzer models down to $-60\text{ }^{\circ}\text{C}$ have been developed by Spencer [33] and modified by Marion [34] for the hexary oceanic system. Thereby, the dielectric constant of water had to be treated as an adjustable parameter, because reliable values below $-30\text{ }^{\circ}\text{C}$ are not available.

On the basis of partial molal volumes Monnin [35] used the Pitzer equations to describe the pressure dependence of the calcium sulfate solubility up to 1 kbar and 200 °C in solutions of sodium chloride. Recently, the treatment was extended to SrSO₄ and BaSO₄ within the hexary oceanic system [36].

FITTING PROCEDURES FOR THE PITZER MODEL

The equations of the model have been described many times [20–30,37]. Adjustable parameters are the virial coefficients $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ (for 2-2 and electrolytes of higher valency) and C_{ca}^ϕ describing interactions between cation c and anion a in binary system solutions and $\theta_{cc'}$, $\theta_{aa'}$, $\psi_{cc'a}$, and $\psi_{aa'c}$ for the ternary solutions. In general, all parameters are temperature-dependent. The ideal fitting scheme for parameter estimation is pointed out in Fig. 1. It consists of a determination of the coefficients $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$, C_{ca}^ϕ from the concentration dependence of activity data (including enthalpies, heat capacities) in unsaturated binary systems at temperatures of interest and concentrations reaching solubility limits as near as possible. The resulting thermodynamic solution model is then used to calculate thermodynamic solubility constants of simple salts or salt hydrates from solubility data in binary systems. For multicomponent systems parameters $\theta_{cc'}$, $\theta_{aa'}$, $\psi_{cc'a}$, and $\psi_{caa'}$ have to be determined from activity data of unsaturated solutions of all ternary salt(1)-salt(2)-water subsystems. From the complete solution model then the remaining solubility constants of double or triple salts can be calculated from solubility data in ternary or higher component systems. Despite several new series of isopiestic [38–44] and enthalpic [45–51] measurements in unsaturated solutions the modeler is mostly forced to leave the ideal scheme because of missing data, especially for ternary solutions. In these cases solubility data itself represent the most important source of solute activities, if simple salts crystallize and their thermodynamic solubility constants are known as shown in Fig. 2a. For solubility diagrams dominated by large crystallization branches of double salts (Fig. 2b) mixing parameters and solubility constants have to be fitted simultaneously. Thus, solubility constants get more or less the character of an adjustable parameter. Other reasons giving rise to further compromises and specific routes in the model development are varying accuracy of data in different subsystems, missing binary system data in certain temperature intervals, and unequal distribution of available data with respect to composition, temperature,

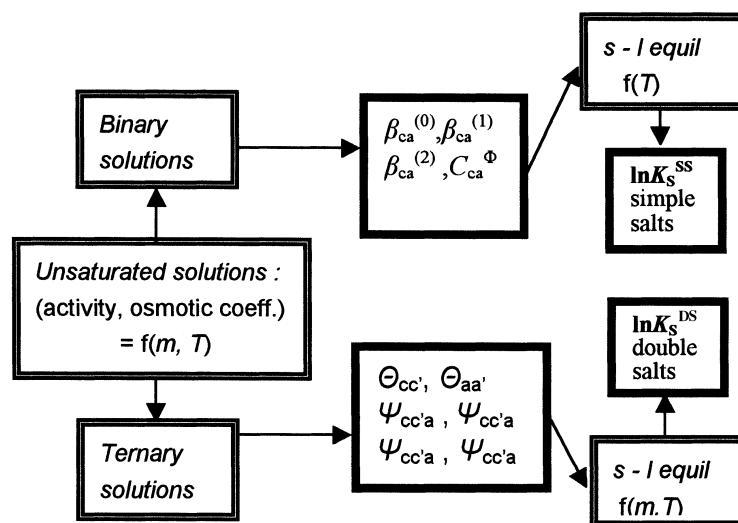


Fig. 1 Ideal fitting scheme for Pitzer model.

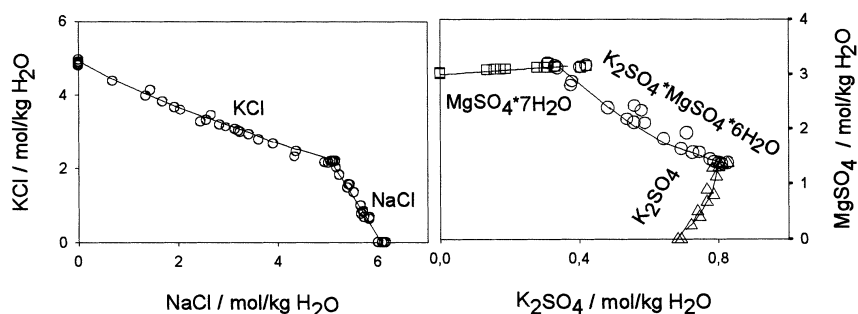


Fig. 2 Typical solubility isotherms with simple and double salt branches: a) system NaCl–KCl–H₂O, $t = 25$ °C; b) system K₂SO₄–MgSO₄–H₂O, $t = 25$ °C.

and subsystems. The situation becomes even more complicated in the case of solid solution formation (for instance, in Na₂SO₄–K₂SO₄–H₂O at $t > 50$ °C). All these aspects apply to the hexary oceanic salt system. Consequently, the fitting procedure and the resulting parameter set depend on the purpose of the model development.

HIGH-TEMPERATURE MODEL OF THE HEXARY SYSTEM

At temperatures above 120 °C solubility data of MgSO₄– and CaSO₄– containing systems of oceanic salts are sparse or absent. The construction of complete solubility diagrams and the evaluation of phase stabilities for minerals like polyhalite, löweite, or syngenite in multicomponent solutions is not possible. Therefore, the Pitzer approach was used to combine available data with our own solubility determinations in the systems Na₂SO₄–MgSO₄–H₂O, K₂SO₄–MgSO₄–H₂O and KCl–K₂SO₄–H₂O at 150 and 200 °C [52] as well as preliminary data in the K₂SO₄–MgSO₄–CaSO₄–H₂O system [53] to develop a robust model for interpolation and extrapolation of solubilities. From the work of Greenberg and Möller [29,30] it follows that over extended temperature ranges the largest number of parameters results from temperature coefficients. Therefore, we tried to keep temperature functions as simple as possible. For double salts the number of unknown temperature coefficients of solubility constants can be reduced (mostly to one), if a thermodynamic cycle is applied as shown for langbeinite in Fig. 3.

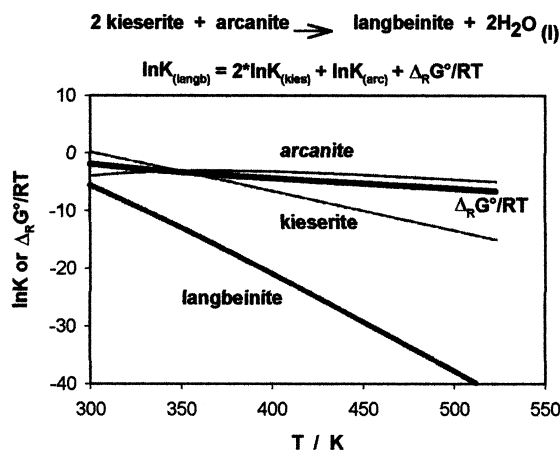


Fig. 3 Temperature dependence of solubility constants of simple salts, double salts, and reaction term ($\Delta_R G^0/RT$).

In this way, $\ln K_S^{DS}$ of the double salt (DS) is composed of $\ln K_S^{SS}$ of the simple salts (SS) and a solid-state reaction term ($\Delta_R G^\circ/RT$). The latter is usually small and often can be considered as constant or as a linear function of T . By this method the temperature functions of $\ln K_S$ of langbeinite, syngenite, pentasalt, and polyhalite were fixed, and ternary Pitzer coefficients could be derived from a small number of solubility data [52]. Selected results of model calculations are shown in Figs. 4 and 5. The variation of kieserite solubility in $MgCl_2$ solutions at $t=140$ and 200 °C is shown in Fig. 4.

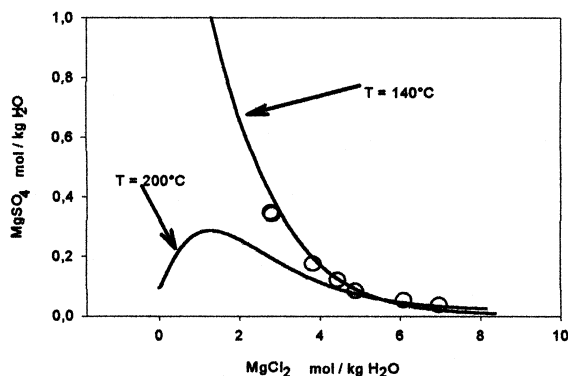


Fig. 4 Solubility isotherm of kieserite in the system $MgCl_2$ - $MgSO_4$ - H_2O ; — calculated ○ experimental data.

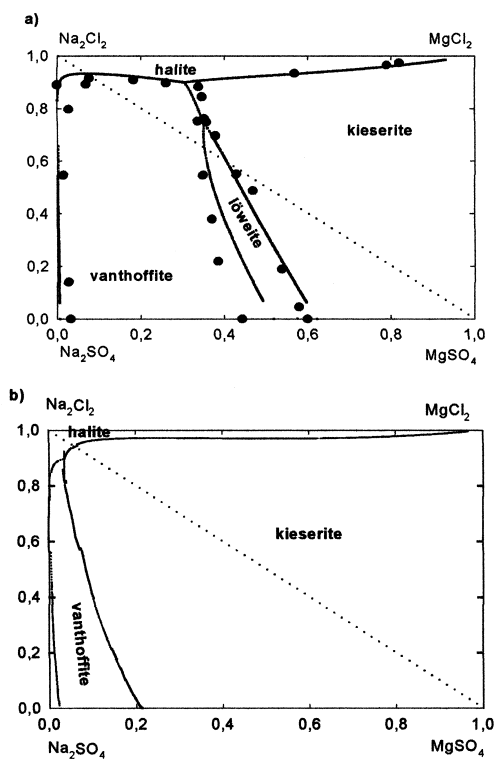


Fig. 5 Jänecke diagram of the system Na^+ , Mg^{2+}/Cl^- , SO_4^{2-} - H_2O ; a) $t = 150$ °C; b) $t = 200$ °C; Mole fraction scale; ● experimental data — calculated diagonal section line.

At high temperatures $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ behaves like a sparingly soluble salt as can be seen for the curve at $t = 200^\circ\text{C}$. For the reciprocal system $\text{Na}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$ a calculated phase diagram in Jänecke coordinates is compared with available data at $t = 150^\circ\text{C}$. Reasonable agreement can be stated (Fig. 5a). Figure 5b gives a prediction of the phase equilibria at 200°C in this system.

The calculation suggests that at these high temperatures (Fig. 5b) kieserite can co-exist with halite, which is not possible at lower temperatures (Fig. 5a). Similar calculations using the model for the hexary system predict instability of the mineral polyhalite in contact with halite saturated solutions at $t > 160^\circ\text{C}$ [63].

AMBIENT TEMPERATURE MODEL OF THE QUINARY SYSTEM $\text{Na}^+, \text{K}^+, \text{Mg}^{2+} // \text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$

In contrast to the situation at $t > 120^\circ\text{C}$, there are thousands of solubility data between 0 and 120°C . However, especially for sulfates, data are quite scattered and a number of contradictions exists for data sets from different authors. One aim of this model development was to apply Pitzer's equations as an evaluation tool for data quality. Thus, a fitting procedure was chosen, which follows as close as possible the ideal scheme described above. In particular, an attempt was made to avoid the usual fitting of Pitzer's mixing coefficients and solubility constants. From a database of about 6000 solubility data in ternary systems most of the mixing coefficients and solubility constants of double salts have been estimated between 0 and 120°C . As far as possible at $t = 25^\circ\text{C}$ the temperature functions of parameters and solubility constants were fixed at the values given by Harvie, Möller, and Weare [27]. Maximum CaCl_2 concentration was limited to $4 \text{ mol/kg H}_2\text{O}$. For more detailed informations and explanations the reader is referred to [54]. Deviation plots for the activity products of all minerals in all systems (more than 15 000 data points) showed general agreement with the model. In Figs. 6–8 typical plots are pre-

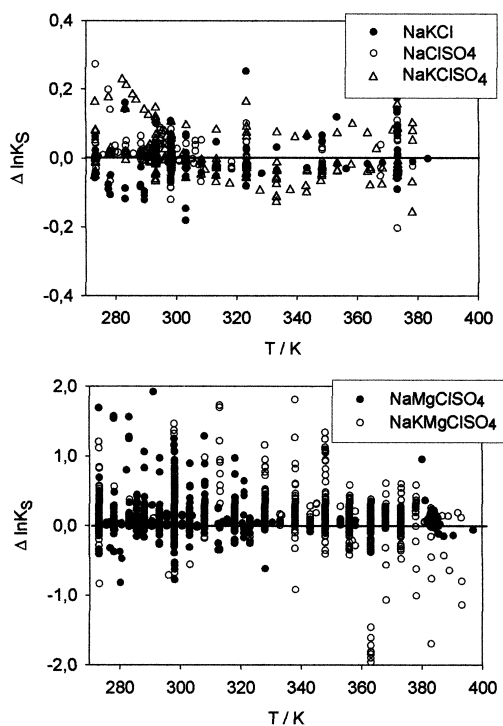


Fig. 6 Deviation plots of solubility products for halite in different systems.

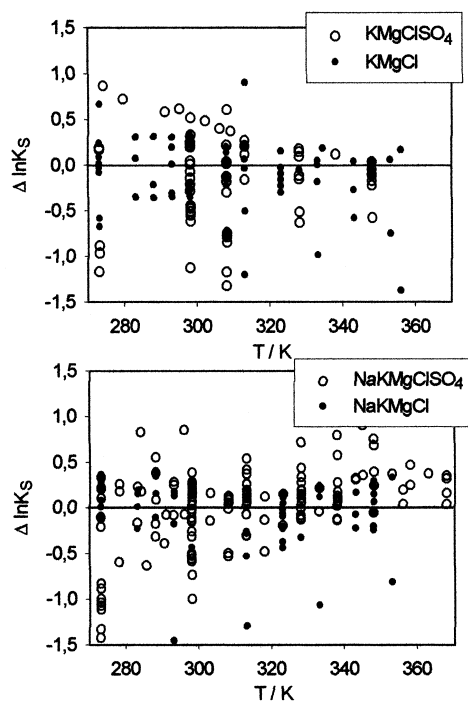


Fig. 7 Deviation plots of the solubility products of carnallite in different systems.

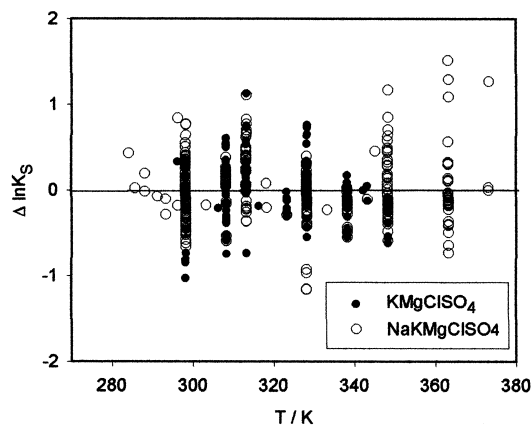


Fig. 8 Deviation plots of solubility products of kainite in different systems.

sented for halite, carnallite, and kainite. However, the work with Pitzer's model revealed some problems. One problem is connected with the deficiency of activity data in unsaturated ternary solutions. Most of the mixing coefficients had to be derived from solubilities. Solubility data itself are not equally distributed along the temperature scale. This is demonstrated for the ternary sulfate systems in Fig. 9. Only solubilities of simple salts or hydrates are suited for mixing parameter estimations. But

from the statistics in Fig. 9 the large portion of double salt data points can be recognized. Difficulties arising from avoiding simultaneous fitting of the mixing parameter $\Psi_{cc'a}$ and $\ln K_S$ of a double salt are demonstrated at the example of the system $\text{KCl}-\text{MgCl}_2-\text{H}_2\text{O}$. Figure 10 shows a section of some solubility isotherms in this system. At first, only experimental points located on the crystallization branches of the simple salts KCl and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were used for the estimation of Ψ_{KMgCl} . The model was then used to calculate the solubility constant of carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, along the crystallization branch of carnallite. The thin lines in Fig. 10 give the results of this fit. At low temperatures ($t \leq 40^\circ\text{C}$) the experimental points are reproduced, but between 40 and 100°C systematic differences appear. The correct composition of the co-existence points of sylvite/carnallite is not predicted. Repeating the fitting procedure and including simultaneous adjusting of Ψ_{KMgCl} and $\ln K_{S(\text{carnallite})}$ of course improves the fit as can be seen from the heavy lines in Fig. 10. However, this prevents the use of the equations for evaluation of data quality of the carnallite isotherms or the location of the 2-salt points sylvite/carnallite.

Nevertheless, the derived model represents a first useful description of the quinary system in the given temperature interval. As an example for the description of multiphase equilibria the calculated solution compositions for the important paragenesis Q (halite, sylvite, carnallite, kainite) are compared with results from other data compilations in Fig. 11. Whereas general coincidence of data can be stat-

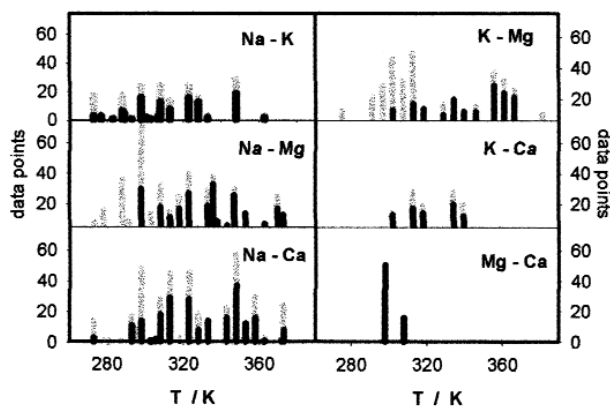


Fig. 9 Distribution of solubility data in ternary sulfate systems. — Simple salts crystallizing — double salts crystallizing.

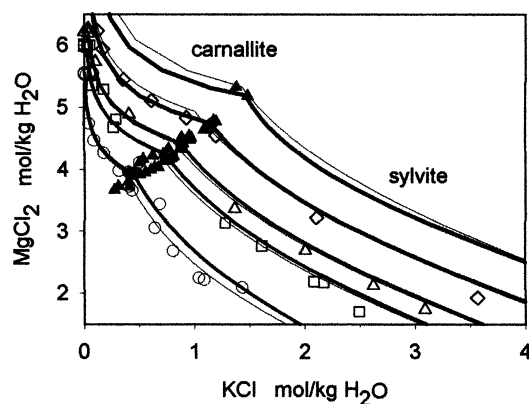


Fig. 10 Sections of solubility isotherms in the system $\text{KCl}-\text{MgCl}_2-\text{H}_2\text{O}$, temperatures from bottom to top: 0°C , 35°C , 50°C , 75°C , 100°C ; filled triangles: 2-salt points carnallite/sylvite; thin lines: [62], heavy lines: new model [54].

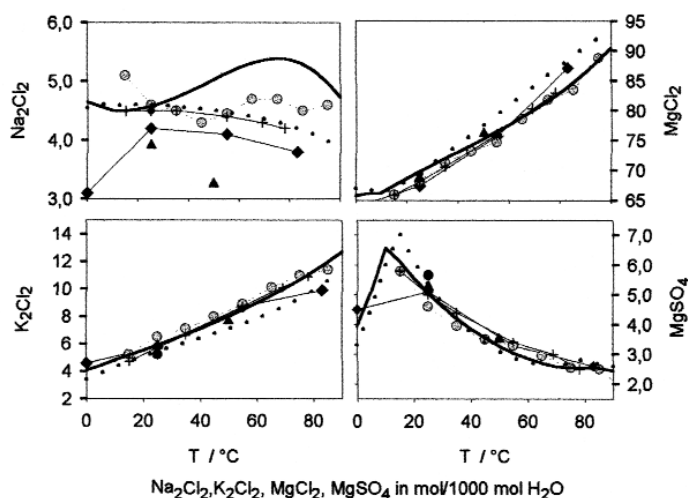


Fig. 11 Temperature dependence of paragenesis Q (halite, sylvite, carnallite, kainite): ◆ Autenrieth [5] ● Beck [9,10] ▲ Cohen-Adad [61] ● Harvie, Möller, Weare [27] old model [62] — new model [54].

ed, the differences between the authors' evaluations are much larger than the analytical accuracy available, for instance, in modern geochemical investigations today. Thus, it would be worthwhile to discard a larger number of scattered experimental data, however, at present such a step cannot be justified on the basis of the model. Besides the shortcomings in availability of solution data, the restrictions of the Pitzer model itself at very high ionic strengths ($I > 8$) and missing guidance for the temperature dependence of ionic interactions prevent unambiguous selection of consistent data. In order to overcome the limits in ionic strength, recently it was suggested to introduce ionic strength dependence also for the ternary parameters C^{ϕ} and Ψ_{ijk} [55]. This again increases the number of adjustable parameters and, consequently, the number of data points necessary for their estimation.

COHEN-ADAD APPROACH

Within the activities of IUPAC commission V.8 solid-liquid equilibrium data are compiled and critical evaluated. For binary salt-water systems an approach proposed by Cohen-Adad [56] was applied, which in essence is based on the mass action law and consists of a description of the temperature dependence of the ionic mole fraction product of every existing solid phase. The mathematical form is determined by general thermodynamics

$$\ln(xK_S) = A_0 + A_1*(1/T) + A_2*\ln(T) + A_3*T + A_4*T^2 \quad (1)$$

Often a break-off can be made after the second or third term of eq 1. In a multicomponent solution the composition dependence of the parameters A_i has to be described in form of a power series eq 2 [57].

$$A_i(X_i, X_j, \dots) = \sum \sum X_i X_j \{ a^{ij} + \sum \sum U_k^n \{ (a^{ijk})_n + \dots \} \} \quad (2)$$

where, for instance, the term $\sum \sum U_k^n (a^{ijk})_n$ denotes the contribution to A_i arising from interactions in all ternary subsystems where the salt consisting of ion i and j crystallizes. This scheme can be extended to arbitrary high complexity. The values of the higher component terms of A_i decrease quite fast with the number of components.

For several years already a large project for data compilation of major oceanic salt systems has proceeded in the Commission's subcommittee on solid-liquid solubilities. In view of the broad success of Pitzer equations it was not obvious which modeling approach would be more appropriate for a critical evaluation of all experimental data of the hexary system of oceanic salts and its subsystems. The double salt $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was chosen to demonstrate the capability of the Cohen-Adad method. The solubility curves of this salt show strong curvatures as a function of temperature and potassium content of the solutions. A three-dimensional view of a fit of the solubility product is given in Fig. 12. The ion mole fraction product $xK_S(\text{carnallite})$ calculated from experimental data of all available sources according to eqs 3-4 scatter around a smooth function (eq 4) with much less curvature than the solubility curves itself. The deviation plots in Fig. 13 demonstrate the absence of trends in the scatter of data.

$$xK_{S(\text{carnallite})} = X_{\text{K}} \cdot X_{\text{Mg}} \cdot (X_{\text{Cl}})^3 \cdot (X_{\text{H}_2\text{O}})^6 \quad (3)$$

with

$$X_{\text{K}} = n_{\text{K}} / \sum n_{\text{cations}} \quad ; \quad X_{\text{Mg}} = n_{\text{Mg}} / \sum n_{\text{cations}} \quad (3a)$$

$$X_{\text{Cl}} = n_{\text{Cl}} / \sum n_{\text{anions}} \quad ; \quad X_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} / \sum n_{\text{species}} \quad (3b)$$

$$xK_{S(\text{carnallite})} = A_0 + A_1 \cdot X_{\text{K}} \cdot X_{\text{Mg}} + A_2 \cdot (X_{\text{K}} \cdot X_{\text{Mg}})^2 + A_3 \cdot X_{\text{Na}} + A_4 / T + (A_5 + A_6 \cdot X_{\text{K}} \cdot X_{\text{Mg}}) \cdot \ln(T) + A_7 / (X_{\text{K}} \cdot X_{\text{Mg}}) \quad (4)$$

where n denotes mole numbers.

In this manner the $xK_S = f(T, X_{\text{K}})$ surface is described from -20°C until the incongruent melting point of the double salt at 167°C by eq 4. The equation contains seven parameters for the ternary system and only one parameter more (here A_3) for the quaternary system $\text{NaCl}-\text{KCl}-\text{MgCl}_2-\text{H}_2\text{O}$. Based on the experience in dealing with both approaches the number of adjustable parameters for the quinary oceanic system within 0 and 120°C is estimated to be between 200 and 220 for either approach, assuming comparable description quality of solubility data. If the temperature interval is enlarged the number of parameters will increase more markedly in the case of the Pitzer model. This

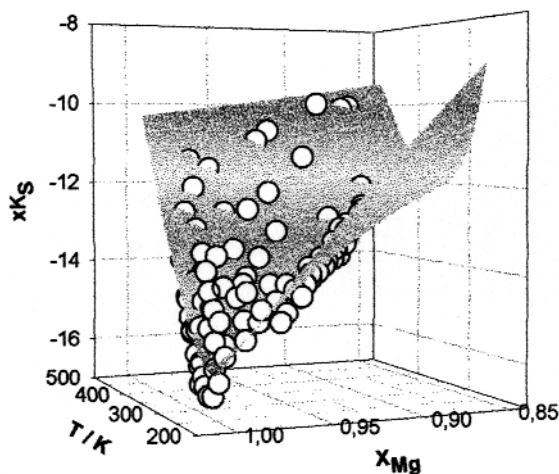


Fig. 12 3D plot of the mole fraction solubility product xK_S of carnallite in the system $\text{KCl}-\text{MgCl}_2-\text{H}_2\text{O}$; points: experimental data; surface: model.

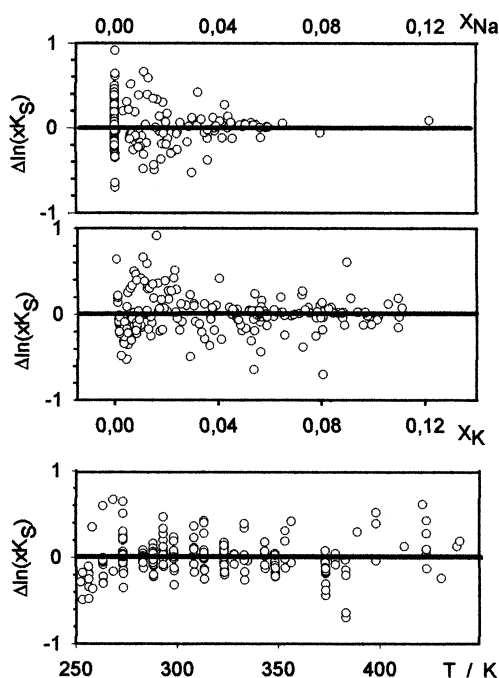


Fig. 13 Deviation plots of the mole fraction solubility products of carnallite in the system NaCl–KCl–MgCl₂–H₂O.

is because Cohen-Adad formalism focuses on the solid phases. Consequently, only the thermodynamic behavior at compositions and temperatures near the saturation limits of the solids is relevant. For instance, MgCl₂-containing salts (MgCl₂·6H₂O, KCl·MgCl₂·6H₂O) will only exist in solutions of high concentration of MgCl₂, and thus, solutions with low MgCl₂ contents must not be considered for the corresponding equations of these salts, which diminishes the number of adjustable parameters. On the other hand, the Cohen-Adad approach does not yield a thermodynamic model of the complete system, especially in the case of unsaturated solutions, which prevents linking with thermodynamic measurements in solutions.

CONCLUSIONS

At present, there are not sufficient thermodynamic solution data for the ternary oceanic salt systems available to apply Pitzer's equations as a more selective evaluation criterion of solubility data. Solubility data in higher component systems itself can be considered as a valuable source of activity data. However, the existing solubility data had been produced to draw mono-variant curves in solubility diagrams, which means for higher component systems simultaneous equilibria of two, three, or more solid phases with the solution were investigated. Solubility determinations of single salts in multicomponent solutions would be more appropriate for thermodynamic modeling, because this allows enhanced accuracy and more equal distributed data in the composition space. For solubility and thermodynamic solution data of high accuracy, extended forms of the Pitzer equations have to be applied, which increases the number of adjustable parameters.

One drawback of Pitzer's equations represents the large number of temperature coefficients in the ion interaction parameters, because the model gives no guidance in this respect. At present, the

Cohen-Adad approach can be considered as a most practical way for modeling solubility data. Opposite to the Pitzer model it gives guidance in the temperature dependence of model parameters, however, not in composition dependence. The number of adjustable parameters of both approaches is comparable. Clearly, models with guidance in composition and temperature dependence are needed. First attempts were made on the basis of local composition [58] and UNIQUAC models [59,60], but these models were not tested in detail with respect to the necessary description quality of oceanic salt systems.

ACKNOWLEDGMENTS

The author received financial support from "Bundesamt für Strahlenschutz", "Bundesministerium für Bildung, Forschung und Technologie" (projects 02 E 8361; 02 E 9319; 02 E 9330), from INCO COPERNICUS Program of EC (project PL 964379) and from IUPAC. I am also indebted to Prof. Roger Cohen-Adad for helpful discussions.

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