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# Thermodynamics of Vapor-Liquid and Liquid-Liquid Equilibria in Aqueous Systems Containing Organic Solvents and Salts

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# Thermodynamics of Vapor-Liquid and Liquid-Liquid Equilibria in Aqueous Systems Containing Organic Solvents and Salts

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## Abstract:

A semi-empirical 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 step-wise 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.

## 1. 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 /1-24/. 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 and coworkers /25,26/ have presented a semi-empirical 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 /27-30/, but they are also restricted to intermediate salt concentrations.

This work presents an alternate semi-empirical 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, i.e. with much less energy than that required in a triple-effect evaporator /31-33/.

## 2. 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.

$$E \rightarrow \nu_C C + \nu_A A \tag{2.1}$$

where $\nu_C$ and $\nu_A$ are the stoichiometric coefficients. Let

$$\nu = \nu_C + \nu_A \quad . \tag{2.2}$$

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

$$x_k = \frac{n_k}{\sum_l n_l} \quad . \tag{2.3}$$

The sum includes all ionic and molecular species.

The chemical potential $\mu_E$ of the electrolyte is related to those of the ions by

$$\mu_E = \nu_C \mu_C + \nu_A \mu_A \quad . \tag{2.4}$$

For ions C and A, we introduce activity coefficients $\gamma_C$ and $\gamma_A$ based on the complete-dissociation mole fractions:

$$\mu_E = \nu_C \left[\mu_C^\theta + RT \ln(x_C \gamma_C)\right] + \nu_A \left[\mu_A^\theta + RT \ln(x_A \gamma_A)\right] \tag{2.5}$$

where superscript $\Theta$ 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

$$\gamma_C \rightarrow 1 \quad \text{as} \quad x_C \rightarrow 0 \quad \text{and} \quad x_1 \rightarrow 1 \tag{2.6}$$

and

$$\gamma_A \rightarrow 1 \quad \text{as} \quad x_A \rightarrow 0 \quad \text{and} \quad x_1 \rightarrow 1. \tag{2.7}$$

The standard state for every ion is always a hypothetical ideal 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 is different 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 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

$$\mu_E = \nu \mu_\pm = \nu_C \mu_C + \nu_A \mu_A \tag{2.8}$$

$$\mu_\pm = \mu_\pm^\theta + RT \ln(\gamma_\pm x_\pm) \tag{2.9}$$

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

$$\gamma_{\pm} = [\gamma_C^{\nu_C} \gamma_A^{\nu_A}]^{1/\nu} \tag{2.10}$$

$$x_{\pm} = [x_C^{\nu_C} x_A^{\nu_A}]^{1/\nu} \ . \tag{2.11}$$

For the chemical potential in the standard state,

$$\nu \mu_{\pm}^{\theta} = \nu_C \mu_C^{\theta} + \nu_A \mu_A^{\theta} \ . \tag{2.12}$$

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

$$\mu_1 = \mu_1^{\theta} + RT \ln (x_1 \gamma_1) \tag{2.13}$$

$$\mu_2 = \mu_2^{\theta} + RT \ln (x_2 \gamma_2) \ . \tag{2.14}$$

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 $\gamma_1$ and $\gamma_2$ are normalized by

$$\gamma_1 \rightarrow 1 \quad \text{as} \quad x_1 \rightarrow 1 \tag{2.15}$$

$$\gamma_2 \rightarrow 1 \quad \text{as} \quad x_2 \rightarrow 1 \ . \tag{2.16}$$

The Gibbs energy of the real solution is given by

$$G = n_1 \mu_1 + n_2 \mu_2 + n_C \mu_C + n_A \mu_A \ . \tag{2.17}$$

The Gibbs energy of the ideal solution is defined by

$$G^{ideal} = \sum_k n_k \mu_k^{\theta} + RT \sum_k n_k \ln (x_k) \ . \tag{2.18}$$

The excess Gibbs energy $G^E$ is defined by

$$G^E = G - G^{ideal} \ . \tag{2.19}$$

Substituting in Equation 2.17 the activity coefficients defined in equations 2.5, 2.13 and 2.14, the excess Gibbs energy is given by

$$G^E = RT \sum_k n_k \ln (\gamma_k) \ . \tag{2.20}$$

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

$$RT \ln(\gamma_k) = \left(\frac{\partial G^E}{\partial n_k}\right)_{T,P,n_{j\neq k}} . \tag{2.21}$$

Upon adopting a model for $G^E$, equation 2.21 gives activity coefficients for single ions. However, experimental measurements always give the chemical potential of an electrically neutral assembly of ions; i.e. 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

$$\ln(\gamma_\pm) = \frac{1}{\nu}\left[\nu_C \ln(\gamma_C) + \nu_A \ln(\gamma_A)\right] . \tag{2.22}$$

Vapor-Liquid Equilibrium

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

$$\mu_1^V = \mu_1^L \quad \text{and} \quad \mu_2^V = \mu_2^L . \tag{2.23}$$

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

Equation 2.23 can be rewritten in terms of fugacities. Neglecting the Poynting correction :

$$\varphi_1 y_1 P = \gamma_1 x_1 P_1^{sat} \varphi_1^{sat} \tag{2.24}$$

$$\varphi_2 y_2 P = \gamma_2 x_2 P_2^{sat} \varphi_2^{sat} \tag{2.25}$$

where $\varphi_i^{sat}$ is the vapor-phase fugacity coefficient of pure component i at saturation and $\varphi_i$ 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 /34/. Fugacity coefficients are calculated from an expression based on the virial equation truncated after the second virial coefficient /35/.

Activity coefficients $\gamma_1$ and $\gamma_2$ are obtained from a model for $G^E$, using equation 2.21.

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

$$\mu_1' = \mu_1'' \tag{2.26}$$

$$\mu_2' = \mu_2'' \tag{2.27}$$

$$\mu_E' = \mu_E'' \tag{2.28}$$

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

With the definition of the mean ionic properties (equations 2.8 - 2.12), equation 2.28 can be replaced by

$$\mu_\pm' = \mu_\pm'' \quad . \tag{2.29}$$

Introducing activity coefficients defined in equations 2.9, 2.13 and 2.14, the equations for liquid-liquid phase equilibrium are

$$\left[\mu_1^\theta + RT \ln ( x_1 \gamma_1 )\right]' = \left[\mu_1^\theta + RT \ln ( x_1 \gamma_1 )\right]'' \tag{2.30}$$

$$\left[\mu_2^\theta + RT \ln ( x_2 \gamma_2 )\right]' = \left[\mu_2^\theta + RT \ln ( x_2 \gamma_2 )\right]'' \tag{2.31}$$

$$\left[\mu_\pm^\theta + RT \ln( x_\pm \gamma_\pm )\right]' = \left[\mu_\pm^\theta + RT \ln( x_\pm \gamma_\pm)\right]'' \quad . \tag{2.32}$$

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

$$(x_1 \gamma_1)' = (x_1 \gamma_1)'' \tag{2.33}$$

$$(x_2 \gamma_2)' = (x_2 \gamma_2)'' \tag{2.34}$$

$$(x_\pm \gamma_\pm)' = (x_\pm \gamma_\pm)'' \tag{2.35}$$

where the activity coefficients are found from excess Gibbs energy $G^E$ as indicated by equation 2.21. The mean-ionic activity coefficient $\gamma_\pm$ is obtained from equation 2.22. The simplicity of equation 2.35 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 ".

## 3. 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 (e.g. Van Laar) or by "chemical" theories (ion solvation), or both. 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 /36/.

Short-range forces between ions and solvent molecules are frequently described by formation of semi-stable complexes; this formation is called solvation. Experimental studies on ion solvation in the gas phase /37,38/ 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 /39,40/. Also, computer simulations /41-43/ 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 /44-47/. Spectroscopic measurements in liquid mixtures of two solvents and a salt show preferential solvation of one solvent around the ion /48-50/. 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 /16/ and Schönert /17/, 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 /51/. 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 in Section 3.2.

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

$$G^E = G^{E^{chem}} + G^{E^{phys}} + G^{E^{LR}} \quad . \tag{3.1}$$

where superscript LR stand for long-range. Using equations 2.21 and 2.22, equation 3.1 provides activity coefficients of the form

$$\ln(\gamma_r) = \ln(\gamma_r^{chem}) + \ln(\gamma_r^{phys}) + \ln(\gamma_r^{LR}) \quad . \tag{3.2}$$

where r stand for 1, 2 or ±.

The three contributions in Equation 3.1 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.

### 3.1 Chemical Contribution

As indicated in Section 2, 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 /16/ 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 /12,13,52,53/. 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 /45,46/.

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 | |
|---|---|---|
| $C_0 + i\ (\text{solvent } 1) + j\ (\text{solvent } 2) \leftrightarrow C_{i,j}$ | $K_{i,j}$ | (3.1.1) |

Here $C_0$ 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 (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 /16/ and Schönert /17/.

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

$$\frac{G^{E^{chem}}}{RT} = n_1 \ln(\gamma_1^{chem}) + n_2 \ln(\gamma_2^{chem}) + n_C \ln(\gamma_C^{chem}) + n_A \ln(\gamma_A^{chem}) \qquad (3.1.2)$$

with the activity coefficients $\gamma_k^{chem}$ given in Appendix I.

For the solvent components, we obtain

$$\ln(\gamma_1^{chem}) = \ln\left(\frac{\xi_1^f}{x_1}\right) \qquad (3.1.3)$$

and

$$\ln(\gamma_2^{chem}) = \ln\left(\frac{\xi_2^f}{x_2}\right) \qquad (3.1.4)$$

where $\xi_s$ is the "true" mole fraction of species s at chemical equilibrium with the total mole number of all species $n^t$

$$\xi_s = \frac{n_s}{n^t} . \tag{3.1.5}$$

For the cation,

$$\ln(\gamma_C^{chem}) = \ln\left(\frac{\xi_{C_0}}{x_C}\right) + \ln(\Sigma^\theta) \tag{3.1.6}$$

where $\Sigma^\Theta$ is defined by

$$\Sigma^\theta = \sum_{i=0}^{N} K_{i,j=0} \tag{3.1.7}$$

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 /45/. We choose N = 12 for bivalent cations.

Similarly for the anion,

$$\ln(\gamma_A^{chem}) = \ln\left(\frac{\xi_{A_0}}{x_A}\right) \tag{3.1.8}$$

In equation 3.1.8 the last term in equation 3.1.6 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

$$\ln(\gamma_\pm^{chem}) = \frac{1}{\nu}\left[\nu_C \ln(\gamma_C^{chem}) + \nu_A \ln(\gamma_A^{chem})\right] \tag{3.1.9}$$

The chemical equilibrium constants must now be specified. To reduce the number of adjustable parameters, we assume not only that the cation is solvated while the anion is not, but in addition, 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 ($k^o$) for each solvent-salt pair at a fixed temperature. This statistical argument is given in Appendix III.

## 3.2 Physical Contribution

Interactions between water and cosolvent are expressed by an extended equation of the type suggested by van Laar /54/ and by Scatchard and Hamer /55/. 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

$$\frac{G^{E^{phys}}_{(1,2)}}{n^T RT} = q\ \phi_1\phi_2\ [\,A + B\,\phi_2 + C\,\phi_1\phi_2\,] \tag{3.2.1}$$

where the volume fractions are defined by

$$\phi_k = \frac{q_k\ x_k}{q} \qquad\qquad q = \sum_k x_k\, q_k \tag{3.2.2}$$

and where $q_k$ is a volume parameter, taken from Reid /34/ and Bondi /56/ 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 equation 3.2.1 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

$$n^T = n_1 + n_2 + n_C + n_A \tag{3.2.3}$$

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

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 /5/.

For the water-salt binary mixture we assume

$$\frac{G^{E^{phys}}_{(1\text{-}I)}}{n^T RT} = x_1 x_I \beta_1 \tag{3.2.4}$$

and for the cosolvent-salt mixture

$$\frac{G^{E^{phys}}_{(2\text{-}I)}}{n^T RT} = x_2 x_I \beta_2 \tag{3.2.5}$$

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

$$x_I = x_C + x_A \quad . \tag{3.2.6}$$

Here $\beta_1$ and $\beta_2$ 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

$$\frac{G^{E^{phys,(sym)}}}{n^T R T} = q\,\phi_1\,\phi_2\,\left[A(1 + b\,x_I) + B\,\phi_2 + C\,\phi_1\,\phi_2\right] + x_1\,x_I\,\beta_1 + x_2\,x_I\,\beta_2 \tag{3.2.7}$$

where b is the the only ternary parameter. In equation 3.2.7, as indicated by superscript (sym), the standard states for all components are the pure liquids. To use equation 3.2.7 in combination with the other contributions to the excess Gibbs energy in equation 3.1, equation 3.2.7 must be normalized to the standard state for the ions defined in section 2. This normalization is easily achieved by

$$\frac{G^{E^{phys}}}{n^T R T} = \frac{G^{E^{phys,(sym)}}}{n^T R T} - x_I \ln(\gamma_I^{\infty}) = \frac{G^{E^{phys,(sym)}}}{n^T R T} - x_I \beta_1 \qquad (3.2.8)$$

The properly normalized physical contribution to $G^E$ is

$$\frac{G^{E^{phys}}}{n^T R T} = q \phi_1 \phi_2 \left[A(1 + b x_I) + B \phi_2 + C \phi_1 \phi_2\right] + x_1 x_I \beta_1 + x_2 x_I \beta_2 - x_I \beta_1 \ . \qquad (3.2.9)$$

For the ions, parameters $q_k$ are calculated using crystallographic radius $r_k$ /45/

$$q_k = \frac{(4/3)\ \pi r_k^3}{v_{ref} / N_{Av}} \ . \qquad (3.2.10)$$

where $N_{Av}$ is Avogadro's number and $v_{ref} = v(CH_2) = 15.17\ cm^3/mole$ /57/. 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 equation 3.2.9, $q_I$ is found from

$$q_I = (q_C v_C + q_A v_A) / v \ . \qquad (3.2.11)$$

Activity coefficients $\gamma^{(phys)}$ are obtained using equation 3.2.1 and 3.2.9. Expressions for these activity coefficients are given in Appendix IV.

## 3.3 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 $\mu_1$ and $\mu_2$. To maintain consistency, we need to convert the activity coefficients from the McMillan-Mayer to the Lewis-Randall framework. Pailthorpe /58/ describes conversion for a single-solvent system and Cardoso and O'Connell /36/ 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 indicated in Section 2, 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 /59/. 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

$$RT \ln(\gamma_1^{LR}) = -(\bar{v}_1) \cdot \Pi^{DH} \tag{3.3.1}$$

$$RT \ln(\gamma_2^{LR}) = -(\bar{v}_2) \cdot \Pi^{DH} \tag{3.3.2}$$

These equations are essentiallly equivalent to equation 12 in /36/ and to equation 918.3 in /60/.

Long-range forces are responsible for a (Debye-Hückel) osmotic pressure designated by $\Pi^{DH}$; it is given by/61/:

$$\frac{\Pi^{DH}}{kT} = -\frac{\kappa^3 f(\kappa d)}{24\pi} \tag{3.3.3}$$

$$f(\kappa d) = \frac{3}{(\kappa d)^3}\left[1 + \kappa d - \frac{1}{1+\kappa d} - 2\ln(1 + \kappa d)\right] \tag{3.3.4}$$

The Debye length is $\kappa^{-1}$. Its inverse square is given by

$$\kappa^2 = \frac{4\pi e^2 \left(\sum_k x_k z_k^2\right)}{kTDv} \tag{3.3.5}$$

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

$$\ln(\gamma_k^{LR}) = - \frac{z_i^2 \, e^2}{2 D k T} \frac{\kappa}{1 + \kappa d} . \qquad (3.3.6)$$

This equation is essentially equivalent to equation 13a in /36/ and equation 918.10 in /60/.

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

$$\ln(\gamma_\pm^{LR}) = - \frac{|z_C \, z_A| \, e^2}{2 D k T} \frac{\kappa}{1 + \kappa d} . \qquad (3.3.7)$$

The dielectric constant of the mixture is calculated by a volume-fraction mixing rule /62/:

$$D = \phi_1 D_1 + \phi_2 D_2 \qquad (3.3.8)$$

where $\phi$ is the volume fraction on a salt-free basis. Akhadov /63/ gives experimental dielectric constants of some pure and mixed liquids.

In equation 3.3.5, the molar volume of the mixture v is approximated by the molar volume of the salt-free mixture, using additivity (Amagat's Law).

## 4. 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

$$\langle \Delta Q \rangle = \left[ \sum_{l}^{J} \left| Q_l^{(exp)} - Q_l^{(calc)} \right| \right] / J \tag{4.1}$$

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 ($k^o$) and the other ($\beta$) is for the physical contribution. Figures 1 and 2 illustrate the relative magnitudes of contributions to the activity coeffcients 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 only important 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.

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

$$\ln(k_1^o) = a_1 + b_1 / T \tag{4.2}$$

and

$$\ln(k_2^o) = a_2 + b_2 / T \tag{4.3}$$

where a and b are adjustable parameters. Physical parameters $\beta_1$ and $\beta_2$ 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 regression, parameters A, B and C in equation 3.2.9 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. The first (denoted by a), gives results predicted by parameters that are only obtained from binary data. In the second 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 to $k_2^0 = -0.846$. 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 $\beta_2$ for the cosolvent-salt binary system. If no data are available for the binary cosolvent-salt system, we must find $\beta_2$ 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 /80/

$$\langle \Delta z \rangle = \sqrt{\frac{\sum_{l}^{J} \sum_{r}^{M} \left[ ( z_{l,r}^{'(exp)} - z_{l,r}^{'(calc)} )^2 + ( z_{l,r}^{''(exp)} - z_{l,r}^{''(calc)} )^2 \right]}{2\,J\,M}} \qquad [\text{mol}\,\%] \qquad (4.4)$$

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

$$z_r = \frac{n_r}{n_1 + n_2 + n_E} \qquad (4.5)$$

Figures 5a,b,c 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; that 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 described in 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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## Nomenclature

| | |
|---|---|
| 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 |
| <N> | average solvation number |
| $N_{Av}$ | Avogadro Number |
| P | pressure |
| T | absolute temperature |
| d | distance of closest approach between two ions |
| e | elementary charge |
| k | Boltzmann constant |
| $k^o$ | 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

| | |
|---|---|
| $\phi$ | volume fraction |
| $\gamma$ | activity coefficient |
| $\varphi$ | fugacity coefficient |
| $\kappa$ | inverse Debye length |
| $\mu$ | chemical potential |
| $\nu$ | stoichiometric coefficient |
| $\xi$ | true mole fraction |
| $\Pi$ | osmotic pressure |

superscripts

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

subscripts

| | |
|---|---|
| A | anion |
| C | cation |
| calc | calculated |
| 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 |
| o | unsolvated |

## Figure Captions

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

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

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

Figure 4: Vapor-liquid equilibria for the system water/isopropanol/lithium bromide at 75°C /69/

Figure 5: Liquid-liquid equilibria for the system water/n-butanol/sodium chloride at 25°C /78/

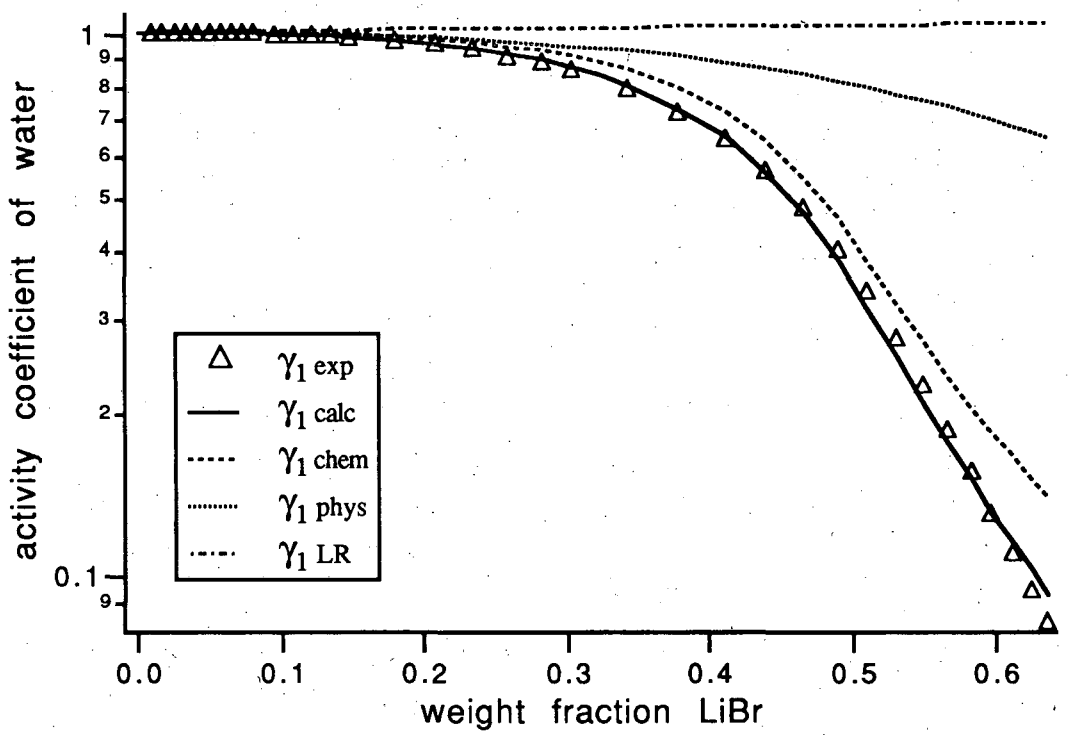
activity coefficient of water
1
9
8
7
6
5
4
3
2
0.1
9
0.0
0.1
0.2
0.3
0.4
0.5
0.6
weight fraction LiBr
γ1 exp
γ1 calc
γ1 chem
γ1 phys
γ1 LR

Figure 1

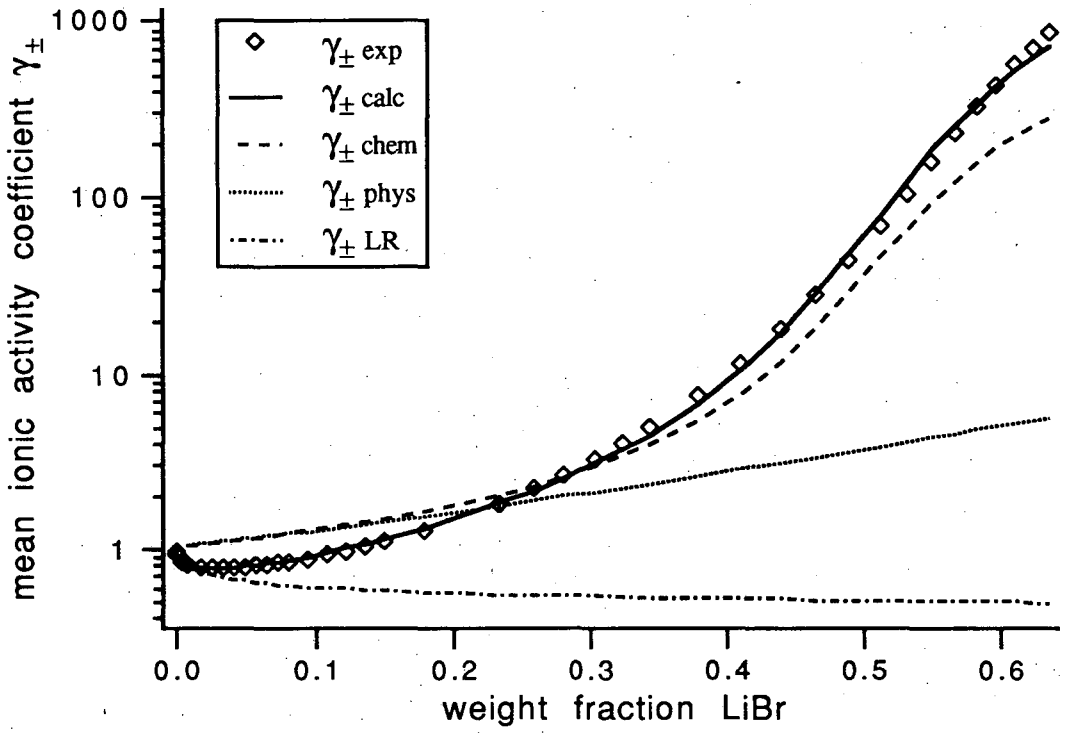
1000
100
10
1
mean ionic activity coefficient $\gamma_\pm$
$\gamma_\pm$ exp
$\gamma_\pm$ calc
$\gamma_\pm$ chem
$\gamma_\pm$ phys
$\gamma_\pm$ LR
0.0
0.1
0.2
0.3
0.4
0.5
0.6
weight fraction LiBr

Figure 2

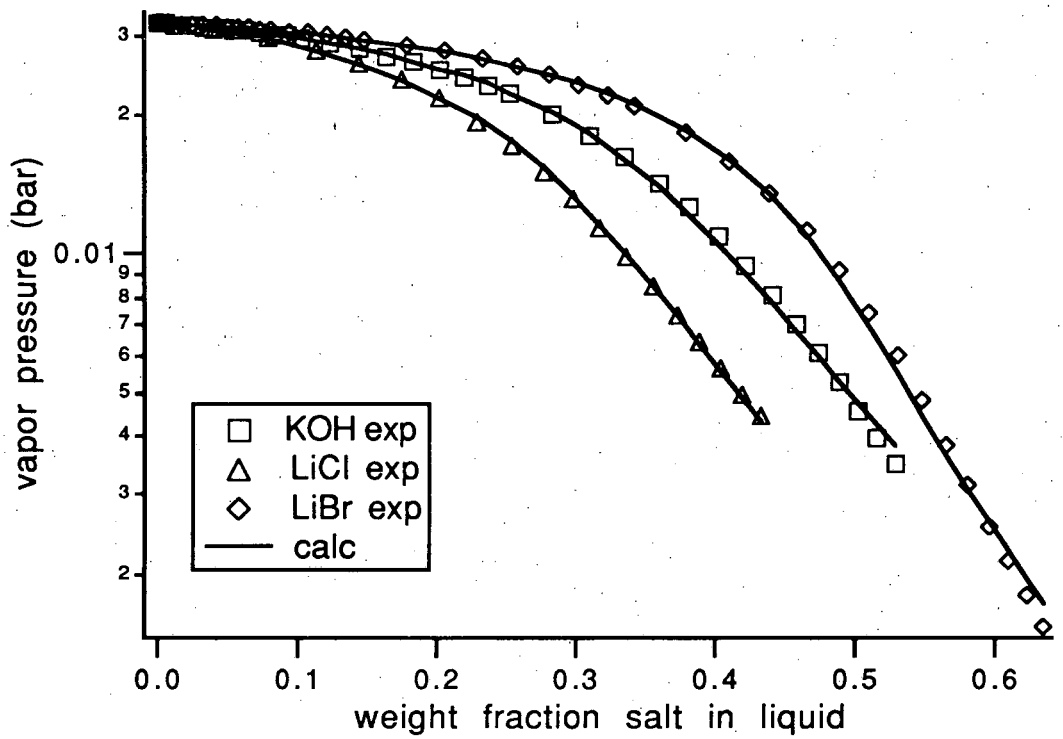
vapor pressure (bar)
3
2
0.01
9
8
7
6
5
4
3
2
KOH exp
LiCl exp
LiBr exp
calc
0.0
0.1
0.2
0.3
0.4
0.5
0.6
weight fraction salt in liquid

Figure 3

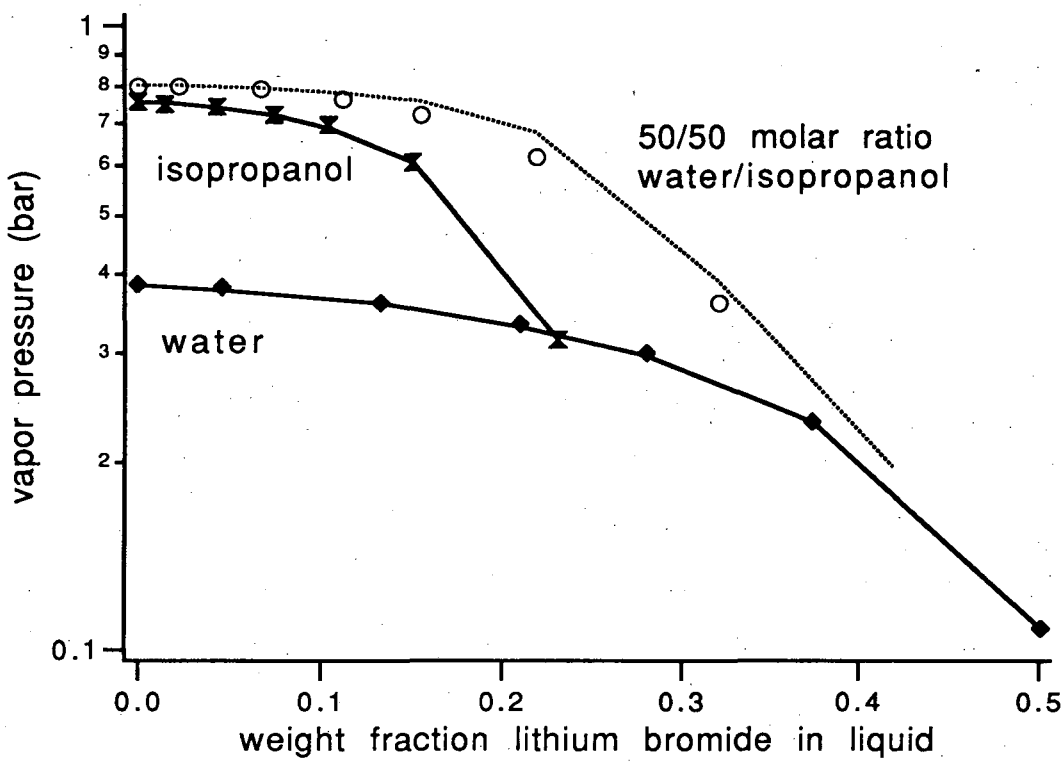
1
9
8
7
6
5
4
3
2
0.1
vapor pressure (bar)
isopropanol
water
50/50 molar ratio
water/isopropanol
0.0
0.1
0.2
0.3
0.4
0.5
weight fraction lithium bromide in liquid

Figure 4

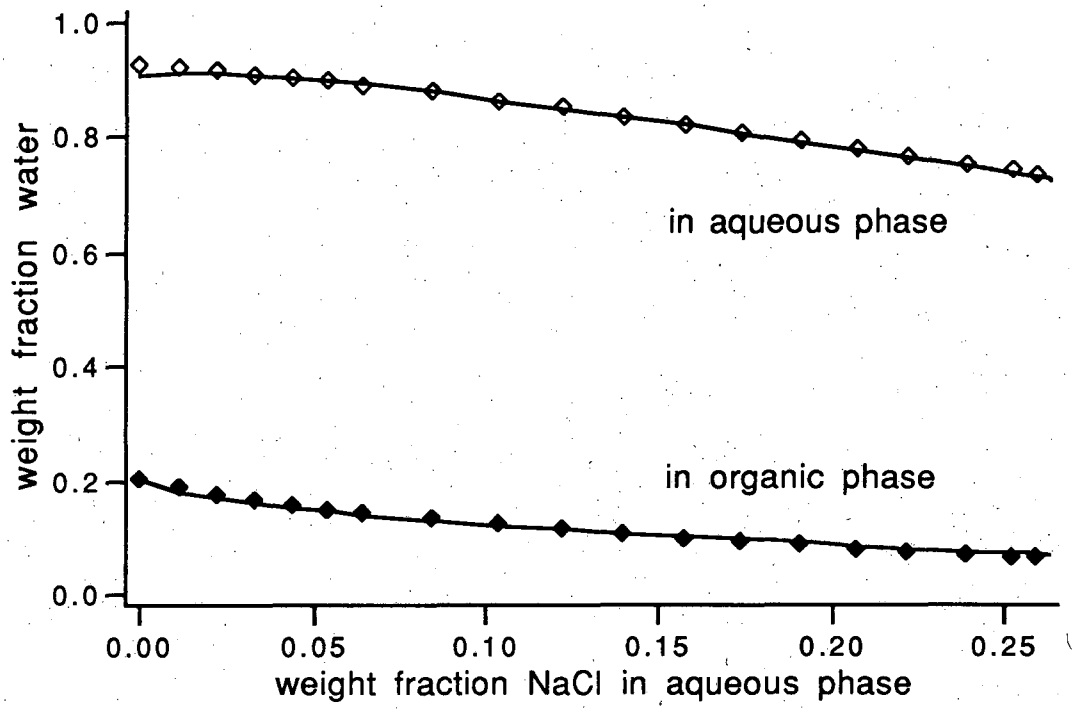
1.0
0.8
0.6
0.4
0.2
0.0
weight fraction water
in aqueous phase
in organic phase
0.00
0.05
0.10
0.15
0.20
0.25
weight fraction NaCl in aqueous phase

Figure 5a

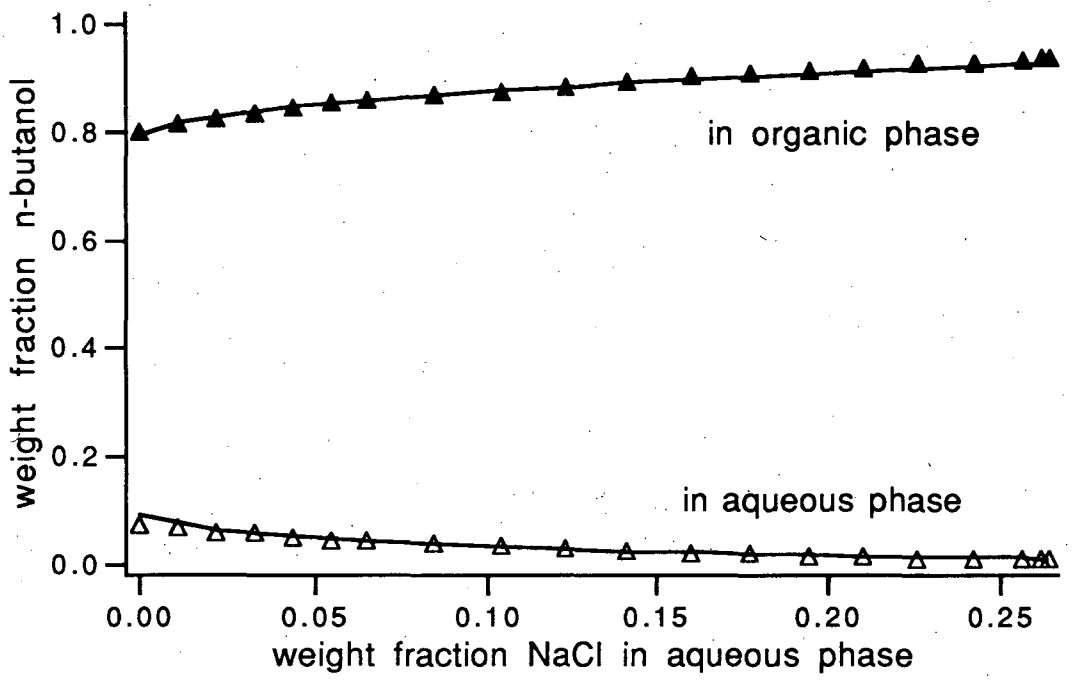
1.0
0.8
0.6
0.4
0.2
0.0
weight fraction n-butanol
in organic phase
in aqueous phase
0.00
0.05
0.10
0.15
0.20
0.25
weight fraction NaCl in aqueous phase

Figure 5b

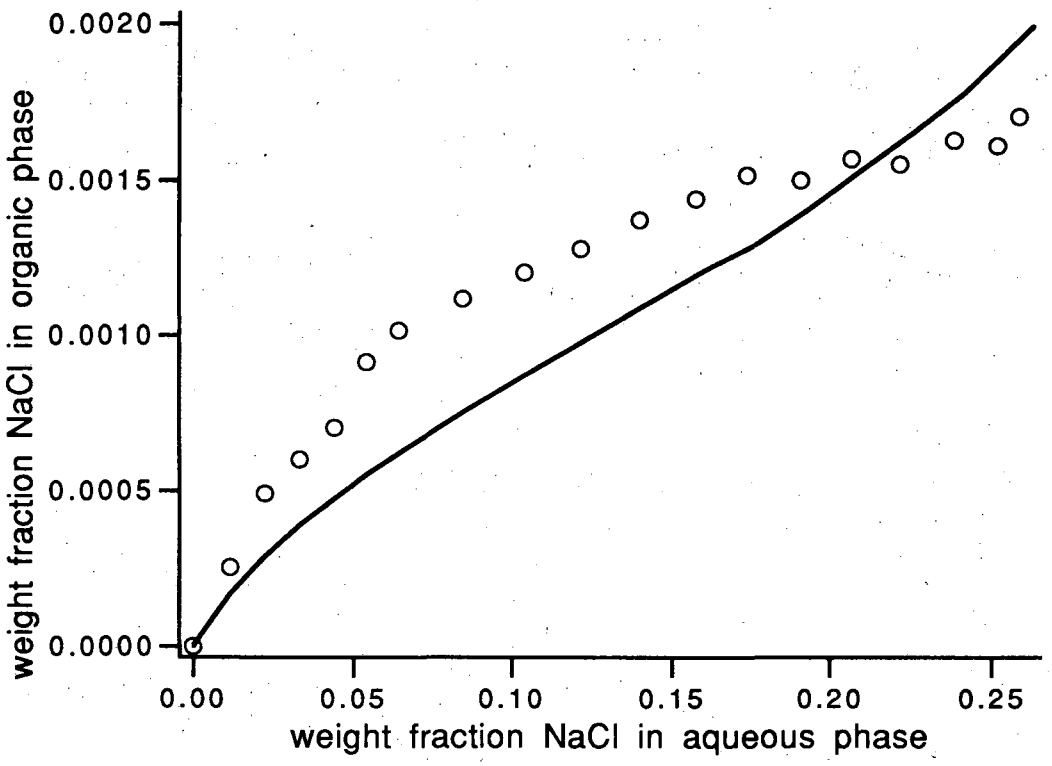
0.0020
0.0015
0.0010
0.0005
0.0000
weight fraction NaCl in organic phase
0.00
0.05
0.10
0.15
0.20
0.25
weight fraction NaCl in aqueous phase

Figure 5c

| | | | |
|---|---|---|---|
| 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 |

Table 1a: Volume Parameter q for solvents. These parameters are dimensionless because they are normalized by $v(CH_2) = 15.17\ cm^3/mole$.

| 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 |

Table 1b: Volume parameters q for ions normalized by $v(CH_2)$. Crystallographic radii are from/45/

| Salt | t [°C] | max. wt% Salt | $\ln(k_1^o)$ | $\beta_1$ | <Δp> [ %] | reference |
|---|---|---|---|---|---|---|
| KBr | 25 | 39.6 | -0.399 | 0.0 | 0.1 | /64/ |
| KOH | 25 | 52.9 | 1.859 | -1.374 | 1.2 | /64/ |
| LiBr | 25 | 63.5 | 2.587 | -2.559 | 1.7 | /64/ |
| LiBr | 75 | 50.8 | 1.936 | -3.000 | 0.1 | /72/ |
| LiCl | 25 | 43.3 | 1.808 | -2.214 | 1.1 | /64/ |
| LiCl | 60 | 34.2 | 1.500 | -2.254 | 0.5 | /64/ |
| LiCl | 75 | 42.8 | 1.863 | 0.0 | 3.9 | /72/ |
| NaCl | 25 | 26.4 | 1.314 | 0.410 | 0.1 | /64/ |
| $CaCl_2$ | 25 | 52.6 | 0.968 | -3.218 | 0.9 | /73/ |
| $MgCl_2$ | 25 | 36.1 | 1.434 | -3.950 | 0.9 | /74/ |

Table 2a: Results and Parameters for Aqueous Salt Solutions

| System | t [°C] | max. wt% Salt | $\ln(k_2^o)$ | $\beta_2$ | <Δp> [ %] | reference |
|---|---|---|---|---|---|---|
| Methanol/LiCl | 60 | 23.9 | 1.019 | -2.650 | 0.9 | /65/ |
| Methanol/LiBr | 30 | 58.2 | 2.804 | -1.413 | 3.3 | /66/ |
| Methanol/$CaCl_2$ | 25 | 22.6 | 0.656 | 0.0 | 1.7 | /75,84/ |
| Isopropanol/LiBr | 75 | 23.6 | 2.529 | 3.045 | 0.3 | /72/ |
| Isopropanol/LiCl | 75 | 12.6 | -1.550 | 0.0 | 1.8 | /72/ |

Table 2b: Results and Parameters for Nonaqueous Salt Solutions

| System | t [°C] | max. wt% Salt | $a_1/a_2$ | $b_1/b_2$ | $\beta_1/\beta_2$ | $\langle\Delta p\rangle$ [ %] | reference |
|---|---|---|---|---|---|---|---|
| Water/LiBr | 20-170 | 70 | -1.319 | 1164 | -2.559 | 2.1 | /67,76,77/ |
| Water/NaCl | 0-110 | 28 | -0.883 | 655 | 0.410 | 0.2 | /64,68/ |
| Water/$K_2CO_3$ | 25-90 | 51 | -4.988 | 2525 | 0.078 | 0.6 | /78/ |
| Methanol/LiBr | -10-200 | 60 | -2.827 | 1707 | -1.413 | 3.2 | /66,69,76,77/ |

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

| Cosolvent | t [°C] | A | B | C | <Δ p> [ %] | <Δy> [ %] | reference |
|---|---|---|---|---|---|---|---|
| Methanol | 30 | 0.360 | 0.136 | 0.0 | 1.3 | 0.4 | /79/ |
| Methanol | 60 | 0.512 | 0.044 | 0.0 | 0.7 | 0.5 | /65/ |
| Isopropanol | 75 | 0.992 | 0.206 | -0.370 | 0.1 | 0.4 | /72/ |

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

| Cosolvent and Salt | t [°C] | max. wt% salt | b | <Δp> [ %] | <Δy> [ %] | reference | |
|---|---|---|---|---|---|---|---|
| Isopropanol/LiBr | 75 | 52 | 0.0 | 4.7 | 1.1 | /72/ | a) |
| | | | -0.564 | 3.7 | 0.9 | | b) |
| Methanol/LiCl | 60 | 30 | 0.0 | 6.3 | 4.0 | /72/ | a) |
| | | | 4.03 | 2.5 | 1.4 | | b) |
| Methanol/LiBr | 30 | 61 | 0.0 | 15.5 | 5.1 | /69,76,77/ | a) |
| | | | 7.20 | 5.2 | 5.1 | | b) |
| Isopropanol/LiCl | 75 | 33 | 0.0 | 3.3 | 0.8 | /72/ | a) |
| | | | 0.390 | 3.1 | 0.6 | | b) |
| Isopropanol/$CaCl_2$ | 75 | 49 | 0.0 | 6.6 | 1.2 | /72/ | |

Table 5: Results for Ternary Aqueous Vapor-Liquid Equilibria

| Cosolvent | t [°C] | A | B | C | <Δp [%] | <Δy> [%] | <Δz> [%] | reference |
|---|---|---|---|---|---|---|---|---|
| n-butanol | 25 | 1.285 | 0.388 | -1.276 | 1.6 | 0.7 | 0.02 | /79,80/ |
| i-butanol | 25 | 1.331 | 0.526 | -1.535 | 0.6 | 0.9 | 0.02 | /79,90/ |
| n-propanol | 25 | 0.971 | 0.350 | -0.118 | 1.5 | 1.8 | - | /79,80/ |
| i-propanol | 25 | 0.841 | 0.499 | -0.277 | 0.3 | 0.5 | - | /79,80/ |
| acetonitrile | 25 | 1.320 | 0.701 | -0.634 | 2.1 | 2.2 | - | /79/ |
| 2-butanone | 25 | 1.028 | 0.717 | -0.546 | 7.0 | 2.3 | 0.03 | /83/ |

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

| Cosolvent and Salt | t [°C] | max. wt% salt | β2 | b | <Δ z> [ %] | reference |
|---|---|---|---|---|---|---|
| n-butanol/NaCl | 25 | 26 | 3.396 | 1.382 | 0.7 | /81/ |
| i-butanol/NaCl | 25 | 26 | 3.102 | 1.400 | 1.3 | /81/ |
| n-propanol/NaCl | 25 | 26 | 2.724 | 2.625 | 1.7 | /81/ |
| i-propanol/NaCl | 25 | 26 | 2.963 | 2.984 | 1.0 | /81/ |
| acetonitrile/KBr | 25 | 29 | 2.591 | 0.0 | 1.1 | /82/ |
| 2-butanone/$CaCl_2$ | 25 | 44 | 3.366 | 0.0 | 1.5 | /83/ |

Table 7: Results for Ternary Aqueous Liquid-Liquid Systems

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## Appendix I

Derivation of activity coefficients from the chemical model

As indicated in section 3.1, 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 | |
|---|---|---|
| $C_0 + i\ (\text{solvent } 1) + j\ (\text{solvent } 2) \rightarrow C_{i,j}$ | $K_{i,j}$ | (AI.1) |

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 /16/ and Schönert /17/.

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.

$$n_1^t = n_1^f + \sum_{i=0}^{N} \sum_{j=0}^{N-i} i\, n_{C_{i,j}} \tag{AI.2}$$

$$n_2^t = n_2^f + \sum_{i=0}^{N} \sum_{j=0}^{N-i} j\, n_{C_{i,j}} \tag{AI.3}$$

and the total number of cations is

$$n_C^t = \sum_{i=0}^{N} \sum_{j=0}^{N-i} n_{C_{i,j}} . \tag{AI.4}$$

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

$$n^t = n_1^f + n_2^f + \sum_{i=0}^{N} \sum_{j=0}^{N-i} n_{C_{i,j}} + n_A . \tag{AI.5}$$

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

$$\xi_1^f = \frac{n_1^f}{n^t} \qquad \xi_2{}^f = \frac{n_2^f}{n^t} \quad . \tag{AI.6}$$

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

$$\frac{a_{C_{i,j}}}{a_{C_0}\ (a_1{}^f)^i\ (a_2{}^f)^j} = K_{i,j} \tag{AI.7}$$

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

$$a_k = \xi_k \quad . \tag{AI.8}$$

The ratio of solvated cations to unsolvated cations is

$$\frac{n_{C_{i,j}}}{n_{C_o}} = K_{i,j} \cdot \left(\xi_1^f\right)^i \cdot \left(\xi_2^f\right)^j \quad . \tag{AI.9}$$

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

$$n_1^b = n_{C_0} \cdot \sum_{i=0}^{N} \sum_{j=0}^{N-i} i \cdot K_{i,j} \cdot \left(\xi_1^f\right)^i \cdot \left(\xi_2^f\right)^j \tag{AI.10}$$

and

$$n_2^b = n_{C_0} \cdot \sum_{i=0}^{N} \sum_{j=0}^{N-i} j \cdot K_{i,j} \cdot \left(\xi_1^f\right)^i \cdot \left(\xi_2^f\right)^j \tag{AI.11}$$

with the short-hand notation $\sigma$ for the double sums in equations AI.10 and AI.11, this gives

$$n_1^b = n_{C_0} \cdot \sigma_1 \tag{AI.12}$$

and

$$n_2^b = n_{C_0} \cdot \sigma_2 \quad . \tag{AI.13}$$

We first note that the total number of cations is

$$n_C^t = n_{C_0} \cdot \sum_{i=0}^{N} \sum_{j=0}^{N-i} K_{i,j} \cdot \left(\xi_1^f\right)^i \cdot \left(\xi_2^f\right)^j \tag{AI.14}$$

and the double sum in equation AI.14 abreviated by $\Sigma$ gives

$$n_C^t = n_{C_0} \cdot \Sigma \quad . \tag{AI.15}$$

We then define the average solvation numbers

$$\langle N_1 \rangle = \frac{n_1^b}{n_C^t} = \frac{\sigma_1}{\Sigma} \tag{AI.16}$$

and

$$\langle N_2 \rangle = \frac{n_2^b}{n_C^t} = \frac{\sigma_2}{\Sigma} \; . \tag{AI.17}$$

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.

$$\xi_1^f = \frac{n_1^f}{n^t} = \frac{n_1^t - n_1^b}{\left[n_1^t - n_1^b\right] + \left[n_2^t - n_2^b\right] + n_C^t + n_A} \tag{AI.18}$$

and

$$\xi_2^f = \frac{n_2^f}{n^t} = \frac{n_2^t - n_2^b}{\left[n_1^t - n_1^b\right] + \left[n_2^t - n_2^b\right] + n_C^t + n_A} \; . \tag{AI.19}$$

With the average solvation numbers, we obtain

$$\xi_1^f = \frac{n_1^t - \langle N_1 \rangle n_C^t}{\left[n_1^t - \langle N_1 \rangle n_C^t\right] + \left[n_2^t - \langle N_2 \rangle n_C^t\right] + n_C^t + n_A} \tag{AI.20}$$

and

$$\xi_2^f = \frac{n_2^t - \langle N_2 \rangle n_C^t}{\left[n_1^t - \langle N_1 \rangle n_C^t\right] + \left[n_2^t - \langle N_2 \rangle n_C^t\right] + n_C^t + n_A} \tag{AI.21}$$

using the mole fractions based on complete dissociation

$$\xi_1^f = \frac{x_1 - \langle N_1 \rangle x_C}{\left[x_1 - \langle N_1 \rangle x_C\right] + \left[x_2 - \langle N_2 \rangle x_C\right] + x_C + x_A} \tag{AI.22}$$

and

$$\xi_2^f = \frac{x_2 - \langle N_2 \rangle x_C}{\left[x_1 - \langle N_1 \rangle x_C\right] + \left[x_2 - \langle N_2 \rangle x_C\right] + x_C + x_A} \; . \tag{AI.23}$$

For the mole fraction of the unsolvated ions we have

$$\xi_{C_o} = \frac{n_{C_0}}{n^t} = \frac{n_{C_0}}{\left[n_1^t - \langle N_1 \rangle n_C^t\right] + \left[n_2^t - \langle N_2 \rangle n_C^t\right] + n_C^t + n_A} \tag{AI.24}$$

Using equation AI.15, and using the complete-dissociation mole fractions, we obtain

$$\xi_{C_o} = \frac{x_C / \Sigma}{\left[x_1 - \langle N_1 \rangle x_C\right] + \left[x_2 - \langle N_2 \rangle x_C\right] + x_C + x_A} \quad . \tag{AI.25}$$

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

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

$$\mu_1 = \mu_1^f \tag{AI.26}$$

and

$$\mu_2 = \mu_2^f \quad . \tag{AI.27}$$

For the chemical contribution to the activity coefficient

$$\mu_1^\theta + RT \ln(x_1 \gamma_1^{chem}) = \mu_1^{f\theta} + RT \ln(\xi_1^f) \tag{AI.28}$$

and

$$\mu_2^\theta + RT \ln(x_2 \gamma_2^{chem}) = \mu_2^{f\theta} + RT \ln(\xi_2^f) \quad , \tag{AI.29}$$

we obtain for the solvents

$$\ln(\gamma_1^{chem}) = \ln\left(\frac{\xi_1^f}{x_1}\right) \tag{AI.30}$$

and

$$\ln(\gamma_2^{chem}) = \ln\left(\frac{\xi_2^f}{x_2}\right) \tag{AI.31}$$

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

Similar to equations AI.26 and AI.27, for the chemical potential of the cations

$$\mu_C = \mu_{C_0} \quad . \tag{AI.32}$$

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

$$\gamma_C = 1 \quad \text{as} \quad x_C \rightarrow 0 \quad x_1 \rightarrow 1 \quad . \tag{AI.33}$$

Using activity coefficients we obtain:

$$\mu_C = \mu_C^\theta + RT \ln ( x_C \gamma_C^{chem}) = \mu_{C_0}^\theta + RT \ln ( \xi_{C_0}) \quad . \tag{AI.34}$$

The chemical contribution to the activity coefficients of the cations is

$$\ln (\gamma_C^{chem}) = \ln ( \frac{\xi_{C_0}}{x_C}) + \frac{1}{RT} \left[\mu_{C_0}^\theta - \mu_C^\theta\right] \quad . \tag{AI.35}$$

The last term in equation AI.35 gives the connection between the symetrically normalized chemical model and the standard state defined on the unsymetrical convention. The last term in brackets at infinite dilution in water is given by

$$\frac{1}{RT} \left[\mu_{C_0}^\theta - \mu_C^\theta\right] = \lim_{\substack{x_C \rightarrow 0 \\ x_W \rightarrow 1}} \left[ \ln( \frac{x_C \gamma_C^{chem}}{\xi_{C_0}}) \right] \tag{AI.36}$$

$$\frac{1}{RT} \left[\mu_{C_0}^\theta - \mu_C^\theta\right] = \ln (\Sigma^\theta) \quad . \tag{AI.37}$$

With $\Sigma$ defined in equation AI.15,

$$(\Sigma^\theta) = \sum_{i=0}^{N} K_{i,\, j=0} \tag{AI.38}$$

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

$$\ln (\gamma_C^{chem} ) = \ln ( \frac{\xi_{C_0}}{x_C}) + \ln ( \Sigma^\theta) \tag{AI.39}$$

and in the same way, for the anion

$$\ln (\gamma_A^{chem} ) = \ln ( \frac{\xi_{A_0}}{x_A}) \quad . \tag{AI.40}$$

In equation AI.40 the last term in equation AI.39 does not appear because we assumed that the anion is unsolvated (All equilibrium constants are zero).

The mean ionic activity coefficient is found from

$$\ln(\gamma_{\pm}^{chem}) = \frac{1}{\nu}\left[\nu_C \ln(\gamma_C^{chem}) + \nu_A \ln(\gamma_A^{chem})\right] \quad . \qquad \text{(AI.41)}$$

## Appendix II

<u>Contribution of the chemical model to the excess Gibbs energy</u>

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 equation 2.17:

$$G = n_1 \mu_1 + n_2 \mu_2 + n_C \mu_C + n_A \mu_A \quad . \qquad \text{(AII.1)}$$

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

$$G^{chem} = n_1^f \mu_1^f + n_2^f \mu_2^f + \sum_{i=0}^{N}\sum_{j=0}^{N-i} n_{C_{i,j}} \mu_{C_{i,j}} + \sum_{i=0}^{N}\sum_{j=0}^{N-i} n_{A_{i,j}} \mu_{A_{i,j}} \quad . \qquad \text{(AII.2)}$$

The chemical equilibrium condition gives

$$\mu_{C_{i,j}} = \mu_{C_0} + i\ \mu_1^f + j\ \mu_2^f \qquad \text{(AII.3)}$$

and

$$\mu_{A_{i,j}} = \mu_{A_0} + i\ \mu_1^f + j\ \mu_2^f \quad . \qquad \text{(AII.4)}$$

By combining equation AII.3, AII.4 and AII.2 we obtain

$$G^{chem} = \left\{ n_1^f + \sum_{i=0}^{N} \sum_{j=0}^{N-i} i \; n_{C_{i,j}} + \sum_{i=0}^{N} \sum_{j=0}^{N-i} i \; n_{A_{i,j}} \right\} \mu_1^f$$
$$+ \left\{ n_2^f + \sum_{i=0}^{N} \sum_{j=0}^{N-i} j \; n_{C_{i,j}} + \sum_{i=0}^{N} \sum_{j=0}^{N-i} j \; n_{A_{i,j}} \right\} \mu_2^f \qquad \text{(AII.5)}$$
$$+ \left\{ \sum_{i=0}^{N} \sum_{j=0}^{N-i} n_{C_{i,j}} \right\} \mu_{C_0} + \left\{ \sum_{i=0}^{N} \sum_{j=0}^{N-i} n_{A_{i,j}} \right\} \mu_{A_0} \; .$$

Using the mass balance this gives

$$G^{chem} = \{n_1\} \mu_1^f + \{n_2\} \mu_2^f + \{n_C\} \mu_{C_0} + \{n_A\} \mu_{A_0} \qquad \text{(AII.6)}$$

Comparing equation AII.6 and AII.1 gives the following relations

$$\mu_1 = \mu_1^f \qquad \text{(AII.7)}$$

$$\mu_2 = \mu_2^f \qquad \text{(AII.8)}$$

$$\mu_C = \mu_{C_0} \qquad \text{(AII.9)}$$

$$\mu_A = \mu_{A_0} \qquad \text{(AII.10)}$$

The Gibbs energy of the ideal mixture is defined by equation 2.18

$$G^{ideal} = n_1 \mu_1^\theta + n_2 \mu_2^\theta + n_C \mu_C^\theta + n_A \mu_A^\theta + RT \sum_k n_k \ln(x_k) \qquad \text{(AII.11)}$$

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

$$\mu_k = \mu_k^\theta + RT \ln( x_k \gamma_k^{chem}) \; . \qquad \text{(AII.12)}$$

The excess Gibbs energy is given as

$$G^{E^{chem}} = G^{chem} - G^{ideal} \; . \qquad \text{(AII.13)}$$

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

$$\frac{G^{E^{chem}}}{RT} = n_1 \ln(\gamma_1^{chem}) + n_2 \ln(\gamma_2^{chem}) + n_C \ln(\gamma_C^{chem}) + n_A \ln(\gamma_A^{chem}) \ . \qquad \text{(AII.14)}$$

With the equations for the activity coefficients (AI.30,AI.31,AI.39 and AI.40), we obtain

$$\frac{G^{E^{chem}}}{n^T RT} = x_1 \ln(\frac{\xi_1^f}{x_1}) + x_2 \ln(\frac{\xi_2^f}{x_2}) + x_C \ln(\frac{\xi_{C_0}}{x_C} \Sigma_C^\theta) + x_A \ln(\frac{\xi_{A_0}}{x_A} \Sigma_A^\theta) \qquad \text{(AII.15)}$$

## Appendix III

<u>Calculation of chemical equilibrium constants</u>

For a binary solvent-salt system with the equilibrium

$$C_0 + i \text{ (solvent)} \leftrightarrow C_i \ . \qquad \text{(AIII.1)}$$

As proposed by Schönert /17/, the equilibrium constant $K_i$ can be written in the form

$$\ln(K_i) = i \ln(k^0) + \ln \binom{N}{i} \qquad \text{(AIII.2)}$$

with the binomial coefficient defined by

$$\binom{N}{i} = \frac{N!}{i! \cdot (N-i)!} \qquad \text{(AIII.3)}$$

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

To extend equation AIII.2 for the equilibrium constant to multisolvent systems, we use the multinomial coefficient.

For the equilibrium constants in the ternary mixture, defined in equation 3.1.1, we write

$$\ln(K_{ij}) = i \cdot \ln(k_1^0) + j \cdot \ln(k_2^0) + \ln\binom{N}{ij} \qquad \text{(AIII.4)}$$

with the multinomial coefficient defined by

$$\binom{N}{ij} = \left(\frac{N!}{i! \cdot j! \cdot (N-i-j)!}\right) . \qquad \text{(AIII.5)}$$

Equation AIII.4 gives the equilibrium constant for the formation of each possible solvate. For a binary solvent-salt mixture, equation AIII.4 reduces to equation AIII.2 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 AIII.4 permits calculations of mixed solvates in the ternary mixture using only equilibrium constants obtained from binary solvent-salt data.

## Appendix IV

<u>Derivation of the activity coefficients from the physical contribution</u>

The physical contribution to the excess Gibbs energy is given in equation 3.2.9 as

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

where the volume fractions are defined by

$$\phi_k = \frac{q_k\,x_k}{q} \qquad q = \sum_k x_k\,q_k \qquad \text{(AIV.2)}$$

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

$$\ln(\gamma_1^{phys}) = A\, q_1 [\phi_2 - \phi_1\phi_2] + B\, q_1 [\phi_2^2 - 2\, \phi_1\phi_2^2] + C\, q_1 [2\, \phi_1\phi_2^2 - 3\, \phi_1^2\phi_2^2] + Ab\, q_1 \left[\phi_2 x_I - \phi_1\phi_2 x_I (1 + \frac{q}{q_1})\right] + x_I^2 \beta_1 + x_2 x_I (\beta_1 - \beta_2) \quad \text{(AIV.3)}$$

$$\ln(\gamma_2^{phys}) = A\, q_2 [\phi_1 - \phi_1\phi_2] + B\, q_2 [2\, \phi_1\phi_2 - 2\, \phi_1\phi_2^2] + C\, q_2 [2\, \phi_1^2\phi_2 - 3\, \phi_1^2\phi_2^2] + Ab\, q_2 \left[\phi_1 x_I - \phi_1\phi_2 x_I (1 + \frac{q}{q_2})\right] + x_I^2 \beta_2 + x_1 x_I (\beta_2 - \beta_1) \quad \text{(AIV.4)}$$

$$\ln(\gamma_I^{phys}) = A\, q_I [-\phi_1\phi_2] + B\, q_I [-2\, \phi_1\phi_2^2] + C\, q_I [-3\, \phi_1^2\phi_2^2] + Ab\, [\phi_1\phi_2 q - \phi_1\phi_2 x_I (q_I + q)] + x_I^2 \beta_1 + x_2^2 \beta_2 + x_1 x_2 (\beta_1 + \beta_2) - \beta_1 \quad \text{(AIV.5)}$$

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

$$\gamma_C^{phys} = \gamma_A^{phys} = \gamma_I^{phys} \; . \quad \text{(AIV.6)}$$

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

$$\ln(\gamma_1^{\infty}) = q_1 (A + B) \quad \text{(AIV.7)}$$

$$\ln(\gamma_2^{\infty}) = q_2 (A) \quad \text{(AIV.8)}$$

## Appendix V

<u>Parameter estimation</u>

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 equation 3.2.1 and 3.2.9 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 equation 3.2.9 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

$$F = \sum_{l}^{J} ( Q_l^{(exp)} - Q_l^{(calc)} )^2 \qquad \text{(AV.1)}$$

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

$$F = \sum_{l}^{J} \sum_{r}^{M} ( z_{l,r}^{'(exp)} - z_{l,r}^{'(calc)} )^2 + ( z_{l,r}^{''(exp)} - z_{l,r}^{''(calc)} )^2 \qquad \text{(AV.2)}$$

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:

$$z_r = \frac{n_r}{n_1 + n_2 + n_E} \qquad \text{(AV.3)}$$

To obtain the objective function AV.2, the liquid compositions in the two phases have to be calculated by solving the isothermal liquid-liquid flash problem. Therefore a modified subroutine from /35/ 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

$$F_{init} = \sum_{l}^{J} \sum_{k}^{M} (x_{l,k}^{'(exp)} \gamma_{l,k}^{'(calc)} - x_{l,k}^{''(exp)} \gamma_{l,k}^{''(calc)} )^2 \qquad \text{(AV.4)}$$

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 AV.2 is minimized.

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