Thermodynamics of Phase Equilibria in Aqueous-Organic Systems with Salt

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A semiempirical thermodynamic method is developed to establish a framework for calculating vapor-liquid and liquid-liquid equilibria in ternary systems containing water, an organic solvent, and a salt. Careful attention is given to precise definition of standard states. Short-range ion-solvent forces are taken into account primarily by a chemical-equilibrium method based on stepwise ion solvation; however, physical contributions also contribute. Water-cosolvent nonideality is described by an extended equation of the van Laar form. Long-range electrostatic forces between ions are taken into account by an extended Debye-Hückel equation with corrections for transferring from a McMillan-Mayer to a Lewis-Randall framework.

The new method is illustrated with results for several systems including saturated aqueous mixtures of LiBr or LiCl with methanol where the salt concentration exceeds 20 molal. The method developed here is of particular interest for process calculations in extractive crystallization, a low-energy operation for producing salt from aqueous solution.

Introduction

While the chemical engineering literature has given extensive attention to the thermodynamics of multicomponent vapor-liquid and liquid-liquid equilibria of mixtures containing nonelectrolytes, much less attention has been given to such equilibria for systems containing a salt dissolved in a mixed solvent.

Binary aqueous salt mixtures have been studied for many years; in addition to extensive experimental results, there exists a variety of theoretical descriptions: Debye and Hückel (1923); Glückauf (1955); Robinson and Stokes (1970); Pitzer (1971); Bromley (1973); Pitzer (1973); Stokes and Robinson (1973); Blum (1975); Olivares and McQuarrie (1975); Triolo et al. (1976); Pitzer (1977); Blum (1980); Planche and Renon (1981); Nesbit (1982); Ball et al. (1985); Ball and Planche et al. (1985); Engels (1985); Schönert (1986); Copeman and Stein (1987); Blum (1988); Liu et al. (1989); Melchior and Basset (1990); Haghtalab and Vera (1991); Clegg and Pitzer (1992). But these descriptions are not easily extended to ternary mixtures containing one salt and two solvents, especially when that mixture leads to two liquid phases and hence liquid-liquid equilibria where all three components are present in both phases. Chen et al. (1982, 1986) have presented a semiempirical method for calculating both vapor-liquid and liquid-liquid in such ternary systems restricted to salt concentrations of about 6 molal. Other models have been developed for the representation of ternary vapor-liquid equilibria (Hala, 1969; Maurer, 1983; Renon, 1986; Sander et al., 1986), but they are also restricted to intermediate salt concentrations.

This work presents an alternate semiempirical method for calculating vapor-liquid and liquid-liquid equilibria in systems similar to those considered by Chen and coworkers. The new method presented here differs from previously published methods in two ways. First, the major contribution to nonideality arising from short-range ion-solvent forces is here ascribed to chemical equilibria leading to solvated ions; physical contributions constitute only a minor contribution, whereas in Chen's and other work they are dominant. Second, it is this "chemical" feature of the new method which permits representation of experimental data to very high salt concentrations; it is applicable to saturated salt solutions where the salt concentration can reach 20 molal or more. The new method does not use the Born equation for changing from one reference state to another, primarily because the Born equation often gives poor results when compared to experiment; sometimes the Born equation gives a partial Gibbs energy that is qualitatively incorrect with the wrong sign.

The new method necessarily contains adjustable parameters.

For a ternary system (one salt, two solvents), all but one of these parameters can be obtained from pure-component or binary data.

Following a terse summary of electrolyte-solution thermodynamics, the new method is derived with all mathematical details omitted; these are given in appendices. Illustrative results are given for several binary and ternary systems.

Liquid-liquid equilibria for ternary systems containing one salt and two solvents are of particular interest for the recently-developed unit operation called extractive crystallization. This operation provides a method for removing a salt from aqueous solution with a minimum of energy, that is, with much less energy than that required in a triple-effect evaporator (Weingaertner et al., 1991; Brenner et al., 1992; Ting et al., 1992).

Thermodynamic Background

Consider a ternary system containing water (1), an organic cosolvent (2), and a salt. Since we are concerned with solutions of strong electrolytes, we assume complete dissociation of electrolyte E into cations C and anions A:

$$E \rightarrow \nu_C C + \nu_A A \tag{1}$$

where ν_C and ν_A are the stoichiometric coefficients. Let

$$\nu = \nu_C + \nu_A. \tag{2}$$

For any species k, the mole fraction x_k, based on the assumption of complete dissociation, is related to the mole numbers n by:

$$x_k = \frac{n_k}{\sum_l n_l}. \tag{3}$$

The sum includes all ionic and molecular species.

The chemical potential μ_E of the electrolyte is related to those of the ions by:

$$\mu_E = \nu_C \mu_C + \nu_A \mu_A. \tag{4}$$

For ions C and A, we introduce activity coefficients γ_C and γ_A based on the complete-dissociation mole fractions:

$$\mu_E = \nu_C[\mu_C^\ominus + \mathrm{RT}\ \ln(x_C\gamma_C)] + \nu_A[\mu_A^\ominus + \mathrm{RT}\ \ln(x_A\gamma_A)] \tag{5}$$

where superscript Θ denotes the standard state. Regardless of solvent, the standard state for the cation is a hypothetical ideal dilute solution *in water* when $x_C = 1$, at system temperature and pressure. Similarly, the standard state for the anion is a hypothetical ideal dilute solution *in water* when $x_A = 1$. In the hypothetical ideal dilute solution, $\gamma_A = \gamma_C = 1$ for all x. In the real solution, the activity coefficients are normalized by:

$$\gamma_C \rightarrow 1 \quad \text{as} \quad x_C \rightarrow 0 \quad \text{and} \quad x_1 \rightarrow 1 \tag{6}$$

and

$$\gamma_A \rightarrow 1 \quad \text{as} \quad x_A \rightarrow 0 \quad \text{and} \quad x_1 \rightarrow 1. \tag{7}$$

The standard state for every ion is always a hypothetical ideal dilute solution at unit mole fraction in water, even in the ternary mixture or in the water-free organic solvent. This standard state is convenient for liquid-liquid phase-equilibrium calculations where the water/solvent ratio in one phase differs from that in the other. The standard state of the ions is hypothetical, but the physical properties of the ions at infinite dilution in water are clearly defined and experimentally accessible.

It is a common misconception that the standard state for the solute is the infinitely dilute solution. (That is not correct: the chemical potential of the solute at infinite dilution is $-\infty$.) The standard state of the solute is the hypothetical ideal dilute solution at a fixed concentration, usually unit concentration. In this work, unit concentration for the cation means $x_C = 1$; similarly, unit concentration for the anion means $x_A = 1$.

In defining the standard state used here, the word hypothetical is important. In the real world, it is not possible to have a solution which is simultaneously dilute and at a solute mole fraction equal to unity. In an ideal dilute solution, the chemical potential of solute i is described by the equation $\mu_i = \mu_i^\ominus + \mathrm{RT}\ \ln\ x_i$, where it is understood that x_i is small compared to unity. From experimental data when x_i is small, it is possible to obtain information about $\mu_i^\ominus$. The definition of μ_i is valid even if x_i approaches unity, although in that event the ideal dilute solution is no longer real but becomes hypothetical.

In the equations above, cation and anion appear as separate species. However, only the chemical potential of the electrically neutral salt is experimentally accessible. This follows from the condition of electroneutrality for every phase. Following long-standing convention, we use the mean ionic activity coefficient, denoted by subscript $\pm$.

For the chemical potential of the salt, we write:

$$\mu_E = \nu\mu_\pm = \nu_C\mu_C + \nu_A\mu_A \tag{8}$$

$$\mu_\pm = \mu_\pm^\ominus + \mathrm{RT}\ \ln(\gamma_\pm x_\pm) \tag{9}$$

where $\gamma_\pm$ and $x_\pm$ are defined by:

$$\gamma_\pm = [\gamma_C^{\nu_C}\gamma_A^{\nu_A}]^{1/\nu} \tag{10}$$

$$x_\pm = [x_C^{\nu_C}x_A^{\nu_A}]^{1/\nu}. \tag{11}$$

For the chemical potential in the standard state,

$$\nu\mu_\pm^\ominus = \nu_C\mu_C^\ominus + \nu_A\mu_A^\ominus. \tag{12}$$

The chemical potential of water and cosolvent are expressed also in terms of complete-dissociation mole fractions:

$$\mu_1 = \mu_1^\ominus + \mathrm{RT}\ \ln(x_1\gamma_1) \tag{13}$$

$$\mu_2 = \mu_2^\ominus + \mathrm{RT}\ \ln(x_2\gamma_2). \tag{14}$$

Here, the chemical potential in the standard state is that of pure liquid water or that of pure liquid cosolvent at system temperature and pressure. Activity coefficients γ_1 and γ_2 are normalized by:

$$\gamma_1 \rightarrow 1 \quad \text{as} \quad x_1 \rightarrow 1 \tag{15}$$

$$\gamma_2 \rightarrow 1 \quad \text{as} \quad x_2 \rightarrow 1. \tag{16}$$

The Gibbs energy of the real solution is given by:

$$G = n_1\mu_1 + n_2\mu_2 + n_C\mu_C + n_A\mu_A. \tag{17}$$

The Gibbs energy of the ideal solution is defined by:

$$G^{\text{ideal}} = \sum_k n_k\mu_k^\Theta + \text{RT} \sum_k n_k \ln(x_k). \tag{18}$$

The excess Gibbs energy G^E is defined by:

$$G^E = G - G^{\text{ideal}}. \tag{19}$$

Substituting in Eq. 17 the activity coefficients defined in Eqs. 5, 13 and 14, the excess Gibbs energy is given by:

$$G^E = \text{RT} \sum_k n_k \ln(\gamma_k). \tag{20}$$

The activity coefficients of water, cosolvent, cation and anion are related to G^E by:

$$\text{RT} \ln(\gamma_k) = \left(\frac{\partial G^E}{\partial n_k}\right)_{T,P,n_{j\neq k}}. \tag{21}$$

Upon adopting a model for G^E, Eq. 21 gives activity coefficients for single ions. However, experimental measurements always give the chemical potential of an electrically neutral assembly of ions: experimental data give $\ln(\gamma_\pm)$.

To obtain $\ln(\gamma_\pm)$ from a model for G^E, we first calculate $\ln(\gamma_C)$ and $\ln(\gamma_A)$, and then use:

$$\ln(\gamma_\pm) = \frac{1}{\nu} [\nu_C \ln(\gamma_C) + \nu_A \ln(\gamma_A)]. \tag{22}$$

Vapor-liquid equilibrium

The condition for phase equilibrium between vapor and liquid is given by:

$$\mu_1^V = \mu_1^L \quad \text{and} \quad \mu_2^V = \mu_2^L. \tag{23}$$

where superscript V stands for vapor and L for liquid. We assume that there is no salt in the vapor.

Equation 23 can be rewritten in terms of fugacities. Neglecting the Poynting correction:

$$\varphi_1 y_1 P = \gamma_1 x_1 P_1^{\text{sat}} \varphi_1^{\text{sat}} \tag{24}$$

$$\varphi_2 y_2 P = \gamma_2 x_2 P_2^{\text{sat}} \varphi_2^{\text{sat}} \tag{25}$$

where φ_i^{sat} is the vapor-phase fugacity coefficient of pure component i at saturation and φ_i is the fugacity coefficient of i in the mixture; P is the total pressure and P_i^{sat} is the vapor pressure of pure liquid i, all at system temperature T.

For the systems discussed later, the vapor pressure of the pure liquid is given by the Wagner equation (Reid et al., 1987). Fugacity coefficients are calculated from an expression based on the virial equation truncated after the second virial coefficient (Prausnitz, 1980). At the low pressures encountered in this work, corrections for gas-phase nonideality are negligible.

Activity coefficients γ_1 and γ_2 are obtained from a model for G^E, using Eq. 21.

Liquid-liquid equilibrium

It is more difficult to describe liquid-liquid equilibria than vapor-liquid equilibria because salt appears in both phases. The condition for phase equilibrium is given by:

$$\mu_1' = \mu_1'' \tag{26}$$

$$\mu_2' = \mu_2'' \tag{27}$$

$$\mu_E' = \mu_E'' \tag{28}$$

where superscripts $'$ and $''$ denote the two liquid phases.

With the definition of the mean ionic properties (Eqs. 8-12), Eq. 28 can be replaced by:

$$\mu_\pm' = \mu_\pm''. \tag{29}$$

Introducing activity coefficients defined in Eqs. 9, 13 and 14, the equations for liquid-liquid phase equilibrium are:

$$[\mu_1^\Theta + \text{RT} \ln(x_1\gamma_1)]' = [\mu_1^\Theta + \text{RT} \ln(x_1\gamma_1)]'' \tag{30}$$

$$[\mu_2^\Theta + \text{RT} \ln(x_2\gamma_2)]' = [\mu_2^\Theta + \text{RT} \ln(x_2\gamma_2)]'' \tag{31}$$

$$[\mu_\pm^\Theta + \text{RT} \ln(x_\pm\gamma_\pm)]' = [\mu_\pm^\Theta + \text{RT} \ln(x_\pm\gamma_\pm)]''. \tag{32}$$

Using the previously defined standard-state chemical potentials, the equations of liquid-liquid equilibrium simplify to:

$$(x_1\gamma_1)' = (x_1\gamma_1)'' \tag{33}$$

$$(x_2\gamma_2)' = (x_2\gamma_2)'' \tag{34}$$

$$(x_\pm\gamma_\pm)' = (x_\pm\gamma_\pm)'' \tag{35}$$

where the activity coefficients are found from excess Gibbs energy G^E as indicated by Eq. 21. The mean-ionic activity coefficient $\gamma_\pm$ is obtained from Eq. 22. The simplicity of Eq. 35 follows from defining the standard state for each ion as the hypothetical ideal dilute solution in *water* at unit mole fraction for *both* phase $'$ and phase $''$.

A Model for G^E

Molecular-thermodynamic models for liquid mixtures of nonelectrolytes express deviations from ideality arising from short-range interactions. In electrolyte solutions there exist, in addition, long-range electrostatic forces that lead to significant deviations from ideal-solution behavior; these long-range interactions are particularly important at low salt concentrations. The effect of short-range forces can be described by "physical" theories (such as Van Laar) and/or by "chemical" theories (ion solvation). The effect of long-range forces is taken into account by an extended Debye-Hückel theory. Because the long-range contribution is defined in the McMillan-Mayer framework, it must be converted to the Lewis-Randall framework as discussed by Cardoso and O'Connell (1987).

Short-range forces between ions and solvent molecules are frequently described by formation of semistable complexes, which is called solvation. Experimental studies on ion solvation in the gas phase (Dzidic and Kebarle, 1970; Kebarle, 1977) have shown that solvated ions are indeed chemical complexes. Enthalpies and entropies for consecutive solvation steps have been measured. Using measured equilibrium constants, Pitzer developed a model for NaCl in steam (Pitzer, 1983; Pitzer and Tanger, 1989). Also, computer simulations (Claverie et al., 1978; Mezei and Beveridge, 1981; Chandrasekhar et al., 1984) indicate that, in the liquid phase, ions form complexes with water and other polar solvents due to the strong electrostatic attraction between the charged ion and the polar solvent molecules (Conway, 1981; Enderby and Neilson, 1981; Marcus, 1985; Ben Naim, 1987). Spectroscopic measurements in liquid mixtures of two solvents and a salt show preferential solvation of one solvent around the ion (Covington and Dunn, 1989; Sacco et al., 1991; Eaton et al., 1992). In aqueous solutions of organic solvents, ions solvate with both water and cosolvent but usually water is the preferred component for solvation. Following Stokes and Robinson (1973) and Schönert (1986), we use a stepwise chemical equilibrium to describe the primary short-range nonideality arising from interactions between ions and solvent molecules.

In the absence of salt, interactions between water and cosolvent are given by an expansion of the Wohl type (Wohl, 1946). In this expression we must introduce a term that reflects how the salt modifies interactions between water and cosolvent beyond those accounted for by the formation of ion-solvation complexes, as discussed previously.

Following these ideas, it is convenient to write G^E as a sum of three contributions:

$$G^E = G^{E^{\text{chem}}} + G^{E^{\text{phys}}} + G^{E^{LR}}. \tag{36}$$

where superscript LR stands for long-range. Using Eqs. 21 and 22, Eq. 36 provides activity coefficients of the form:

$$\ln(\gamma_r) = \ln(\gamma_r^{\text{chem}}) + \ln(\gamma_r^{\text{phys}}) + \ln(\gamma_r^{LR}) \tag{37}$$

where r stands for 1, 2 or ±.

The three contributions in Eq. 36 are discussed in the following sections.

In this work, at this stage of development, the three contributions are calculated independently. The chemical contribution concerns the formation of "true" solvated-ion species, "free" water, and "free" organic solvent. However, the physical and long-range contributions do not consider the existence of these "true" species. A self-consistent model, which considers "true" species in all three contributions, would be prohibitively complex mathematically and, what is worse, would include far too many adjustable parameters.

At low salt concentrations, the long-range contribution is important, but as salt concentration rises, that contribution becomes increasingly small compared to the others. At intermediate and high salt concentrations, the chemical contribution is usually much more important than the physical contribution, as illustrated later.

Chemical contribution

As indicated earlier, we assume complete dissociation of the electrolyte E into cations C and anions A. To reduce the number of adjustable parameters, we follow Stokes and Robinson (1973) by assuming that only the cation is solvated. This assumption is also used in most statistical-mechanical descriptions of electrolyte solutions where the radius of the cation is taken as the solvated radius (Ball and Planche et al., 1985; Copeman and Stein, 1986; Copeman and Stein, 1987; Gering et al., 1989). For many typical salts, the ion-dipole forces between cation and polar solvent molecules are much higher than those for the anion due to the smaller size of the cation (Conway, 1981; Marcus, 1985).

The fundamental assumption of the chemical model is a stepwise solvation with a characteristic equilibrium constant $K_{i,j}$ for each solvation step:

Equilibrium	Equilibrium Constant	
$C_0 + i$ (solvent 1) $+ j$ (solvent 2) $\leftrightarrow C_{i,j}$	K_{ij}	(36a)

Here C_0 represents the unsolvated cation; $C_{i,j}$ is the solvated cation with i molecules of solvent 1 (water) and j molecules of solvent 2 (cosolvent). In chemical equilibrium, we have a variety of different solvates. In the equations below, we use a notation similar to that of Stokes and Robinson (1973) and Schönert (1986).

As shown in Appendix II, the excess Gibbs energy arising from the chemical model can be written as:

$$\frac{G^{E^{\text{chem}}}}{\text{RT}} = n_1 \ln(\gamma_1^{\text{chem}}) + n_2 \ln(\gamma_2^{\text{chem}}) + n_C \ln(\gamma_C^{\text{chem}}) + n_A \ln(\gamma_A^{\text{chem}}) \tag{36b}$$

with the activity coefficients γ_k^{chem} given in Appendix I.

For the solvent components, we obtain:

$$\ln(\gamma_1^{\text{chem}}) = \ln\left(\frac{\xi_1^f}{x_1}\right) \tag{36c}$$

and

$$\ln(\gamma_2^{\text{chem}}) = \ln\left(\frac{\xi_2^f}{x_2}\right) \tag{36d}$$

where ξ_s is the "true" mole fraction of species s at chemical equilibrium with the total mole number of all species n':

$$\xi_s = \frac{n_s}{n'}. \tag{36e}$$

For the cation,

$$\ln(\gamma_C^{\text{chem}}) = \ln\left(\frac{\xi_{C_0}}{x_C}\right) + \ln(\Sigma^{\Theta}) \tag{36f}$$

where Σ^{Θ} is defined by:

$$\Sigma^{\Theta} = \sum_{i=0}^{N} K_{i,j=0} \tag{36g}$$

In this summation, i refers to the number of water molecules in the solvated ion, where the unsolvated ion is also included ($K_{0,0} = 1$). N is the number of binding sites per ion. We choose $N = 5$ for monovalent cations. Experimentally obtained solvation numbers, determined from Stokes radii indicate higher solvation numbers for multivalent cations (Marcus, 1985). We choose $N = 12$ for bivalent cations.

Similarly, for the anion,

$$\ln(\gamma_A^{\text{chem}}) = \ln\left(\frac{\xi_{A_0}}{x_A}\right) \tag{36h}$$

In Eq. 36h, the last term in Eq. 36f does not appear because we assumed the anion to be unsolvated. (For the anion, all equilibrium constants are zero.)

For the chemical contribution to the mean ionic activity coefficient, we have:

$$\ln(\gamma_\pm^{\text{chem}}) = \frac{1}{\nu}\left[\nu_C \ln(\gamma_C^{\text{chem}}) + \nu_A \ln(\gamma_A^{\text{chem}})\right] \tag{36i}$$

The chemical equilibrium constants must now be specified. To reduce the number of adjustable parameters, we assume that the cation is solvated although the anion is not, while we interrelate the equilibrium constants for the individual solvation steps by a statistical argument which accounts for the number of possible arrangements in the solvation shell. We then retain only one adjustable equilibrium-constant parameter (k^0) for each solvent-salt pair at a fixed temperature. This statistical argument is given in Appendix III.

Physical contribution

Interactions between water and cosolvent are expressed by an extended equation of the type suggested by van Laar (1910) and by Scatchard and Hamer (1935). This extended equation is useful for simultaneous representation of liquid-liquid and vapor-liquid data for salt-free aqueous-organic systems.

For the salt-free binary system, we propose:

$$\frac{G_{(1,2)}^{E^{\text{phys}}}}{n^T RT} = q\phi_1\phi_2[A + B\phi_2 + C\phi_1\phi_2] \tag{37a}$$

where the volume fractions are defined by:

$$\phi_k = \frac{q_k x_k}{q} \qquad q = \sum_k x_k q_k \tag{37b}$$

and where q_k is a volume parameter, taken from Reid et al. (1987) and Bondi (1968) for water and cosolvent. Table 1a shows q parameters used in this work. The summation includes water and cosolvent for the salt-free system. Later, when Eq. 37a is extended to the ternary system, cation and anion are also included in the summation. The total number of moles n^T is defined as:

$$n^T = n_1 + n_2 + n_C + n_A \tag{37c}$$

and reduces to the mole numbers of water and cosolvent for the salt-free system.

Table 1a. Volume Parameter q for Solvents*

Water	0.92	Propanol	2.78
Methanol	1.43	Butanol	3.45
Acetonitrile	1.87	Acetone	2.57
Ethanol	2.11	2-Butanone	3.25

*These parameters are dimensionless because they are normalized by $v(CH_2) = 15.17\ \text{cm}^3/\text{mol}$.

Table 1b. Volume Parameters q for Ions Normalized by $v(CH_2)$*

Ion	r [nm]	q	Ion	r [nm]	q
Li^+	0.060	0.036	Cl^-	0.181	0.987
Na^+	0.095	0.143	Br^-	0.195	1.234
K^+	0.133	0.392	OH^-	0.140	0.457
Ca^{2+}	0.099	0.162	CO_3^{2-}	0.185	1.053

*Crystallographic radii are from Marcus (1985).

For solvent-salt binaries, physical interactions between solvent molecules and ions are taken into account by a simple expression. Empirical tests have shown that this interaction is preferably expressed by mole rather than volume fractions. The ion-molecule interactions are expressed as proposed by Pitzer (1991).

For the water-salt binary mixture, we assume:

$$\frac{G_{(1-I)}^{E^{\text{phys}}}}{n^T RT} = x_1 x_I \beta_1 \tag{37d}$$

and for the cosolvent-salt mixture:

$$\frac{G_{(2-I)}^{E^{\text{phys}}}}{n^T RT} = x_2 x_I \beta_2 \tag{37e}$$

where x_I is the sum of the mole fractions of cation and anion:

$$x_I = x_C + x_A. \tag{37f}$$

Here β_1 and β_2 are specific interaction coefficients, respectively, for the water-salt and the cosolvent-salt systems. These coefficients are determined from salt/single-solvent data.

All coefficients in the chemical and physical contributions to G^E can be obtained from binary data alone. Therefore, when the long-range contribution is added, the model could predict phase equilibria in ternary systems. Using only pure-component and binary data to fix model parameters, fair predicted results have been obtained for ternary vapor-liquid equilibria. However, representation of ternary data can be improved by taking into account the direct effect of salt on interactions between water and cosolvent.

The physical contribution to the excess Gibbs energy of the ternary system is given by:

$$\frac{G^{E^{\text{phys, (sym)}}}}{n^T RT} = q\phi_1\phi_2[A(1 + bx_I) + B\,\phi_2 + C\phi_1\phi_2] + x_1 x_I \beta_1 + x_2 x_I \beta_2 \tag{37g}$$

where b is the only ternary parameter. In Eq. 37g, as indicated by superscript (sym), the standard states for all components are the pure liquids. To use Eq. 37g in combination with the other contributions to the excess Gibbs energy in Eq. 36, Eq. 37g must be normalized to the standard state for the ions defined earlier. This normalization is easily achieved by:

$$\frac{G^{E^{\text{phys}}}}{n^T\,\text{RT}}=\frac{G^{E^{\text{phys, (sym)}}}}{n^T\,\text{RT}}-x_I\,\ln(\gamma_I^{\infty})=\frac{G^{E^{\text{phys, (sym)}}}}{n^T\,\text{RT}}-x_I\beta_1 \tag{37h}$$

The properly normalized physical contribution to G^E is:

$$\frac{G^{E^{\text{phys}}}}{n^T\,\text{RT}}=q\phi_1\phi_2[A(1+bx_I)+B\phi_2+C\phi_1\phi_2] + x_1x_I\beta_1+x_2x_I\beta_2-x_I\beta_1. \tag{37i}$$

For the ions, parameters q_k are calculated using crystallographic radius r_k (Marcus, 1985):

$$q_k=\frac{(4/3)\pi r_k^3}{v_{\text{ref}}/N_{Av}}. \tag{37j}$$

where N_{Av} is Avogadro's number and $v_{\text{ref}}=v(\text{CH}_2)=15.17\ \text{cm}^3/\text{mol}$ (Abrams and Prausnitz, 1975). For convenience, all q parameters are normalized (as UNIQUAC r parameters) using the volume of CH_2. Table 1b shows q parameters for ions used in this work. For calculation of the activity coefficients from Eq. 37i, q_I is found from:

$$q_I=(q_C\nu_C+q_A\nu_A)/\nu. \tag{37k}$$

Activity coefficients $\gamma^{(\text{phys})}$ are obtained using Eqs. 37a and 37i. Expressions for these activity coefficients are given in Appendix IV.

Long-range interactions

The chemical and physical contributions to the Gibbs energy describe the short-range interactions. They are obtained within the Lewis-Randall framework, where the independent variables are temperature T, pressure P, and the mole numbers of all species n_k. However, the long-range interactions, represented by the Debye-Hückel expression, are calculated in the McMillan-Mayer framework. Here the independent variables are temperature T, volume V, the mole numbers of the solute species n_j, and the chemical potentials of the solvents μ_1 and μ_2. To maintain consistency, we need to convert the activity coefficients from the McMillan-Mayer to the Lewis-Randall framework. Pailthorpe et al. (1984) describe conversion for a single-solvent system, and Cardoso and O'Connell (1987) show a method for conversion for a mixed-solvent system with one salt.

The McMillan-Mayer framework considers a mixed-solvent solution of one salt as an effective one-component system where the mixed solvent appears only as a dielectric medium. The standard state for each ion is always the ideal dilute solution in the solvent mixture at unit mole fraction. As mentioned previously, the standard state for each ion is the ideal dilute solution in water at unit mole fraction. This apparent discrepancy is inherent in the McMillan-Mayer framework, as pointed out by Wu and Lee (1992). Fortunately, this apparent discrepancy has no significance because we are here concerned only with long-range forces. Therefore, the two standard states are identical; when only long-range forces are considered, the chemical potential of an ion in an ideal dilute solution in water is the same as that in an ideal dilute solution of some other solvent, provided only that the mole fraction of ion in one solvent is identical to that in the other. Regardless of solvent, the activity coefficient of ion k due to long-range forces is always normalized by $\gamma_k^{LR}\rightarrow 1$ as $x_k\rightarrow 0$.

For solvents 1 and 2, the long-range contributions to the activity coefficients in the Lewis-Randall framework are given by:

$$\text{RT}\,\ln(\gamma_1^{LR})=-(\bar{v}_1)\cdot\Pi^{\text{DH}} \tag{38a}$$

$$\text{RT}\,\ln(\gamma_2^{LR})=-(\bar{v}_2)\cdot\Pi^{\text{DH}} \tag{38b}$$

These equations are essentially equivalent to Eq. 12 in Cardoso and O'Connell (1987) and to Eq. 918.3 in Fowler and Guggenheim (1952).

Long-range forces are responsible for a Debye-Hückel osmotic pressure designated by Π^{DH}; it is given by McQuarrie (1973):

$$\frac{\Pi^{\text{DH}}}{kT}=-\frac{\kappa^3 f(\kappa d)}{24\pi} \tag{38c}$$

$$f(\kappa d)=\frac{3}{(\kappa d)^3}\left[1+\kappa d-\frac{1}{1+\kappa d}-2\,\ln(1+\kappa d)\right] \tag{38d}$$

The Debye length is κ^{-1}. Its inverse square is given by:

$$\kappa^2=\frac{4\pi e^2\left(\sum_k x_k z_k^2\right)}{kTDv} \tag{38e}$$

Here, e is the elementary charge, z_k is the charge on ion k, d is the distance of closest approach between two ions, k is the Boltzmann constant, D is the dielectric constant, and v is the molar volume of the mixture. We set $d=0.4$ nm. Index k in the summation includes all ionic species (cations and anions). In the absence of other information, the partial molar volumes of the solvents are approximated by pure-component volumes. The partial molar volume of the salt is neglected; therefore, the conversion between the McMillan-Mayer and the Lewis-Randall system does not appear.

The long-range activity coefficient of ion k in the Lewis-Randall system is given by:

$$\ln(\gamma_k^{LR})=-\frac{z_i^2 e^2}{2DkT}\frac{\kappa}{1+\kappa d}. \tag{38f}$$

This equation is essentially equivalent to Eq. 13a in Cardoso and O'Connell (1987) and Eq. 918.10 in Fowler and Guggenheim (1952).

The mean (long-range) ionic activity coefficient is then given by:

$$\ln(\gamma_{\pm}^{LR})=-\frac{|z_C z_A|e^2}{2DkT}\frac{\kappa}{1+\kappa d}. \tag{38g}$$

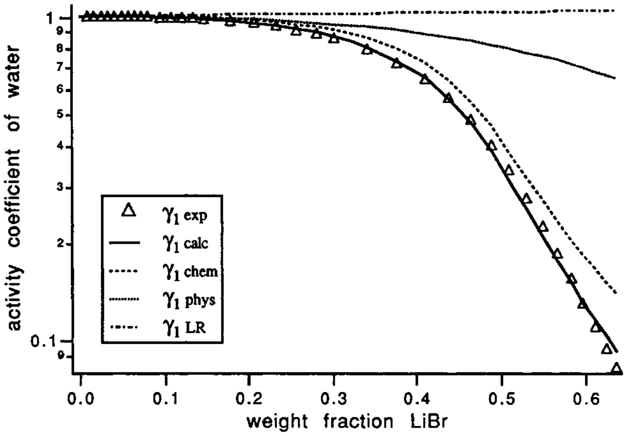

Figure 1. Contributions to the activity coefficient of water for aqueous lithium bromide at 25°C.

The dielectric constant of the mixture is calculated by a volume-fraction mixing rule (Harvey, 1987):

$$D = \phi_1 D_1 + \phi_2 D_2 \tag{38h}$$

where ϕ is the volume fraction on a salt-free basis. Akhadov (1981) gives experimental dielectric constants of some pure and mixed liquids.

In Eq. 38e, the molar volume of the mixture v is approximated by the molar volume of the salt-free mixture, using additivity (Amagat's Law).

Results and Discussion

Model parameters are obtained by regression of experimental data as discussed in Appendix V. Results are represented by the average deviation between experimental (exp) and calculated (calc) quantities:

$$\langle \Delta Q \rangle = \left[\sum_{l}^{J} \left| Q_l^{(\text{exp})} - Q_l^{(\text{calc})} \right| \right] / J \tag{39}$$

where Q is the pressure P, or the vapor mole fraction y or the logarithm of the mean ionic activity coefficient $\ln(\gamma_\pm)$. J is the number of experimental data.

Solvent-salt binary systems

For representation of binary solvent-salt data, two adjustable parameters are needed: one parameter is for the chemical contribution (k^0) and the other (β) is for the physical contribution. Figures 1 and 2 illustrate the relative magnitudes of contributions to the activity coefficients of water and salt in an aqueous solution of lithium bromide at 25°C. The chemical contribution is dominant at high salt concentration. The long-range contribution is important only at low salt concentrations and has little effect on the water activity coefficient.

The model gives good agreement between experimental and calculated vapor pressures as shown in Figure 3. Tables 2a and 2b give model parameters and average deviations for some aqueous and nonaqueous salt solutions.

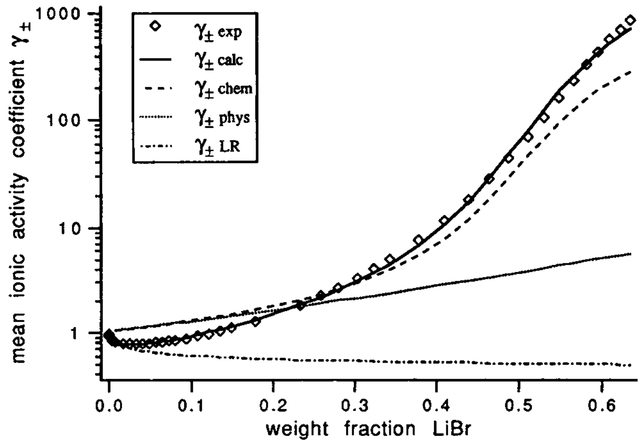

Figure 2. Contributions to the mean ionic activity coefficient for aqueous lithium bromide at 25°C.

Temperature dependence of parameters

To represent the vapor pressures of salt solutions as a function of temperature, we assume for the temperature dependence of the equilibrium constants:

$$\ln(k_1^0) = a_1 + b_1/T \tag{40}$$

and

$$\ln(k_2^0) = a_2 + b_2/T \tag{41}$$

where a and b are adjustable parameters. Physical parameters β_1 and β_2 are taken as temperature-independent.

Table 3 summarizes the representation of vapor pressures of some binary aqueous and nonaqueous salt solutions over a range of temperatures.

Ternary systems with water, alcohol, and salt

For calculation of ternary-phase equilibria, binary data are required not only for the two salt-containing binaries but also for the salt-free binary system: either vapor-liquid or liquid-liquid equilibrium data or, preferably, both. By data regres-

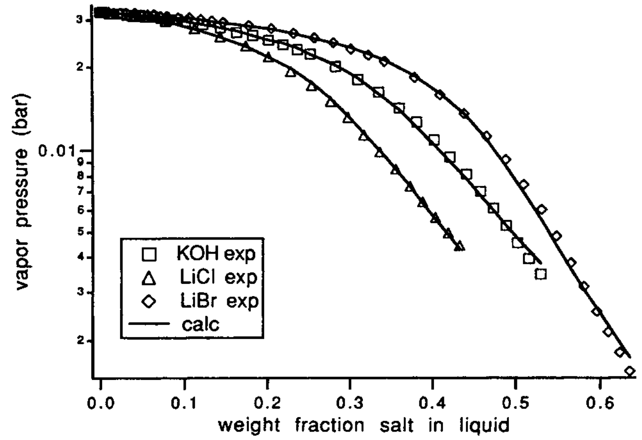

Figure 3. Vapor pressures of aqueous solutions of LiBr, LiCl and KOH at 25°C.

Table 2a. Results and Parameters for Aqueous Salt Solutions

Salt	t [°C]	Max. wt. % Salt	$\ln(k_1^0)$	β_1	$\langle \Delta p \rangle$ [%]	Ref.
KBr	25	39.6	−0.399	0.0	0.1	1
KOH	25	52.9	1.859	−1.374	1.2	1
LiBr	25	63.5	2.587	−2.559	1.7	1
LiBr	75	50.8	1.936	−3.000	0.1	2
LiCl	25	43.3	1.808	−2.214	1.1	1
LiCl	60	34.2	1.500	−2.254	0.5	1
LiCl	75	42.8	1.863	0.0	3.9	2
NaCl	25	26.4	1.314	0.410	0.1	1
$CaCl_2$	25	52.6	0.968	−3.218	0.9	3
$MgCl_2$	25	36.1	1.434	−3.950	0.9	4

1 = Hammer and Wu (1972) 3 = Staples and Nuttal (1977)
2 = Sada and Morisue (1975) 4 = Goldberg and Nuttal (1978)

Table 2b. Results and Parameters for Nonaqueous Salt Solutions

System	t [°C]	Max. wt. % Salt	$\ln(k_2^0)$	β_2	$\langle \Delta p \rangle$ [%]	Ref.
Methanol/LiCl	60	23.9	1.019	−2.650	0.9	1
Methanol/LiBr	30	58.2	2.804	−1.413	3.3	2
Methanol/$CaCl_2$	25	22.6	0.656	0.0	1.7	4, 5
Isopropanol/LiBr	75	23.6	2.529	3.045	0.3	3
Isopropanol/LiCl	75	12.6	−1.550	0.0	1.8	3

1 = Hala (1983) 4 = Bixon et al. (1979)
2 = Renz (1980) 5 = Kumagae et al. (1992)
3 = Sada and Morisue (1975)

sion, parameters A, B and C in Eq. 37i are obtained. For many vapor-liquid equilibria, only two adjustable parameters (A and B) are required to represent the data. However, to fit also liquid-liquid equilibria, a third parameter (C) is usually necessary.

Vapor-liquid equilibria

Table 4 shows results and parameters for some salt-free binary mixtures. Table 5 gives vapor-liquid equilibrium results for some ternary systems with water, alcohol and salt. Two cases are shown: case a gives results predicted by parameters obtained only from binary data; in case b, the ternary coefficient is regressed from ternary vapor-liquid equilibrium data.

Ternary results for isopropanol/water/LiCl could be significantly improved when only the chemical equilibrium parameter was used for the binary solvent-salt systems. For the binary system Isopropanol-$CaCl_2$, no data were available. Therefore, the equilibrium constant parameter k_2^0 was obtained from the ternary vapor-liquid equilibrium data; $\ln k_2^0 = -0.846$.

Table 4. Vapor-Liquid Equilibria for Aqueous Salt-free Binary Systems

Cosolvent	t [°C]	A	B	C	$\langle \Delta p \rangle$ [%]	$\langle \Delta y \rangle$ [%]	Ref.
Methanol	30	0.360	0.136	0.0	1.3	0.4	2
Methanol	60	0.512	0.044	0.0	0.7	0.5	3
Isopropanol	75	0.992	0.206	−0.370	0.1	0.4	1

1 = Sada and Morisue (1975)
2 = Gmehling and Onken (1977)
3 = Hala (1983)

Figure 4 shows ternary vapor-liquid equilibria for water/isopropanol/lithium bromide at 75°C. The lines, predicted from binary parameters, show good agreement with experiment.

Liquid-liquid equilibria

In liquid-liquid equilibria for typical water-alcohol-salt systems, the solubility of salt in the water-free cosolvent is extremely low. In that event, we assume that the ions form no solvates with the cosolvent: that is, chemical equilibrium parameter k_2^0 is zero. We then have only one adjustable parameter β_2 for the cosolvent-salt binary system. If no data are available for the binary cosolvent-salt system, we must find β_2 from ternary data. Model parameters for binary systems water-salt and water-cosolvent are obtained as outlined for vapor-liquid equilibria. If the salt-free system forms two liquid phases, vapor-liquid and liquid-liquid data are used together to obtain the model parameters. Table 6 gives results for vapor-liquid and liquid-liquid equilibria in salt-free water-organic solvent systems.

Table 7 shows results for liquid-liquid equilibria for some water-alcohol-salt systems. The accuracy of the calculated results is represented by the average deviation $\langle \Delta Z \rangle$ as proposed by Sørensen and Arlt (1980):

$$\langle \Delta z \rangle = \sqrt{\frac{\sum_{l}^{J} \sum_{r}^{M} [(z_{l,r}^{\prime\,(\mathrm{exp})} - z_{l,r}^{\prime\,(\mathrm{calc})})^2 + (z_{l,r}^{\prime\prime\,(\mathrm{exp})} - z_{l,r}^{\prime\prime\,(\mathrm{calc})})^2]}{2JM}} \quad [\mathrm{mol}\ \%] \tag{42}$$

where J is the number of experimental data, M the number of components in the solution ($M = 3$), and z is the mole fraction of water, cosolvent or salt, defined as:

Table 3. Results for Binary Solvent-Salt Solutions over a Range of Temperatures

System	t [°C]	Max. wt. % Salt	a_1/a_2	b_1/b_2	β_1/β_2	$\langle \Delta p \rangle$ [%]	Ref.
Water/LiBr	20-170	70	−1.319	1,164	−2.559	2.1	1, 8, 7
Water/NaCl	0-110	28	−0.883	655	0.410	0.2	4, 2
Water/K_2CO_3	25-90	51	−4.988	2,525	0.078	0.6	3
Methanol/LiBr	−10-200	60	−2.827	1,707	−1.413	3.2	5, 6, 8, 7

1 = Löwer (1960) 3 = Puchkov and Kurochkina (1970) 5 = Renz (1980) 7 = Belherazem (1985)
2 = Kaufmann (1968) 4 = Hammer and Wu (1972) 6 = Eichholz (1982) 8 = Raatschen (1986)

Table 5. Results for Ternary Aqueous Vapor-Liquid Equilibria

Cosolvent and Salt	t [°C]	Max. wt. % Salt	b	$\langle \Delta p \rangle$ [%]	$\langle \Delta y \rangle$ [%]	Ref.	Case
Isopropanol/LiBr	75	52	0.0	4.7	1.1	1	a
			−0.564	3.7	0.9		b
Methanol/LiCl	60	30	0.0	6.3	4.0	1	a
			4.03	2.5	1.4		b
Methanol/LiBr	30	61	0.0	15.5	5.1	2, 3, 4	a
			7.20	5.2	5.1		b
Isopropanol/LiCl	75	33	0.0	3.3	0.8	1	a
			0.390	3.1	0.6		b
Isopropanol/$CaCl_2$	75	49	0.0	6.6	1.2	1	

1 = Sada and Morisue (1975) 3 = Belherazem (1985)
2 = Eichholz (1982) 4 = Raatschen (1986)

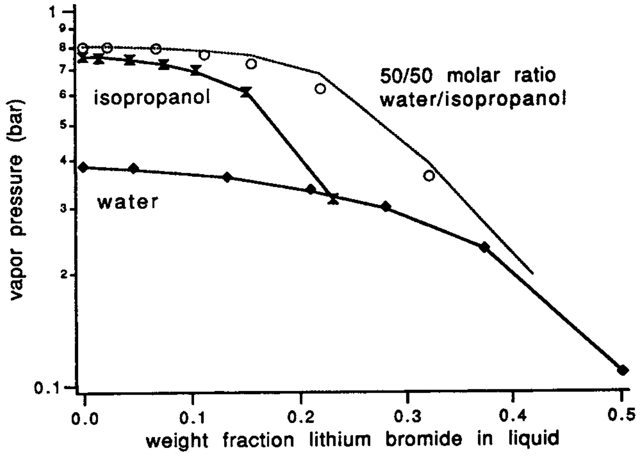

Figure 4. Vapor-liquid equilibria for the system water/isopropanol/lithium bromide at 75°C (Isada and Morisue, 1975).

Lines are calculated; points are experimental.

$$z_r = \frac{n_r}{n_1 + n_2 + n_E} \tag{43}$$

Figures 5a, 5b and 5c show results for ternary liquid-liquid equilibria of water/n-butanol/sodium chloride. Agreement between calculated and experimental data is good. The concentration of the salt in the organic phase is shown on an enlarged scale; the concentration is extremely small and sensitive to tiny errors in the water concentration in the organic phase. Although the deviation for the salt concentration is appreciable, the accuracy is sufficient for most practical purposes.

Conclusion

The framework of this work provides a thermodynamic procedure for calculating vapor-liquid and liquid-liquid equilibria in ternary systems containing two solvents and one salt. The molecular-thermodynamic model developed here gives an approximate, but useful, basis for obtaining good quantitative results from few input data; all adjustable parameters, but one, can be obtained from pure-component and binary data. The model is especially designed to include solutions with high salt contents, as encountered, for example, in extractive-crystallization operations.

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Notation

A = anion
A,B,C = model parameter
C = cation
$C_{i,j}$ = cation solvated with i water and j cosolvent molecules
D = dielectric constant
G = Gibbs energy
K = equilibrium constant
J = number of experimental data points
M = number of components
N = maximum solvation number
$\langle N \rangle$ = average solvation number
N_{Av} = Avogadro Number

Table 6. Vapor-Liquid and Liquid-Liquid Equilibria for Aqueous Salt-free Binary Systems

Cosolvent	t [°C]	A	B	C	$\langle \Delta p \rangle$ [%]	$\langle \Delta y \rangle$ [%]	$\langle \Delta z \rangle$ [%]	Ref.
n-butanol	25	1.285	0.388	−1.276	1.6	0.7	0.02	2, 3
i-butanol	25	1.331	0.526	−1.535	0.6	0.9	0.02	2, 3
n-propanol	25	0.971	0.350	−0.118	1.5	1.8	—	2, 3
i-propanol	25	0.841	0.499	−0.277	0.3	0.5	—	2, 3
acetonitrile	25	1.320	0.701	−0.634	2.1	2.2	—	2
2-butanone	25	1.028	0.717	−0.546	7.0	2.3	0.03	1

1 = Meissner and Stokes (1944)
2 = Gmehling and Onken (1977)
3 = Sørensen and Arlt (1980)

Table 7. Results for Ternary Aqueous Liquid-Liquid Systems

Cosolvent and Salt	t [°C]	Max. wt. % Salt	β_2	b	$\langle \Delta z \rangle$ [%]	Ref.
n-butanol/NaCl	25	26	3.396	1.382	0.7	3
i-butanol/NaCl	25	26	3.102	1.400	1.3	3
n-propanol/NaCl	25	26	2.724	2.625	1.7	3
i-propanol/NaCl	25	26	2.963	2.984	1.0	3
acetonitrile/KBr	25	29	2.591	0.0	1.1	2
2-butanone/$CaCl_2$	25	44	3.366	0.0	1.5	1

1 = Meissner and Stokes (1944) 2 = Renard and Olberg (1952) 3 = De Santis et al. (1976)

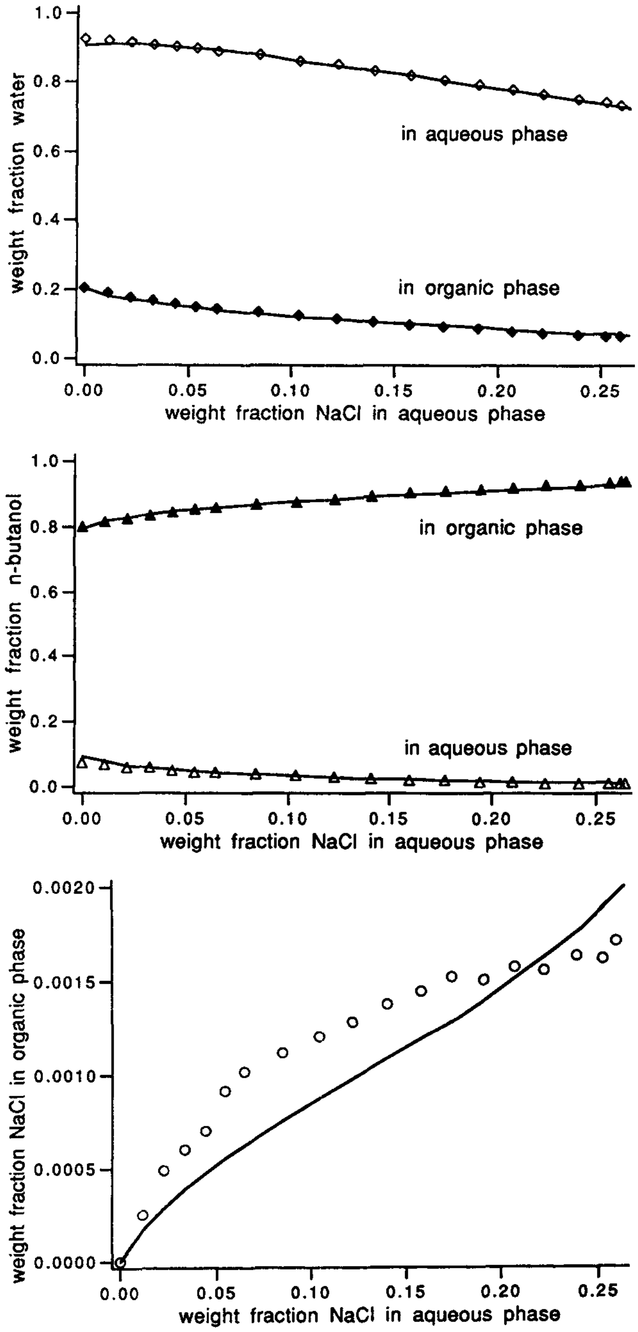

Figure 5. Liquid-liquid equilibria for the system water/*n*-butanol/sodium chloride at 25°C (DeSantis et al., 1976).

Lines are calculated; points are experimental.

P = pressure
T = absolute temperature
d = distance of closest approach between two ions
e = elementary charge
k = Boltzmann constant
k^0 = equilibrium constant parameter
n = mole number
t = temperature in Celsius
x = mole fraction in liquid based on complete dissociation
y = mole fraction in vapor
z = mole fraction in liquid for undissociated components

Greek letters

γ = activity coefficient
ϕ = volume fraction
κ = inverse Debye length
μ = chemical potential
ν = stoichiometric coefficient
ξ = true mole fraction
Π = osmotic pressure
φ = fugacity coefficient

Superscripts

b = bound
chem = chemical contribution
DH = Debye-Hückel
E = excess property
f = free
LR = long-range contribution
phys = physical contribution
sat = saturation
t = total number of true species considering formation of solvates
T = total number of species without formation of solvates
Θ = standard state
∞ = infinite dilution
$'$ = liquid phase 1
$''$ = liquid phase 2

Subscripts

A = anion
calc = calculated
C = cation
exp = experimental
E = electrolyte
i = number of solvated water molecules
j = number of solvated cosolvent molecules
k = index for water, cosolvent, cation and anion
l = index for water, cosolvent, cation and anion
r = index for water, cosolvent and salt (and mean ionic properties)
1 = water
2 = organic solvent
$\pm$ = mean ionic value
0 = unsolvated

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Appendix I: Derivation of Activity Coefficients from the Chemical Model

As indicated earlier, the basic assumption of the chemical model is a stepwise solvation with a typical equilibrium constant $K_{i,j}$ for each step.

Equilibrium	Equilibrium Constant	
$C_0 + i\,(\text{solvent 1}) + j\,(\text{solvent 2}) \rightarrow C_{i,j}$	$K_{i,j}$	(AI1)

where C_0 represents the unsolvated cation and $C_{i,j}$ is the solvated cation with i molecules of solvent 1 (water) and j molecules of solvent 2 (organic cosolvent). In the equations below, we use a notation similar to that of Stokes and Robinson (1973) and Schönert (1986).

The solvent molecules appear either as free (f) or as bound (b) solvent molecules in the solvates. From a mass balance, we obtain the total number of solvent molecules, n_1^t and n_2^t. N is the maximum solvation number:

$$n_1^t = n_1^f + \sum_{i=0}^{N} \sum_{j=0}^{N-i} i n_{C_{i,j}} \tag{AI2}$$

$$n_2^t = n_2^f + \sum_{i=0}^{N} \sum_{j=0}^{N-i} j n_{C_{i,j}} \tag{AI3}$$

and the total number of cations is:

$$n_C^t = \sum_{i=0}^{N} \sum_{j=0}^{N-i} n_{C_{i,j}}. \tag{AI4}$$

The total number of all species in the solution is given by:

$$n^t = n_1^f + n_2^f + \sum_{i=0}^{N} \sum_{j=0}^{N-i} n_{C_{i,j}} + n_A. \tag{AI5}$$

These relations are used to define the mole fractions of the free solvent molecules:

$$\xi_1^f = \frac{n_1^f}{n^t} \qquad \xi_2^f = \frac{n_2^f}{n^t}. \tag{AI6}$$

The chemical equilibrium is expressed in terms of activities (a):

$$\frac{a_{C_{i,j}}}{a_{C_0} (a_1^f)^i (a_2^f)^j} = K_{i,j} \tag{AI7}$$

For all species, the activity is assumed equal to the mole fraction:

$$a_k = \xi_k. \tag{AI8}$$

The ratio of solvated cations to unsolvated cations is:

$$\frac{n_{C_{i,j}}}{n_{C_0}} = K_{i,j} \cdot (\xi_1^f)^i \cdot (\xi_2^f)^j. \tag{AI9}$$

The total number of bound solvent molecules can now be found by:

$$n_1^b = n_{C_0}\cdot\sum_{i=0}^{N}\sum_{j=0}^{N-i} i\cdot K_{i,j}\cdot(\xi_1^f)^i\cdot(\xi_2^f)^j \tag{AI10}$$

and

$$n_2^b = n_{C_0}\cdot\sum_{i=0}^{N}\sum_{j=0}^{N-i} j\cdot K_{i,j}\cdot(\xi_1^f)^i\cdot(\xi_2^f)^j \tag{AI11}$$

with the short-hand notation σ for the double sums in Eqs. AI10 and AI11, this gives:

$$n_1^b = n_{C_0}\cdot\sigma_1 \tag{AI12}$$

and

$$n_2^b = n_{C_0}\cdot\sigma_2. \tag{AI13}$$

We first note that the total number of cations is:

$$n_C^t = n_{C_0}\cdot\sum_{i=0}^{N}\sum_{j=0}^{N-i} K_{i,j}\cdot(\xi_1^f)^i\cdot(\xi_2^f)^j \tag{AI14}$$

and the double sum in Eq. AI14 abbreviated by Σ gives:

$$n_C^t = n_{C_0}\cdot\Sigma. \tag{AI15}$$

We then define the average solvation numbers:

$$\langle N_1\rangle = \frac{n_1^b}{n_C^t} = \frac{\sigma_1}{\Sigma} \tag{AI16}$$

and

$$\langle N_2\rangle = \frac{n_2^b}{n_C^t} = \frac{\sigma_2}{\Sigma}. \tag{AI17}$$

The average solvation numbers describe the number of bound solvent molecules per cation.

From the average solvation numbers we can calculate the "true" mole fractions of the free solvent molecules:

$$\xi_1^f = \frac{n_1^f}{n^t} = \frac{n_1^t - n_1^b}{[n_1^t - n_1^b] + [n_2^t - n_2^b] + n_C^t + n_A} \tag{AI18}$$

and

$$\xi_2^f = \frac{n_2^f}{n^t} = \frac{n_2^t - n_2^b}{[n_1^t - n_1^b] + [n_2^t - n_2^b] + n_C^t + n_A}. \tag{AI19}$$

With the average solvation numbers, we obtain:

$$\xi_1^f = \frac{n_1^t - \langle N_1\rangle n_C^t}{[n_1^t - \langle N_1\rangle\ n_C^t] + [n_2^t - \langle N_2\rangle\ n_C^t] + n_C^t + n_A} \tag{AI20}$$

and

$$\xi_2^f = \frac{n_2^t - \langle N_2\rangle n_C^t}{[n_1^t - \langle N_1\rangle\ n_C^t] + [n_2^t - \langle N_2\rangle\ n_C^t] + n_C^t + n_A} \tag{AI21}$$

using the mole fractions based on complete dissociation

$$\xi_1^f = \frac{x_1 - \langle N_1\rangle\ x_C}{[x_1 - \langle N_1\rangle\ x_C] + [x_2 - \langle N_2\rangle\ x_C] + x_C + x_A} \tag{AI22}$$

and

$$\xi_2^f = \frac{x_2 - \langle N_2\rangle\ x_C}{[x_1 - \langle N_1\rangle\ x_C] + [x_2 - \langle N_2\rangle\ x_C] + x_C + x_A}. \tag{AI23}$$

For the mole fraction of the unsolvated ions we have:

$$\xi_{C_0} = \frac{n_{C_0}}{n^t} = \frac{n_{C_0}}{[n_1^t - \langle N_1\rangle\ n_C^t] + [n_2^t - \langle N_2\rangle\ n_C^t] + n_C^t + n_A} \tag{AI24}$$

Using Eq. AI15 and the complete-dissociation mole fractions, we obtain:

$$\xi_{C_0} = \frac{x_C/\Sigma}{[x_1 - \langle N_1\rangle\ x_C] + [x_2 - \langle N_2\rangle\ x_C] + x_C + x_A}. \tag{AI25}$$

The mole fractions of the free solvents appear implicitly in the equations. Therefore, the chemical equilibrium has to be solved iteratively.

As shown in Appendix II, the condition of chemical equilibrium gives:

$$\mu_1 = \mu_1^f \tag{AI26}$$

and

$$\mu_2 = \mu_2^f. \tag{AI27}$$

For the chemical contribution to the activity coefficient:

$$\mu_1^\Theta + \mathrm{RT}\ \ln(x_1\gamma_1^{\text{chem}}) = \mu_1^{f\Theta} + \mathrm{RT}\ \ln(\xi_1^f) \tag{AI28}$$

and

$$\mu_2^\Theta + \mathrm{RT}\ \ln(x_2\gamma_2^{\text{chem}}) = \mu_2^{f\Theta} + \mathrm{RT}\ \ln(\xi_2^f), \tag{AI29}$$

we obtain for the solvents:

$$\ln(\gamma_1^{\text{chem}}) = \ln\left(\frac{\xi_1^f}{x_1}\right) \tag{AI30}$$

and

$$\ln(\gamma_2^{\text{chem}}) = \ln\left(\frac{\xi_2^f}{x_2}\right) \tag{AI31}$$

where the mole fractions x are based on complete dissociation without solvation and ξ^f is the mole fraction of the free solvent.

Similar to Eqs. AI26 and AI27, for the chemical potential of the cations:

$$\mu_C = \mu_{C_0}. \tag{AI32}$$

By the definition of the standard state of the ions, the activity coefficients are normalized by:

$$\gamma_C = 1 \quad \text{as} \quad x_C \to 0 \quad x_1 \to 1. \tag{AI33}$$

Using activity coefficients we obtain:

$$\mu_C = \mu_C^{\ominus} + \mathrm{RT}\ \ln(x_C\gamma_C^{\mathrm{chem}}) = \mu_{C_0}^{\ominus} + \mathrm{RT}\ \ln(\xi_{C_0}). \qquad \text{(AI34)}$$

The chemical contribution to the activity coefficients of the cations is:

$$\ln(\gamma_C^{\mathrm{chem}}) = \ln\left(\frac{\xi_{C_0}}{x_C}\right) + \frac{1}{\mathrm{RT}}\ [\mu_{C_0}^{\ominus} - \mu_C^{\theta}]. \qquad \text{(AI35)}$$

The last term in Eq. AI35 gives the connection between the symmetrically normalized chemical model and the standard state defined on the unsymmetrical convention. The last term in brackets at infinite dilution in water is given by:

$$\frac{1}{\mathrm{RT}}\ [\mu_{C_0}^{\ominus} - \mu_C^{\ominus}] = \lim_{\substack{x_C \to 0 \\ x_w \to 1}} \left[\ln\left(\frac{x_C\ \gamma_C^{\mathrm{chem}}}{\xi_{C_0}}\right)\right] \qquad \text{(AI36)}$$

$$\frac{1}{\mathrm{RT}}\ [\mu_{C_0}^{\ominus} - \mu_C^{\ominus}] = \ln(\Sigma^{\ominus}). \qquad \text{(AI37)}$$

With Σ defined in Eq. AI15,

$$(\Sigma^{\ominus}) = \sum_{i=0}^{N} K_{i,j=0} \qquad \text{(AI38)}$$

Finally, we derive the chemical contribution to the activity coefficients of the cation:

$$\ln(\gamma_C^{\mathrm{chem}}) = \ln\left(\frac{\xi_{C_0}}{x_C}\right) + \ln(\Sigma^{\ominus}) \qquad \text{(AI39)}$$

and in the same way, for the anion:

$$\ln(\gamma_A^{\mathrm{chem}}) = \ln\left(\frac{\xi_{A_0}}{x_A}\right). \qquad \text{(AI40)}$$

In Eq. AI40, the last term in Eq. AI39 does not appear because we assumed that the anion is unsolvated. (All equilibrium constants are zero.) The mean ionic activity coefficient is found from:

$$\ln(\gamma_{\pm}^{\mathrm{chem}}) = \frac{1}{\nu}\ [\nu_C \ln(\gamma_C^{\mathrm{chem}}) + \nu_A \ln(\gamma_A^{\mathrm{chem}})]. \qquad \text{(AI41)}$$

Appendix II: Contribution of the Chemical Model to the Excess Gibbs Energy

Consider a ternary solution containing water, cosolvent, and salt. Water is indicated by subscript 1 and cosolvent by subscript 2. Electrolyte E is assumed to be completely dissociated into cations C and anions A. The equations are derived generally where both ion species can form solvates.

The Gibbs energy of the real solution is given by Eq. 17:

$$G = n_1\mu_1 + n_2\mu_2 + n_C\mu_C + n_A\mu_A. \qquad \text{(AII1)}$$

The Gibbs energy can also be written as the sum of the chemical potentials of all true species in the chemical equilibrium:

$$G^{\mathrm{chem}} = n_1^f\mu_1^f + n_2^f\mu_2^f + \sum_{i=0}^{N}\sum_{j=0}^{N-i} n_{C_{i,j}}\mu_{C_{i,j}} + \sum_{i=0}^{N}\sum_{j=0}^{N-i} n_{A_{i,j}}\mu_{A_{i,j}}. \qquad \text{(AII2)}$$

The chemical equilibrium condition gives:

$$\mu_{C_{i,j}} = \mu_{C_0} + i\mu_1^f + j\mu_2^f \qquad \text{(AII3)}$$

and

$$\mu_{A_{i,j}} = \mu_{A_0} + i\mu_1^f + j\mu_2^f. \qquad \text{(AII4)}$$

By combining Eqs. AII3, AII4 and AII2 we obtain:

$$\begin{aligned} G^{\mathrm{chem}} = {} & \left\{ n_1^f + \sum_{i=0}^{N}\sum_{j=0}^{N-i} in_{C_{i,j}} + \sum_{i=0}^{N}\sum_{j=0}^{N-i} in_{A_{i,j}} \right\} \mu_1^f \\ & + \left\{ n_2^f + \sum_{i=0}^{N}\sum_{j=0}^{N-i} jn_{C_{i,j}} + \sum_{i=0}^{N}\sum_{j=0}^{N-i} jn_{A_{i,j}} \right\} \mu_2^f \\ & + \left\{ \sum_{i=0}^{N}\sum_{j=0}^{N-i} n_{C_{i,j}} \right\} \mu_{C_0} + \left\{ \sum_{i=0}^{N}\sum_{j=0}^{N-i} n_{A_{i,j}} \right\} \mu_{A_0}. \end{aligned} \qquad \text{(AII5)}$$

Using the mass balance this gives:

$$G^{\mathrm{chem}} = \{n_1\}\ \mu_1^f + \{n_2\}\ \mu_2^f + \{n_C\}\ \mu_{C_0} + \{n_A\}\ \mu_{A_0} \qquad \text{(AII6)}$$

Comparing Eqs. AII6 and AII1 gives the following relations:

$$\mu_1 = \mu_1^f \qquad \text{(AII7)}$$

$$\mu_2 = \mu_2^f \qquad \text{(AII8)}$$

$$\mu_C = \mu_{C_0} \qquad \text{(AII9)}$$

$$\mu_A = \mu_{A_0} \qquad \text{(AII10)}$$

The Gibbs energy of the ideal mixture is defined by Eq. 18:

$$G^{\mathrm{ideal}} = n_1\mu_1^{\ominus} + n_2\mu_2^{\ominus} + n_C\mu_C^{\ominus} + n_A\mu_A^{\ominus} + \mathrm{RT}\ \sum_k n_k \ln(x_k) \qquad \text{(AII11)}$$

As standard state for the solvent components, the pure liquids are used. The standard state for cation and anion is taken as a hypothetical ideal dilute solution in solvent 1 (water) at unit mole fraction, all at system temperature and pressure.

Introducing activity coefficients, the chemical potentials are:

$$\mu_k = \mu_k^{\ominus} + \mathrm{RT}\ \ln(x_k\gamma_k^{\mathrm{chem}}). \qquad \text{(AII12)}$$

The excess Gibbs energy is given as:

$$G^{E^{\text{chem}}} = G^{\text{chem}} - G^{\text{ideal}}. \qquad \text{(AII13)}$$

This gives for the contribution of the chemical model to the Gibbs energy:

$$\frac{G^{E^{\text{chem}}}}{\text{RT}} = n_1 \ln(\gamma_1^{\text{chem}}) + n_2 \ln(\gamma_2^{\text{chem}}) + n_C \ln(\gamma_C^{\text{chem}}) + n_A \ln(\gamma_A^{\text{chem}}). \qquad \text{(AII14)}$$

With the equations for the activity coefficients (AI30, AI31, AI39 and AI40), we obtain:

$$\frac{G^{E^{\text{chem}}}}{n^T\,\text{RT}} = x_1 \ln\left(\frac{\xi_1^f}{x_1}\right) + x_2 \ln\left(\frac{\xi_2^f}{x_2}\right) + x_C \ln\left(\frac{\xi_{C_0}}{x_C}\,\Sigma_C^{\Theta}\right) + x_A \ln\left(\frac{\xi_{A_0}}{x_A}\,\Sigma_A^{\Theta}\right) \qquad \text{(AII15)}$$

Appendix III: Calculation of Chemical Equilibrium Constants

For a binary solvent-salt system with the equilibrium:

$$C_0 + i(\text{solvent}) \leftrightarrow C_i. \qquad \text{(AIII1)}$$

As proposed by Schönert (1986), the equilibrium constant K_i can be written in the form:

$$\ln(K_i) = i \ln(k^0) + \ln \binom{N}{i} \qquad \text{(AIII2)}$$

with the binomial coefficient defined by:

$$\binom{N}{i} = \frac{N!}{i! \cdot (N-i)!} \qquad \text{(AIII3)}$$

$\binom{N}{i}$ is the number of distinguishable ways that i identical molecules can bind with an ion that has N binding sites.

To extend Eq. AIII2 for the equilibrium constant to multisolvent systems, we use the multinomial coefficient.

For the equilibrium constants in the ternary mixture, defined in Eq. 36a, we write:

$$\ln(K_{i,j}) = i \cdot \ln(k_1^0) + j \cdot \ln(k_2^0) + \ln \binom{N}{ij} \qquad \text{(AIII4)}$$

with the multinomial coefficient defined by:

$$\binom{N}{ij} = \left(\frac{N!}{i! \cdot j! \cdot (N-i-j)!}\right). \qquad \text{(AIII5)}$$

Equation AIII4 gives the equilibrium constant for the formation of each possible solvate. For a binary solvent-salt mixture, Eq. AIII4 reduces to Eq. AIII2 with one adjustable parameter. Regressing the equilibrium constants from binary solvent-salt data also fixes the equilibrium constants for the mixed solvates in the ternary system. Equation AIII4 permits calculations of mixed solvates in the ternary mixture using only equilibrium constants obtained from binary solvent-salt data.

Appendix IV: Derivation of the Activity Coefficients from the Physical Contribution

The physical contribution to the excess Gibbs energy is given in Eq. 37i as:

$$\frac{G^{E^{\text{phys}}}}{n^T\,\text{RT}} = q\phi_1\phi_2[A(1 + bx_I) + B\phi_2 + C\phi_1\phi_2] + x_1 x_I \beta_1 + x_2 x_I\, \beta_2 - x_I \beta_1 \qquad \text{(AIV1)}$$

where the volume fractions are defined by

$$\phi_k = \frac{q_k x_k}{q} \qquad q = \sum_k x_k q_k \qquad \text{(AIV2)}$$

The activity coefficients are obtained by taking the derivative of the Gibbs energy with respect to the mole number of each species. This gives:

$$\begin{aligned}\ln(\gamma_1^{\text{phys}}) = {} & Aq_1[\phi_2 - \phi_1\phi_2] + Bq_1[\phi_2^2 - 2\phi_1\phi_2^2] \\ & + Cq_1[2\phi_1\phi_2^2 - 3\phi_1^2\phi_2^2] \\ & + Abq_1\left[\phi_2 x_I - \phi_1\phi_2 x_I \left(1 + \frac{q}{q_1}\right)\right] \\ & + x_I^2\beta_1 + x_2 x_I(\beta_1 - \beta_2)\end{aligned} \qquad \text{(AIV3)}$$

$$\begin{aligned}\ln(\gamma_2^{\text{phys}}) = {} & Aq_2\,[\phi_1 - \phi_1\phi_2] + Bq_2\,[2\phi_1\phi_2 - 2\phi_1\phi_2^2] \\ & + Cq_2\,[2\phi_1^2\phi_2 - 3\phi_1^2\phi_2^2] \\ & + Abq_2\left[\phi_1 x_I - \phi_1\phi_2 x_I \left(1 + \frac{q}{q_2}\right)\right] \\ & + x_I^2\beta_2 + x_1 x_I(\beta_2 - \beta_1)\end{aligned} \qquad \text{(AIV4)}$$

$$\begin{aligned}\ln(\gamma_I^{\text{phys}}) = {} & Aq_I[-\phi_1\phi_2] + Bq_I[-2\phi_1\phi_2^2] + Cq_I[-3\phi_1^2\phi_2^2] \\ & + Ab[\phi_1\phi_2 q - \phi_1\phi_2 x_I(q_I + q)] + x_1^2\beta_1 \\ & + x_2^2\beta_2 + x_1 x_2(\beta_1 + \beta_2) - \beta_1\end{aligned} \qquad \text{(AIV5)}$$

Since we consider cations and anions on an average basis, the ion activity coefficients are identical:

$$\gamma_C^{\text{phys}} = \gamma_A^{\text{phys}} = \gamma_I^{\text{phys}}. \qquad \text{(AIV6)}$$

In the salt free system at infinite dilution, the activity coefficients of solvent components 1 and 2 are:

$$\ln(\gamma_1^{\infty}) = q_1(A + B) \qquad \text{(AIV7)}$$

$$\ln(\gamma_2^{\infty}) = q_2(A) \qquad \text{(AIV8)}$$

Appendix V: Parameter Estimation

For estimation of model parameters, different sets of experimental data are required. For aqueous salt solutions, vapor-pressure data and mean-ionic-activity coefficient data are used. If data are available for the cosolvent-salt system, vapor-pressure data are also used to determine model parameters. The parameters for the salt-free binary mixture A, B and C in Eqs. 37a and 37i are obtained by regressing salt-free vapor-liquid and liquid-liquid equilibrium data.

After fixing all binary model parameters, the model is applied to the ternary mixture. The ternary parameter b in Eq. 37i is now determined by regressing either vapor-liquid or liquid-liquid equilibrium data of the ternary mixture.

The model parameters are obtained by minimizing deviations between experimental and calculated quantities given by the objective function for the vapor-liquid equilibrium data:

$$F=\sum_{l}^{J}\left(Q_l^{(\mathrm{exp})}-Q_l^{(\mathrm{calc})}\right)^2 \tag{AV1}$$

where Q is the type of data used as vapor pressure, vapor composition and mean ionic activity coefficient. J is the number of experimental data points.

In liquid-liquid equilibria the following objective function is used:

$$F=\sum_{l}^{J}\sum_{r}^{M}\left(z_{l,r}'^{(\mathrm{exp})}-z_{l,r}'^{(\mathrm{calc})}\right)^2+\left(z_{l,r}''^{(\mathrm{exp})}-z_{l,r}''^{(\mathrm{calc})}\right)^2 \tag{AV2}$$

where the sum runs over all experimental data points l and all components r. The deviations are expressed in the component mole fractions z for water, cosolvent and salt:

$$z_r=\frac{n_r}{n_1+n_2+n_E} \tag{AV3}$$

To obtain the objective function AV2, the liquid compositions in the two phases have to be calculated by solving the isothermal liquid-liquid flash problem. Therefore a modified subroutine from Prausnitz (1980) was used. Calculation of phase-splitting consumes a high amount of computer time and leads to convergence problems, if the initial estimate of the model parameters is poor. For this reason, an initial estimate of the model parameters is first obtained by using an alternative objective function:

$$F_{\mathrm{init}}=\sum_{l}^{J}\sum_{k}^{M}\left(x_{l,k}'^{(\mathrm{exp})}\,\gamma_{l,k}'^{(\mathrm{calc})}-x_{l,k}''^{(\mathrm{exp})}\,\gamma_{l,k}''^{(\mathrm{calc})}\right)^2 \tag{AV4}$$

where the activity coefficients are calculated with the model equations at phase compositions of the experimental tie lines. With this initial parameter set, the objective function AV2 is minimized.

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