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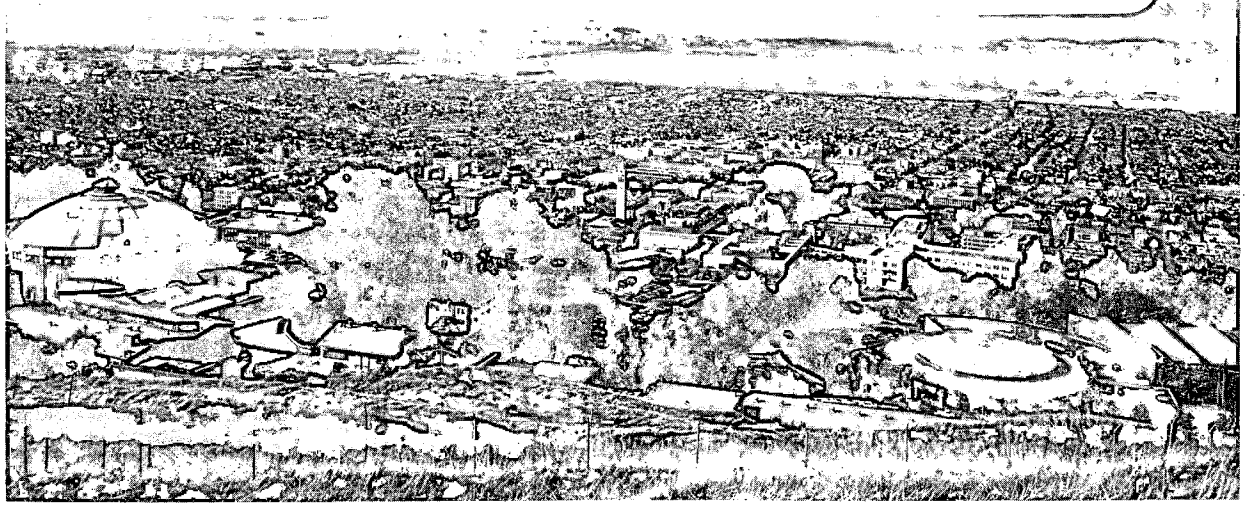

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Prediction of Thermodynamic Properties, Including Solubility Equilibria and Vapor Pressures, for Mixed Aqueous Electrolytes to High Temperatures.

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INTRODUCTION

Aqueous electrolyte solutions play an important role in various industrial processes, including those related to seawater desalination, steam power generation, waste water treatment, geothermal energy development, and hydrometallury. These processes cover a wide range of temperature and pressure conditions, and the aqueous solutions involved are frequently complex in composition. Unfortunately, accurate experimental measurements at the compositions and concentrations encountered in technology, particularly at elevated temperatures and pressures, are extremely difficult and time-consuming to make; consequently, it is desirable to have reliable models for estimating thermodynamic properties of aqueous electrolyte mixtures under these conditions.

A number of different models have been proposed in the literature that treat the thermodynamic properties of electrolyte solutions (see, for example, a review by Zemaitis et al., 1986). The most frequently used at present is the ion-interaction or virial coefficient approach, which was initially developed by Pitzer (1973) and Pitzer and Kim (1974) for aqueous solutions near room temperature. Since the model is based on a general equation for the excess Gibbs energy of the aqueous fluid, any thermodynamic property can be obtained from the appropriate derivatives. Thus the model has been used to describe osmotic and activity coefficients, as well as volumetric and thermal properties (e.g., heat capacity and enthalpy) of aqueous electrolytes. Success of this model when applied to complex and concentrated electrolyte mixtures was initially demonstrated for calculations of equilibria at room temperature between a brine phase and one or more solids by Harvie and Weare (1980). In this study we show that the same success holds over a wider range of temperature conditions. The model is applied to calculations of solubility equilibria, as well as to calculations of vapor pressures of electrolyte mixtures to high temperatures.

REVIEW OF THE ION-INTERACTION MODEL

The basic theoretical rationale for the ion-interaction model has been discussed in several publications (Pitzer, 1973; Pitzer and Kim, 1974; Pitzer, 1979). Briefly, the model starts with a virial expansion of the excess Gibbs energy of the solution:

$$G^{ex}/(n_w RT) = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} + \ldots \quad (1)$$

The first term on the right includes the Debye-Hückel limiting law, I is the ionic strength, n_w is the number of kilograms of solvent, and m_i is the molality of species i.

The parameter λ_{ij} represents the effects of short range interactions between solute particles i and j and is dependent on ionic strength, while μ_{ijk} is a term for triple-ion interactions and is usually taken to be independent of I. These coefficients are not measureable for individual ions, but only in electrically neutral combinations as follows:

$$B_{ca} = \lambda_{ca} + |z_a/2z_c|\lambda_{cc} + |z_c/2z_a|\lambda_{aa} \quad (2)$$

$$C_{ca} = (3/2)(\mu_{cca}/|z_c| + \mu_{caa}|z_a|) \quad (3)$$

$$\Phi_{cc'} = \lambda_{cc'} - (z_{c'}/2z_c)\lambda_{cc} - (z_c/2z_{c'})\lambda_{c'c'} \quad (4)$$

$$\psi_{cc'a} = 6\mu_{cc'a} - (3z_{c'}/z_c)\mu_{cca} - (3z_c/z_{c'})\mu_{c'c'a} \quad (5)$$

where c,c' are cations and a,a' are anions. The B and C terms can be evaluated empirically from data on binary systems, while the Φ and ψ terms arise only for mixed solutions and can best be determined from common-ion mixtures. Other terms in $\Phi_{aa'}$ and $\psi_{caa'}$ arise from permutation of the indices.

In terms of these obsearveable quantities, the equation for the excess Gibbs energy can be rewritten as:

$$G^{ex}/(n_w RT) = f(I) + 2\sum_c \sum_a m_c m_a [B_{ca} + (\sum_c m_c z_c) C_{ca}]$$

$$+ \sum_c \sum_{c'} m_c m_{c'} [\Phi_{cc'} + \sum_a m_a \psi_{cc'a}/2] + \sum_a \sum_{a'} m_a m_{a'} [\Phi_{aa'} + \sum_c m_c \psi_{caa'}/2] \quad (6)$$

From this basic equation expressions can be derived for the various thermodynamic quantities. The equations for osmotic coefficients and for the activity coefficient of cation M are given as follows:

$$(\phi-1) = -\frac{\partial G^{ex}/\partial n_w}{RT \sum_i m_i} = (2/\sum_i m_i)[-A_\phi I^{3/2}/(1+bI^{1/2}) + \sum_c \sum_a m_c m_a (B^\phi_{ca} + ZC_{ca})$$

$$+ \sum_{c<c'} \sum m_c m_{c'} (\Phi^\phi_{cc'} + \sum_a m_a \psi_{cc'a}) + \sum_{a<a'} \sum m_a m_{a'} (\Phi^\phi_{aa'} + \sum_c m_c \psi_{caa'})] \quad (7)$$

and

$$\ln \gamma_M = \frac{1}{RT}\frac{\partial G^{ex}}{\partial m_M} = z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\Phi_{Mc} + \sum_a m_a \psi_{Mca})$$

$$+ \sum_{a<a'} \sum m_a m_{a'} \psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \quad (8)$$

with an analogous expression for the activity coefficient of anion X. z_M is the charge on cation M and b is a universal constant with the value 1.2 $kg^{1/2}$ $mol^{-1/2}$. The double summation indices, c<c' and a<a', denote

the sum over all distinguishable pairs of dissimilar cations or anions The quantity F includes the Debye-Hückel term and other terms as follows:

$$F = -A_\phi[I^{1/2}/(1+bI^{1/2}) + (2/b)\ln(1+bI^{1/2})] + \sum_c \sum_a m_c m_a B'_{ca}$$

$$+ \sum_{c<c'} \sum m_c m_{c'} \Phi'_{cc'} + \sum_{a<a'} \sum m_a m_{a'} \Phi'_{aa'} \tag{9}$$

Also,

$$Z = \sum_i m_i |z_i| \tag{10}$$

$$B^\phi_{ca} = B_{ca} + IB'_{ca} \tag{11}$$

$$\Phi^\phi_{cc'} = \Phi_{cc'} + I\Phi'_{cc'} \tag{12}$$

where B' and Φ' are the ionic strength derivatives of B and Φ.

Since the virial coefficient λ depends on the ionic strength, so do the B's and Φ's. The empirical expressions for this ionic strength dependence of the B terms are given by the following equations:

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\exp(-\alpha_1 I^{1/2}) + \beta^{(2)}_{MX}\exp(-\alpha_2 I^{1/2}) \tag{13a}$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\, g(\alpha_1 I^{1/2}) + \beta^{(2)}_{MX}\, g(\alpha_2 I^{1/2}) \tag{13b}$$

$$B'_{MX} = [\beta^{(1)}_{MX} g'(\alpha_1 I^{1/2}) + \beta^{(2)}_{MX} g'(\alpha_2 I^{1/2})]/I. \tag{13c}$$

where the functions g and g'are given by

$$g(x) = 2[1-(1+x)\exp(-x)]/x^2 \tag{14a}$$

$$g'(x) = -2[1-(1+x+x^2/2)\exp(-x)]/x^2 \tag{14b}$$

$\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ are solute specific parameters which are fit to experimental data on pure electrolytes at varying concentrations at a given P and T. $\beta^{(2)}$ is important only for 2-2 or higher valence electrolytes that show a tendency towards electrostatic ion-pairing. α_1 is usually taken to be 2.0 $kg^{1/2}\ mol^{-1/2}$ for electrolytes in which at least one of the ions is univalent, but other values may be used without undue complication (Holmes and Mesmer, 1986). The optimized values for 2-2 electrolytes at 25°C of α_1 and α_2 are 1.4 and 12 $kg^{1/2}\ mol^{-1/2}$, respectively. There are theoretical reasons, discussed by Phutela and Pitzer (1986), for taking α_2 to be proportional to the Debye-Hückel parameter, A_ϕ, and therefore to depend on the temperature and pressure. However, for our calculations we have found it adequate to take α_1 and α_2 to be independent of T and P.

The terms in Φ and ψ for mixing different ions of the same sign appear only for mixed electrolytes. In the case of the Φ terms, there is a large ionic-strength dependence for unsymmetrical mixing, such as Na^+ and Mg^{2+} or Cl^- and SO_4^{2-}, which arises from long-range forces and is derived from theory (Pitzer, 1975; 1983). Thus the complete expressions for Φ_{ij} are:

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \tag{15a}$$

$$\phi'_{ij} = {}^{E}\theta'_{ij}(I) \tag{15b}$$

$$\phi^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I) \tag{15c}$$

where ${}^{E}\theta(I)$ and ${}^{E}\theta'(I)$ are the forms arising for unsymmetrical mixing effects and depend only on the charges of the ions, on the total ionic strength, and on the density and dielectric constant of the solvent (consequently, on the temperature and pressure). The remaining term θ_{ij} is taken as a constant for any particular pair of cations or anions at a given T and P. Its ionic strength dependence is small and is usually neglected.

Thus the calculation of the thermodynamic properties of electrolyte mixtures reduces to the evaluation of six types of empirical parameters. For osmotic and activity coefficients these are $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C_{MX}, which are evaluated from pure electrolyte data, and θ_{ij} and ψ_{ijk}, which are determined from common-ion mixtures. To calculate activity and osmotic coefficients of aqueous electrolyte mixtures at different temperatures and pressures, we need to know the T and P dependencies of these parameters.

From standard thermodynamics, various functions can be derived from the equation for excess Gibbs energy, such as the excess enthalpy, entropy and heat capacity, as well as the excess volume. These other functions can be determined experimentally and their evaluation yields accurate data on the temperature- or pressure-dependencies of the ion-interaction coefficients. In this respect the model presents a coherent and thermodynamically consistent structure for the evaluation and prediction of electrolyte properties. It also means that there is an extensive array of experimental data from which the model parameters and their temperature functions can be evaluated, including:

1. freezing point depression
2. boiling point elevation
3. vapor pressure
4. isopiestic concentrations
5. E.M.F.
6. enthalpy of dilution
7. enthalpy of mixing
8. enthalpy of solution
9. heat capacity
10. solubility

Measurements that have been most useful at temperatures above 100°C are those of 3,4,6,9, and 10. Likewise, evaluation of volumetric data provides the parameters necessary to calculate the pressure dependencies of electrolyte activity and thermal properties.

Table 1 shows the binary 1:1, 1:2 or 2:1 and 2:2 electrolyte systems for which high temperature data are available. The mixing parameters θ_{ij} and ψ_{ijk} at 25°C were derived by Pitzer and Kim (1974) for many simple ions from the available measurements of activity and osmotic coefficients. Additional values were also obtained by Harvie and Weare (1980) and Harvie et al. (1984) from solubility data. Both θ_{ij} and ψ_{ijk} undoubtedly vary with temperature, and heat of mixing data for some systems give their

Table 1. Binary Electrolyte Solutions with Available High-Temperature Data.

	Temperature range (°C)	Ref.		Temperature range (°C)	Ref.
1:1 Electrolytes			1:2 or 2:1 Electrolytes		
HCl	0 - 375	a,b	Li_2SO_4	0 - 225	f
LiCl	0 - 250	c	Na_2SO_4	0 - 225	f
NaCl	0 - 300	d	K_2SO_4	0 - 225	f
NaI	25 - 100	a	Cs_2SO_4	0 - 225	f
NaOH	0 - 350	e	$MgCl_2$	25 - 200	g,h
KCl	0 - 325	c,j	$CaCl_2$	25 - 200	g,h
CsF	25 - 100	a	$SrCl_2$	25 - 200	g
CsCl	0 - 250	c			
CsI	25 - 100	a	2:2 Electrolytes		
			$MgSO_4$	25 -200	i

[a]Saluja et al. (1986)
[b]Holmes et al. (1987)
[c]Holmes and Mesmer (1983)
[d]Pitzer et al. (1984)
[e]Pabalan and Pitzer (1987)
[f]Holmes and Mesmer (1986)
[g]Phutela et al. (1987)
[h]Holmes et al. (1978)
[i]Phutela and Pitzer (1986b)
[j]Pabalan and Pitzer (forthcoming)

temperature derivatives at 25°C (Phutela and Pitzer, 1986). However, until heat of mixing measurements or activity data for common-ion mixtures become generally available at higher temperatures, we must depend primarily on solubility data for the values of θ_{ij} and ψ_{ijk} at high temperatures. These quantities are both small, however, and for solubility calculations we have found that it was an adequate approximation to keep θ_{ij} at its 25°C value and to assume a simple temperature dependence for ψ_{ijk} (Pabalan and Pitzer, 1987b). Examples of these calculations are given below.

APPLICATIONS

Solubilities of solids

A rigorous test of prediction methods for activity or osmotic coefficients is the calculation of the solubilities of solids in electrolyte solutions. This is especially true for multicomponent systems where the solubilities are strongly affected by the solution composition. Even for two-component systems solubility calculations frequently represent extrapolations of activity or osmotic coefficients outside the range of other experiments since most measurements of thermodynamic properties are made on solutions well below saturation molalities.

Calculations of solubility equilibria, particularly at high temperatures, involves several steps, but the basic theory is well-known. For example, for a hydrated solid with ν_M cations of charge z_M, ν_X anions of charge z_X,

and ν_o molecules of water, the equilibrium constant for the dissolution reaction

$$M^{z_M}_{\nu_M}X^{z_X}_{\nu_X}\cdot\nu_o H_2O = \nu_M M^{+z_M} + \nu_X X^{-z_X} + \nu_o H_2O \tag{16}$$

is given by

$$\ln K = -(\nu_M \mu^o_M + \nu_X \mu^o_X + \nu_o \mu^o_{H_2O})/RT + \mu^o_s/RT \tag{17}$$

where the μ^o_i's represent the standard state chemical potentials of the aqueous ions, of water, or of the solid.

In terms of activities or molalities the equilibrium constant is given by

$$\ln K = \nu_M \ln(m_M\gamma_M) + \nu_X \ln(m_X\gamma_X) + \nu_o \ln(a_{H_2O}) \tag{18}$$

where m_i and γ_i represent the molality and activity coefficient of the aqueous ions, respectively.

The activity of water is related to the osmotic coefficient, ϕ, by the equation

$$\ln a_{H_2O} = -\phi(M_w/1000)\sum_i m_i \tag{19}$$

where M_w is the molecular mass of water and the sum covers all solute species.

To calculate the equilibrium constant at the temperature and pressure of interest we need the chemical potential values at those P's and T's. General tables of standard state chemical potentials at the reference temperature of 25°C and the reference pressure of 1 bar are available from several sources (Robie et al., 1978; Wagman et al., 1982). For high temperature applications, calculations are normally based on the changes of standard chemical potentials from 25°C to the temperature of interest. At constant pressure, this change is given by:

$$(\partial\mu^o_i/\partial T)_P = -S^o_i \tag{20}$$

or,

$$\mu^o_{i,T_f} - \mu^o_{i,T_r} = -S^o_{i,T_r}(T_f - T_r) + \int_{T_r}^{T_f} C^o_{p,i}dT - T\int_{T_r}^{T_f} (C^o_{p,i}/T)dT \tag{21}$$

where S^o_i represents the standard entropy of component i, and $C^o_{p,i}$ is the standard state heat capacity (at constant pressure) which itself is a function of temperature. T_r and T_f are the reference temperature and temperature of interest, respectively.

Thus, if chemical potentials and entropies (or enthalpies) at the reference temperature and heat capacity temperature functions are known, the chemical potentials and equilibrium constants at the temperature of interest can be derived. In the case of water, the chemical potential at T and P can be conveniently calculated from the equations of Haar et al. (1984). For the solids, although there are some inaccuracies or lack of data at high temperatures, their data base is well-organized and given in the compilations of Kelley (1960), Stull and Prophet (1971), Robie et al.

(1978), and Wagman et al. (1982). In the case of the aqueous ions, additivity rules allow us to use standard state heat capacities of neutral electrolytes in calculating equilibrium constants for dissolution reactions. An extensive array of data extending upward in temperature is now available for the most important aqueous solutes, as shown in Table 1.

Figures 1-7 show the results for some of the systems we have looked at (Pabalan and Pitzer, 1987b). For the binary system $NaCl-H_2O$, there is an extensive array of thermodynamic data as reported by Pitzer et al. (1984). Their evaluation of these data yielded a complete set of parameters valid in the region 0-300°C, saturation pressure to 1 kb., and 0-6 m NaCl. NaCl solubilities calculated using these parameters are compared with experimentally measured solubilities in Fig. 1. As shown in the figure there is excellent agreement between calculated and experimental values, with a maximum deviation of 1.5% at 275°C.

An example involving a 2-2 electrolyte is shown in Fig. 2 for $MgSO_4 \cdot nH_2O$ solubility. In this case the parameters used were taken from Phutela and Pitzer (1986b) based on a comprehensive regression of heat capacity, enthalpy, and osmotic coefficient data from 25-200°C for $MgSO_4(aq)$. Figure 2 shows that calculated solubilities are in very good agreement with experimental data to 200°C.

The mixing terms θ_{ij} and ψ_{ijk} are required by the ion-interaction model for calculations in ternary and more complex systems. As mentioned

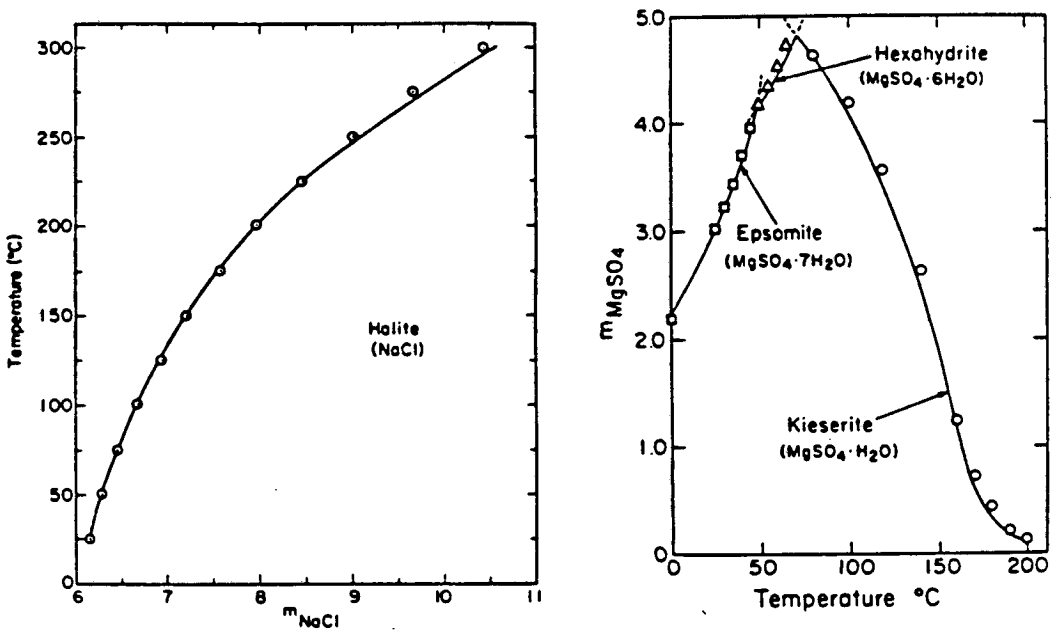

Figure 1. (left) Calculated halite (NaCl) solubilities in the binary $NaCl-H_2O$ system compared to experiment. The solubility data from 75-300°C are from Liu and Lindsay (1972), and those below 75°C are from Linke and Seidell (1965).

Figure 2. (right) Calculated solubilities in the system $MgSO_4-H_2O$ compared to experimental data from Linke and Seidell (1965).

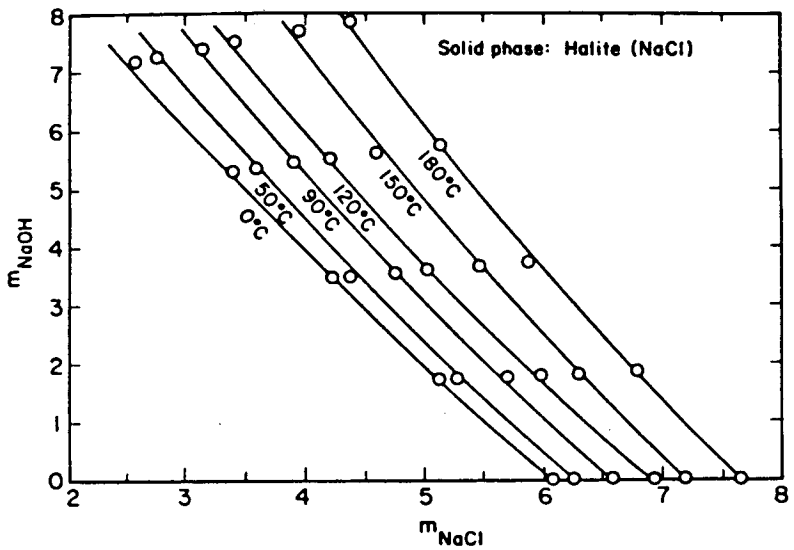

Figure 3. Calculated and experimental solubilities of halite (NaCl) in the ternary system NaCl-NaOH-H_2O. The experimental data were taken from Linke and Seidell (1965).

previously, for solubility calculations we have found it adequate to hold θ_{ij} at its 25°C value and assume a simple temperature dependence for ψ_{ijk}. In most cases the form was: $\psi_{ijk} = A/T + B$. Values of A and B for mixtures in the system Na-K-Mg-Cl-SO_4-OH-H_2O are given in Pabalan and Pitzer (1987b). Calculated solubilities in the system NaCl-NaOH-H_2O are shown in Fig. 3 and indicate good agreement with experimental data from 0-180°C. Agreement is also good between experimental and calculated values for the system NaCl-$MgCl_2$-H_2O to 200°C as shown in Fig. 4. In a few cases constant values of θ_{ij} and ψ_{ijk} are sufficient. An example is shown in Fig. 5 for the system NaCl-Na_2SO_4-H_2O which shows good agreement to 200°C.

The mixing terms θ and ψ complete the parameters necessary to calculate activity or osmotic coefficients in ternary and more complex mixtures. Using the parameters evaluated previously from binary and ternary systems, solubility equilibria in more complex systems can be predicted. An example is shown in Fig. 6 for the quaternary system NaCl-KCl-$MgCl_2$-H_2O at several isotherms. In this diagram the symbols are experimental data from Boecke (1910) and the curves represent predicted values. Fig. 7 shows our results for the quaternary system NaCl-Na_2SO_4-NaOH-H_2O at 150°C. The curves represent predicted solubilities of thenardite (Na_2SO_4) at various molalities of NaOH(aq) and NaCl(aq), and the symbols are experimental data from Schroeder et al. (1935).

Vapor pressures

Vapor pressures of electrolyte mixtures are also of interest in industrial technology. The vapor pressures can be calculated from the osmotic coefficients of the electrolyte solutions and an equation of state for steam. The equation relating vapor pressure and osmotic coefficient is given by Liu and Lindsay (1972):

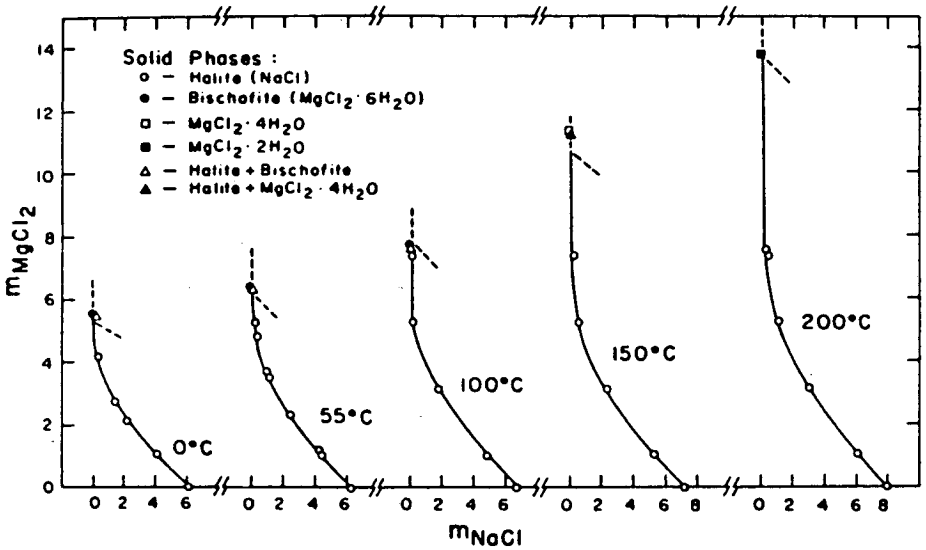

Figure 4. Calculated and experimental solubilities in the $NaCl-MgCl_2-H_2O$ system. Experimental data below 100°C are from Linke and Seidell (1965), while those above 100°C are from Akhumov and Vasil'ev (1932). The dashed curves are extrapolations of the solubilities of either $MgCl_2 \cdot nH_2O$ or NaCl into the supersaturated solution concentration of the other. The intersection of the curves denotes the calculated triple point.

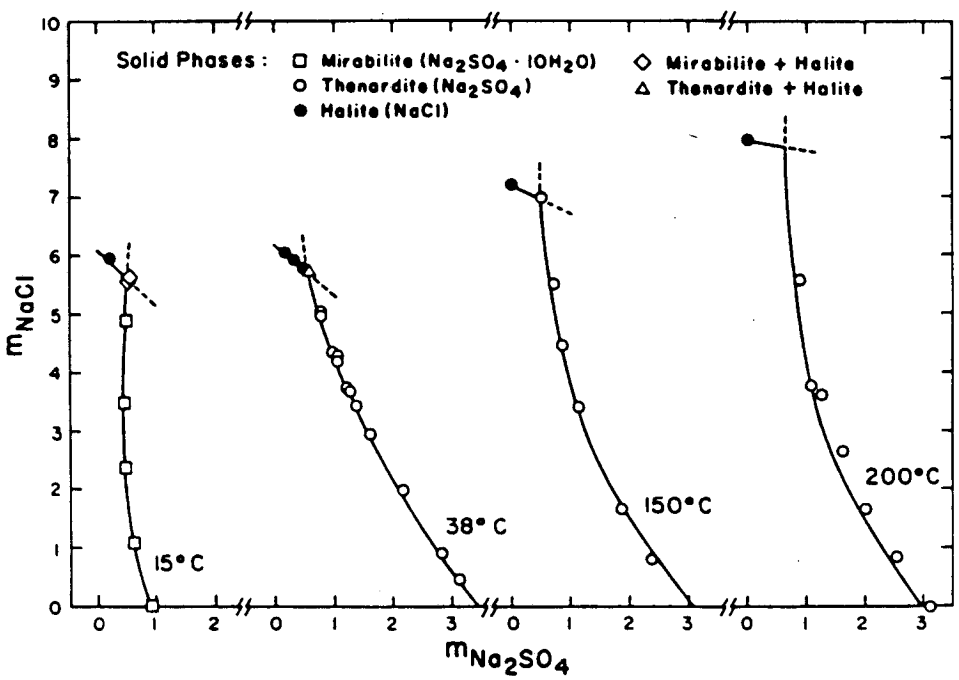

Figure 5. Calculated solubilities in the $NaCl-Na_2SO_4-H_2O$ system compared with experimental data from Linke and Seidell (1965) to 100°C and from Schroeder et al. (1935) at 150°C and above.

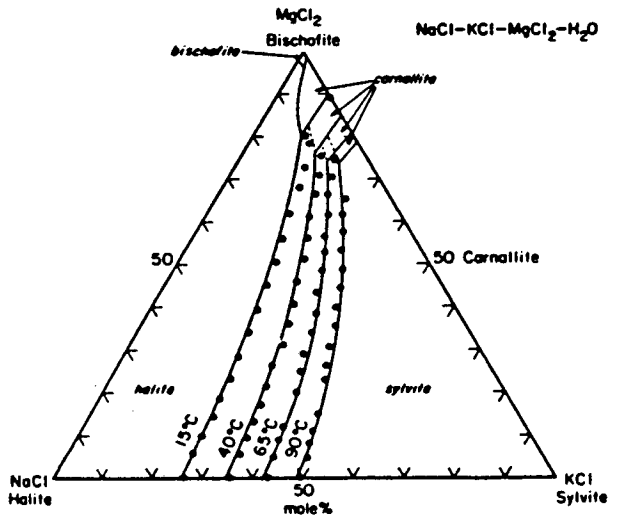

Figure 6. Predicted solubilities in the quaternary system $NaCl-KCl-MgCl_2-H_2O$ at 15, 40, 65, and 90 °C. The solid symbols are experimental data from Boecke (1910).

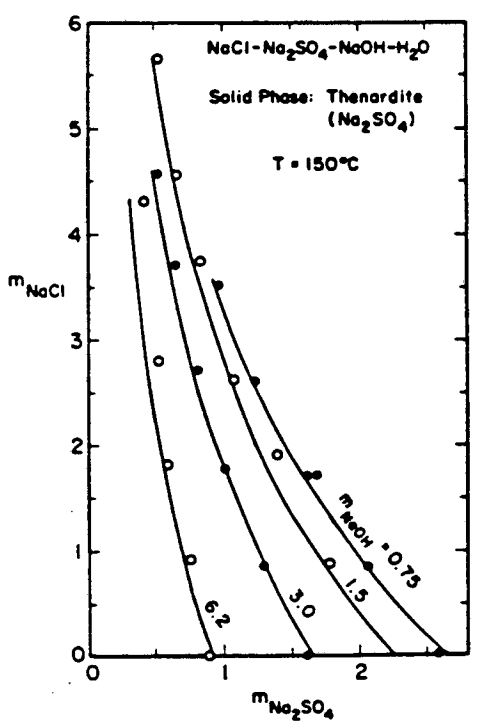

Figure 7. Predicted solubilities of thenardite (Na_2SO_4) in the quaternary system $NaCl-Na_2SO_4-NaOH-H_2O$ at 150 °C. The symbols are experimental data from Schroeder et al. (1935).

$$\phi = \frac{1000}{M_w RT \sum_i m_i} \left[RT \ln\frac{P_o}{P} - \int_P^{P_o} \left(\frac{RT}{P} - V_g\right) dP - \bar{V}_1 (P_o - P) \right] \tag{22}$$

where V_g is the molar volume of water vapor and $\bar{V}_1$ is the partial molar volume of water in the electrolyte solution and is approximated by the molar volume of pure liquid water. P and P_o represent the vapor pressure of the solution and of pure water, respectively. The integral term can be evaluated using the equations of Haar et al. (1984).

Examples of calculated vapor pressures are given in Fig. 8 and Table 2. Figure 8 shows predicted vapor pressures for the ternary system NaCl-Na_2SO_4-H_2O at various temperatures compared with experimental data from Fabuss and Korosi (1966). The figure shows that the calculated values are mostly within the stated experimental uncertainty of 0.1 %. Table 2 compares predicted vapor pressure lowering values to 300°C with data from Liu and Lindsay (1971) for simulated seawater (Na_2SO_4-NaCl-$MgCl_2$-H_2O). The calculated values show excellent agreement with experimental data to 200°C. Calculations above this temperature make use of extrapolations of the temperature functions of the binary ion-interaction parameters for $MgCl_2$(aq) and $MgSO_4$(aq), but agreement is still relatively good to 300°C.

CONCLUSION

The Pitzer ion-interaction model for electrolyte mixtures is shown to be applicable over a wide range of temperature conditions. The model makes use of six types of empirical parameters derived from various experimentally determined electrolyte solution properties or solubilities in binary and ternary systems, but requires no additional parameters to extend the calculations to more complex mixtures. Applications include

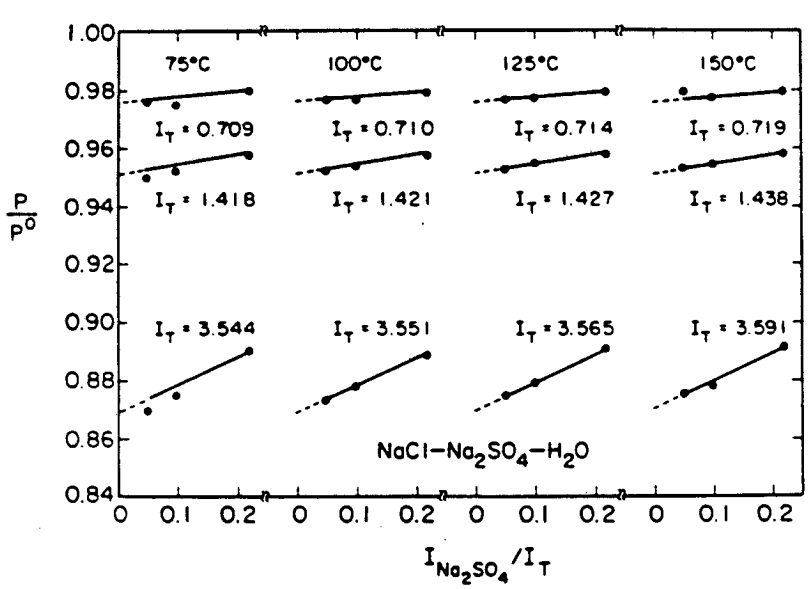

Figure 8. Predicted vapor pressure lowering of NaCl-Na_2SO_4-H_2O mixtures at 75, 100, 125, and 150°C, compared with experimental data from Fabuss and Korosi (1966).

Table 2. Experimental and Predicted Vapor Pressures for Simulated Seawater (Na_2SO_4-NaCl-$MgCl_2$-H_2O)

Temperature (°C)	Concentrate Multiple of Simulated Seawater	Vapor Pressure Lowering $\Delta P = P_o - P$ (mm. Hg) Expt.	Calc.
75	2.8476	15	16
75	5.8158	35	36
100	1.4884	19	21
100	2.8528	41	42
100	5.8377	92	94
106	1.4888	24	26
125	1.4907	46	48
125	2.8630	94	96
125	5.8811	212	212
150	1.4949	95	99
150	2.8813	194	195
150	5.9597	436	434
175	1.5018	181	186
175	2.9128	367	368
175	6.1004	824	820
200	1.5126	323	328
200	2.9630	650	649
200	6.3279	1467	1460
225	1.5291	541	548
225	3.0415	1098	1089
225	6.6980	2517	2499
250	3.1648	1782	1768
250	7.3078	4224	4183
275	3.3622	2844	2810
275	8.3482	7083	6953
300	3.6957	4570	4436
300	10.2027	12244	11391

Actual composition of experimental solutions are given by the concentrations listed below multiplied by the concentrate multiple of simulated seawater given in the second column of the table (data from Liu and Lindsay, 1971):

NaCl = 0.42663 m
Na_2SO_4 = 0.02976 m
$MgCl_2$ = 0.06726 m

calculation of solubility equilibria, as well as vapor pressures of electrolyte mixtures, but the model allows calculation of other quantities relevant to industry, such as total fluid enthalpy, entropy, or volume.

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