Predicting LLE in Mixed-Solvent Electrolyte Systems by an Electrolyte EOS

Julian Youxiang Zuo and Dan Zhang
DB Robinson Research Ltd., Edmonton, Alberta, Canada T6N 1E5

Walter Fürst
Laboratoire Réacteurs et Processus, ENSMP-ENSTA, 75739 Paris, Cedex 15, France

This work extends the previously published aqueous electrolyte equation of state (AEEOS) to predict liquid−liquid equilibria (LLE) of mixed-solvent electrolyte systems. Interaction parameters between ions and organic solvents, and cations and anions were determined by fitting the experimental vapor-pressure data of binary methanol + halide electrolyte mixtures, and then correlated to the cationic Stokes and anionic Pauling diameters. The focus is on the ionic standard/reference state and the standard Gibbs energy for transferring salts from one solvent to another. The methods applied to predict LLE of several ternary water + organic solvent + salt system are to select: 1. the hypothetical ideal gas at unit mol fraction, the system temperature, and 1 bar as the ionic standard state; 2. the infinite dilution in the solvent mixture as the ionic reference state, whose activity coefficients were converted to those at the infinite dilution in pure water by the ionic standard Gibbs energy of transfer. The predicted LLE results agree well with the measured data without any adjusted parameters in fitting the ternary experimental data. The extended AEEOS is comparable to the model of Zerres and Prausnitz, but the latter requires two adjusted parameters in fitting the ternary experimental data for each ternary system.

Introduction

In the past few decades, much progress has been made in representing the thermodynamic properties of electrolyte solutions. However, most of the studies in this field are restricted to aqueous electrolyte systems. Relatively less attention has been given to mixed-solvent electrolyte systems. Furthermore, less emphasis has been put on liquid−liquid equilibria (LLE) than vapor−liquid equilibria (VLE) in mixed-solvent electrolyte systems. An accurate and consistent representation of LLE in mixed-solvent electrolyte systems remains one of the challenging research fields in chemical engineering, as pointed out by Liu and Watanasiri (1996).

To represent phase equilibria in mixed-solvent (or aqueous) electrolyte systems, the excess Gibbs energy function is usually expressed as the sum of a Debye-Hückel (DH) and a short-range term. The UNIQUAC model (Sander et al., 1986; Macedo et al., 1990; Li et al., 1994a), or the UNIFAC model (Kikic et al., 1991; Achard et al., 1994) was employed for the short-range term. As we know, the short-range term is obtained within the Lewis-Randall (LR) framework, while the long-range (DH) term is derived from the McMillan-Mayer (MM) framework. To maintain consistency, the activity coefficients need to be converted from the MM to the LR framework.

Zerres and Prausnitz (1994) developed a thermodynamic framework for calculating VLE and LLE in ternary systems containing water, alcohol, and a salt. Short-range ion-solvent forces are taken into account primarily by a chemical equilibrium method based on stepwise ion solvation. Nonideality of water-cosolvent is described by an extended equation of the van Laar form. Long-range electrostatic forces among ions are taken into account by an extended DH model with corrections for transferring from the MM to the LR framework using the method of Cardoso and O'Connell (1987). The method of Zerres and Prausnitz is powerful because it is ca-

---

Correspondence concerning this article should be addressed to J. Y. Zuo.

pable of simultaneously describing VLE and LLE. However, different ionic reference states were used in the short-range and the long-range term.

Peng et al. (1994) combined the regular solution theory with the DH model to calculate LLE in mixed-solvent electrolyte systems. They also applied different ionic reference states in the short-range and the long-range term. Their results appear not as good as Zerres and Prausnitz's (1994) because the short-range term is too simple.

Liu and Watanasiri (1996) extended the electrolyte NRTL model with an additional term of the Brønsted-Guggenheim (BG) type to represent LLE in mixed-solvent electrolyte systems. The BG term compensates for the inadequacies of the DH and Born equations. However, the model cannot be reduced to the original one that has no BG term for binary electrolyte systems. In addition, five parameters were adjusted to fit the measured ternary LLE data for each water + alcohol + NaCl system.

Up to now, we are not aware of any equations of state (EOS) that have successfully been used to calculate the LLE of mixed-solvent electrolyte systems. In this work, we have extended the AEEOS of Fürst and Renon (1993), which was successfully applied to predict vapor pressures of binary nonaqueous electrolyte systems and VLE of mixed-solvent electrolyte systems by Zuo and Fürst (1997, 1998), to predict LLE of mixed-solvent electrolyte systems. Attention has been given to the ionic standard/reference state and the standard Gibbs energy for transferring salts from one solvent to another.

Extended Aqueous Electrolyte Equation of State of Fürst and Renon

For simplicity, Zerres and Prausnitz's (1994) assumption is followed; that is, a salt is completely dissociated into ions in the liquid phase.

The basis of the extended AEEOS is an expression of the molar Helmholtz energy:

$$\left(\frac{\Delta a}{RT}\right) = \left(\frac{\Delta a}{RT}\right)_{RF} + \left(\frac{\Delta a}{RT}\right)_{SR1} + \left(\frac{\Delta a}{RT}\right)_{\mathrm{BORN}} + \left(\frac{\Delta a}{RT}\right)_{LR} + \left(\frac{\Delta a}{RT}\right)_{SR2}, \qquad (1)$$

where all the terms except the Born term on the righthand side of Eq. 1 are similar to those used by Fürst and Renon (1993) and Zuo and Fürst (1997, 1998). The Born term is added for LLE calculations.

The first two terms on the righthand side of Eq. 1 are the repulsive force (RF) contribution and the first attractive short-range ($SR1$) contribution, respectively. They are similar to the corresponding terms of the SRK EOS modified by Schwartzentruber et al. (1989):

$$\left(\frac{\Delta a}{RT}\right)_{RF} + \left(\frac{\Delta a}{RT}\right)_{SR1} = \sum_i x_i \ln\left(\frac{x_i RT}{P_0(v-b)}\right) + \frac{a^{SR}}{RT(b+c)} \ln\left(\frac{v+c}{v+b+2c}\right), \qquad (2)$$

where the summation runs over all species and $P_0 = 1$ bar. The energy parameters (a^{SR}) and the volume translation parameters (c) of ions are set to zero, because short-range interactions between ions are specifically taken into account in the $SR2$ term and no ionic density data are available to estimate ionic volume translation parameters. Nevertheless, the covolumes (b) of all the species are taken into consideration. The Wong-Sandler mixing rule (1992) with the slightly modified UNIQUAC model is used to estimate a^{SR} and b of mixtures, as was done by Zuo and Fürst (1998). The expressions of a^{SR} and b for pure molecular components and mixtures are given in Appendix A.

For a salt-free system, the last three terms on the righthand side of Eq. 1 vanish as they are specially related to ions. The molar Helmholtz energy of the salt-free system is reduced to Eq. 2. The parameters of pure molecular components are the polar parameters (p_1, p_2, and p_3) and the volume translation parameter (c). They have been determined by fitting the experimental vapor pressure and density data of pure substances, respectively (Boublik et al., 1973; Reid et al., 1987). The values of these parameters are given in Table 1.

For a binary salt-free solvent mixture, there are three adjustable parameters $\tau_{12}^{(0)}$, $\tau_{21}^{(0)}$, and $\tau_{12}^{(1)} = \tau_{21}^{(1)}$ (see Appendix A). They have been determined by fitting the corresponding binary salt-free LLE (if the system forms two liquid phases) and VLE data (Sørensen and Arlt, 1980; Gmehling and Onken, 1977; Meissner and Stokes, 1944; Li et al., 1994b; De Santis et al., 1976a,b), as was done by Zerres and Prausnitz (1994). The values of those parameters are listed in Table 2.

The third term on the righthand side of Eq. 1 is the Born term, which considers that all the ions are discharged in vacuum and recharged in the solvent medium with dielectric constant D_s:

$$\left(\frac{\Delta a}{RT}\right)_{\mathrm{BORN}} = \frac{Ne^2}{4\pi\epsilon_0 RT}\left(\frac{1}{D_s} - 1\right)\sum_i \frac{x_i Z_i^2}{\sigma_i^*}, \qquad (3)$$

Table 1. Parameters (p_1, p_2, p_3, and c) of Pure Solvents

Solvent	p_1	p_2	p_3	$c \times 10^5$ m³/mol
Water	0.023175	4.6462	−8.8079	0.60473
1-Butanol	−0.021111	10.367	−16.625	1.2124
2-Methyl-1-propanol	−0.043565	5.2718	−9.4873	1.3090
2-Butanol	−0.051602	5.7542	−10.394	1.2120
1-Propanol	−0.00038896	−5.0422	24.074	1.0977
2-Propanol	−0.00086686	18.015	5.0466	1.2756
2-Butanone	−0.078486	−19.674	26.314	1.9810

Table 2. Correlated Parameters for Binary Aqueous Salt-Free Systems

Nonaqueous Solvent	$\tau_{12}^{(1)}=\tau_{21}^{(1)}$	$\tau_{12}^{(0)}$	$\tau_{21}^{(0)}$
1-Butanol	−0.6686	0.7949	1.1870
2-Methyl-l-propanol	−0.7234	0.5372	1.5200
2-Butanol	−0.7717	0.6529	1.5670
1-Propanol	−1.2520	0.7018	0.9731
2-Propanol	−0.8943	0.8760	0.7409
2-Butanone	−0.2675	0.2669	1.8980

where e, N, Z and ϵ_0 stand for the protonic charge, the Avogadro number, the ionic charge, and the electric permittivity of free space, respectively; σ_i^* is the diameter of ion i that is different from the ionic size parameter (σ_i) used in the last two terms of Eq. 1. The Born term has been added to correct the standard state of ions. It does not affect the calculation of the osmotic/mean-activity coefficient in the solvent medium and VLE, because it makes no contribution to the solvent fugacity coefficients and ionic activity coefficients at the reference state of the infinite dilution in the solvent medium. However, the Born term is important for the computation of salt solubility and LLE.

The fourth term on the righthand side of Eq. 1 is the long-range (LR) interaction contribution. The simplified mean spherical approximation (MSA) model proposed by Ball et al. (1985) is used

$$\left(\frac{\Delta a}{RT}\right)_{LR}=-\frac{\alpha_{LR}^2}{4\pi}\sum_i\frac{x_iZ_i^2\Gamma}{1+\Gamma\sigma_i}+\frac{\Gamma^3 v}{3\pi N}. \quad (4)$$

The shielding parameter Γ is given by

$$4\Gamma^2=\alpha_{LR}^2\sum_i\frac{x_i}{v}\left(\frac{Z_i}{1+\Gamma\sigma_i}\right)^2 \quad (5)$$

$$\alpha_{LR}^2=\frac{e^2N}{\epsilon_0 DRT}, \quad (6)$$

where D stands for the dielectric constant of the solution, which is expressed as

$$D=1+(D_s-1)\left(\frac{1-\xi_3''}{1-\xi_3''/2}\right). \quad (7)$$

The last term on the righthand side of Eq. 1 is the *SR2* contribution, which takes into account interactions between a molecule and an ion or between two ions:

$$\left(\frac{\Delta a}{RT}\right)_{SR2}=\frac{\sum_i\sum_j x_ix_jW_{ij}}{v(1-\xi_3)}, \quad (8)$$

where at least one of species i and j is an ion; W_{ij} denotes the symmetrical binary interaction parameter between species i and j; ξ_3 is defined as

$$\xi_3=\frac{N\pi}{6}\sum_i\frac{x_i\sigma_i^3}{v}, \quad (9)$$

in which the summation is over all the species. In Eq. 7, ξ_3'' is similar to ξ_3, but the summation is only over ions. The size parameter (σ_i) is related to the covolume (b_i) by

$$\sigma_i=\sqrt[3]{\frac{6b_i}{N\pi}}. \quad (10)$$

Hence, the parameters related to ions are cationic (b_c) and anionic (b_a) covolumes and symmetrical interaction parameters (W_{ij}). As was done by Zuo and Fürst (1997, 1998), the cationic (b_c) and anionic (b_a) covolumes are computed by the correlations:

$$b_c=\lambda_1\left(\sigma_c^{S(\mathrm{aq})}\right)^3+\lambda_2 \qquad \text{and} \qquad b_a=\lambda_1\left(\sigma_a^{P}\right)^3+\lambda_2, \quad (11)$$

where $\sigma_c^{S(\mathrm{aq})}$ represents the cationic Stokes diameter in aqueous solutions, and σ_a^P the anionic Pauling (crystalline) diameter. Therefore, the ionic volumes are independent of solvents.

The interaction parameters (W_{cc} and W_{aa}) between ions with the same sign charges and those (W_{as}) between an anion and a solvent are set to zero owing to the charge repulsive effect and the lower solvation of anions, respectively. Following Fürst and Renon (1993) and Zuo and Fürst (1997, 1998), the symmetrical interaction parameters for cation–solvent pairs (W_{cs}) and for cation–anion pairs (W_{ca}) are correlated to the cationic Stokes diameter (σ^S) in a single solvent and the anionic Pauling diameter (σ^P):

$$W_{cs}=\lambda_3\sigma_c^S+\lambda_4 \qquad \text{and} \qquad W_{ca}=\lambda_5\left(\sigma_c^S+\sigma_a^P\right)^4+\lambda_6. \quad (12)$$

For aqueous electrolyte solutions, Fürst and Renon (1993) determined coefficients $\lambda_1-\lambda_6$ by fitting the measured osmotic coefficient data of the binary aqueous electrolyte systems. For nonaqueous electrolyte solutions, not only λ_5 and λ_6 but also λ_3 and λ_4 have been determined by fitting the experimental vapor pressure data of binary methanol + halide electrolyte mixtures. The experimental data are taken from the same source as in Zuo and Fürst's paper (1997). The values of $\lambda_1-\lambda_6$ and the cationic Stokes diameters in single solvents are given in Tables 3 and 4, respectively.

When the extended AEEOS is applied to a ternary water + organic solvent + salt system, the dielectric constant of the mixed solvent is evaluated by a linear mixing rule over solvent weight fractions. The interaction parameter of the cation–water pair is estimated in terms of the cationic Stokes

Table 3. $\lambda_1-\lambda_6$ of Halide Electrolyte Systems

	λ_i, $\times 10^6$	
i	Water	Nonaqueous Solvent
1	0.10688	0.010688
2	6.5665	6.5665
3	35.090	82.398
4	6.0040	−422.45
5	−0.4304	−0.007162
6	−27.510	−402.90

Table 4. Cationic Stokes and Anionic Pauling Diameters (Å) in Single Solvents at 298.15 K

Solvent	Na^+	K^+	Cl^-	Br^-
Water	3.68	2.5	3.6	3.9
2-Methyl-1-propanol	9.5	6.5	3.6	3.9
1-Butanol	9.5		3.6	3.9
2-Butanol	9.5		3.6	3.9
1-Propanol	8.65		3.6	3.9
2-Propanol	8.65		3.6	3.9
2-Butanone	8.00	6.5	3.6	3.9

diameter in water and the corresponding $\lambda_3-\lambda_6$. Similarly, the interaction parameter of the cation–organic solvent pair is estimated by means of the cationic Stokes diameter in the organic solvent and the corresponding $\lambda_3-\lambda_6$. The interaction parameters for the cation–anion pair that are calculated by Eq. 12 are different because the cationic Stokes diameters and $\lambda_5-\lambda_6$ in both solvents are different. As a result, a mixing rule is required for the interaction parameters of the cation–anion pair (W_{ca}) in the mixed solvent. A linear mixing rule over the salt-free solvent mol fractions is utilized:

$$W_{ca}^{(m)} = \sum_{i=1} x_i^0 W_{ca}^{(i)}, \tag{13}$$

where $W_{ca}^{(i)}$ is the parameter W_{ca} in single solvent i.

The partial derivatives of the dielectric constant of the mixed solvent with respect to solvent mol numbers are not necessary. This is because the mixed solvent in the MSA and Born terms is not treated explicitly and is replaced by a dielectric medium where the mixed solvent is considered to be an effective pseudocomponent solvent.

Ionic Standard and Reference States

The standard state is a state at unit concentration (unit mol fraction is used in this work) with the physical properties at the reference state. As we all know, there are two approaches in representing the nonideality of electrolyte mixtures: the excess Gibbs energy (G^E) approach and the Helmholtz energy (EOS) approach.

The excess Gibbs energy of an electrolyte solution usually combines a DH term with a short-range interaction term. The DH expression is calculated in the MM framework. The independent variables are temperature, volume, the mol numbers of the solute species, and the chemical potentials of the solvents. The short-range term is derived within the LR framework, where the independent variables are temperature, pressure, and the mol numbers of all species. To maintain consistency, the activity coefficients need to be converted from the MM to the LR framework.

The DH (long-range) term, represented by Coulomb forces, considers a mixed-solvent solution of a salt as an effective pseudocomponent system where the mixed solvent appears as a dielectric medium only. The ionic reference state is always the infinite dilution in the dielectric medium, which depends on the composition of the solvent mixture. The DH model is derived on the basis of the Poisson equation of electrostatic theory with a statistical–mechanical distribution formula. It is a theoretical expression without any adjustable parameters (if the distance of the ionic closest approach is appropriate). An infinite dilute electrolyte solution follows the limiting law of Debye and Hückel.

On the other hand, the standard state of all components in the short-range term such as the UNIQUAC and NRTL models is the pure liquid at the system temperature and pressure. To combine the short-range term with the DH term, the short-range excess Gibbs energy must be normalized to the standard state of unsymmetrical convention for all ions. Actually, the reference state of ions in the short-range term can be any state that we select because it is an empirical or semiempirical term, which usually has two or three adjustable parameters for each binary system. Consequently, these adjustable parameters can be used to compensate more or less for the discrepancy of ionic reference states in the long-range and short-range terms.

The infinite dilution in pure water or in the mixed solvent at the system temperature and pressure is the commonly used reference state of ions. For example, Zerres and Prausnitz (1994) and Peng et al. (1994) chose the infinite dilution in pure water as the ionic reference state in the short-range term and assumed that the DH term has the same ionic reference state. They ignored the conversion of the ionic reference state in the long-range (DH) term. This can result in a serious problem for the computation of LLE and salt solubility, which will be discussed later.

In this work, an EOS (Helmholtz energy) approach is employed that is, to a certain extent, different from the G^E approach. However, the same problem also occurs. As in the DH model, the MSA (long-range) term treats the mixed solvent as a dielectric medium. The ionic standard state is the hypothetical ideal dilution in the solvent mixture at unit mol fraction and the system temperature and pressure. On the other hand, the standard state of all species (including ions) in the *RF*, *SR1*, and *SR2* terms of Eq. 1 (except for the MSA and Born terms) is ideal gas at unit mol fraction, and the system temperature and a fixed pressure ($P_0 = 1$ bar) because ions are treated as discharged particle species in the SRK-type EOS. This is apparently a discrepancy, which is related to the standard molar Gibbs energy for transferring salts from one solvent to another. The Born energy can be considered as the energy contribution of electrostatic forces for transferring ions from vacuum to the solvent medium. As we all know, any system approaches ideal gas when pressure approaches zero. Therefore, the Born term converts the ionic standard state of the MSA term to the hypothetical ideal gas at unit mol fraction and the system temperature, and a fixed pressure (1 bar) that is like that in other terms of Eq. 1. Harvey and Prausnitz (1989) used the Born term to convert the ionic standard state to the hypothetical ideal-gas state.

Standard Gibbs Energy for Transferring Salts from One Solvent to Another

According to the thermodynamic relations, for a solution of an electrolyte E in a mixed solvent, the chemical potential of electrolyte E can be expressed as

$$\mu_E = \mu_E^{0(\text{mix})} + \nu RT \ln\left(x_\pm \gamma_\pm^{(\text{mix})}\right) = \mu_E^{0(\text{wat})} + \nu RT \ln\left(x_\pm \gamma_\pm^{(\text{wat})}\right), \tag{14}$$

where $\nu = \nu_c + \nu_a$, ν_c and ν_a are the stoichiometric coefficients of cation c and anion a, respectively; $\mu_E^0 (= \nu_c \mu_c^0 + \nu_a \mu_a^0)$, and $\gamma_\pm$ $(\ln \gamma_\pm = \nu_c/\nu \ln \gamma_c + \nu_a/\nu \ln \gamma_a)$ are the chemical potential at the standard state and the mean activity coefficient, respectively. The superscript (mix) denotes that the ionic standard state is the hypothetical ideal dilution in the solvent mixture at unit concentration and the system temperature and pressure. Similarly, the superscript (wat) represents the hypothetical ideal dilution in pure water (or in a pure organic solvent) at unit concentration and the system temperature and pressure. The ionic mean activity coefficient can be computed in terms of the mean ionic fugacity coefficient ($\phi_\pm$):

$$\gamma_\pm^{(\text{mix or wat})}(T,P,x) = \frac{\phi_\pm(T,P,x)}{\phi_\pm^{\infty(\text{mix or wat})}(T,P,x^\infty)}, \quad (15)$$

where ϕ^∞ is the fugacity coefficient at the reference state of the infinite dilute solution in the solvent mixture (mix) or in pure water (wat).

Equation 14 can be rearranged as

$$\ln \gamma_\pm^{(\text{wat})} = \ln \gamma_\pm^{(\text{mix})} + \frac{\mu_E^{0(\text{mix})} - \mu_E^{0(\text{wat})}}{\nu RT} = \ln \gamma_\pm^{(\text{mix})} + \frac{\Delta G_{E,\text{tr}}^0(\text{wat} \to \text{mix})}{\nu RT}, \quad (16)$$

where $\Delta G_{E,tr}^0(\text{wat} \to \text{mix})$ (which equals $\mu_E^{0(\text{mix})} - \mu_E^{0(\text{wat})}$) is the standard molar Gibbs energy for transferring electrolyte E from water to the mixed solvent. Therefore, the mean activity coefficient referred to water is given by

$$\gamma_\pm^{(\text{wat})} = \gamma_\pm^{(\text{mix})} \exp\left[\frac{\Delta G_{E,\text{tr}}^0(\text{wat} \to \text{mix})}{\nu RT}\right] = \gamma_\pm^{(\text{mix})} \gamma_\pm^{(\text{tr})}(\text{wat} \to \text{mix}), \quad (17)$$

which is the product of two factors: the so-called *salt effect* $\gamma_\pm^{(\text{mix})}$ and the *medium effect* or *transfer coefficient* $\gamma_\pm^{(\text{tr})}(\text{wat} \to \text{mix})$. Since the salt concentration is allowed to decrease and $\gamma_\pm^{(\text{mix})}$ tends to unity at the infinite dilution, $\gamma_\pm^{(\text{wat})}$ will approach $\gamma_\pm^{(\text{tr})}(\text{wat} \to \text{mix})$, which is a characteristic of electrolyte E and the two solvents (wat) and (mix). Equation 17 converts the mean activity coefficients from one standard state to another through the standard Gibbs energy of transfer. The conversion expressions of mean activity coefficients and the standard Gibbs energy of transfer among different concentration scales are given in Appendix B.

As pointed out by Marcus (1985), several experimental methods can be used to obtain the standard Gibbs energy of transfer, such as the EMF measurement on suitable electrochemical cells, the measurement of the distribution of electrolyte E between virtually immiscible solvents, and the measurement of salt solubility.

In the next section we evaluate the effect of the ionic reference states on mean ionic activity coefficients and the standard Gibbs energy of transfer according to the measured data in the open literature.

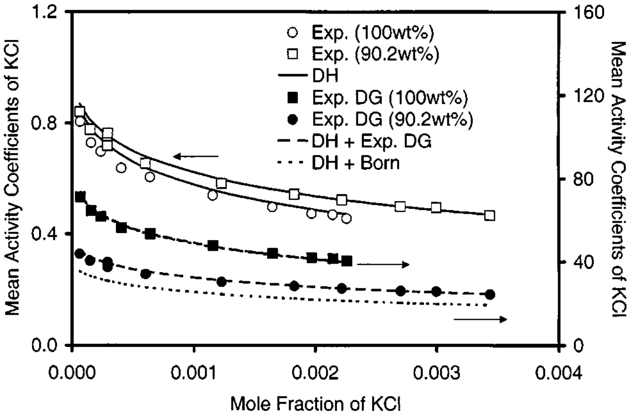

Figure 1. Molar mean activity coefficients in the methanol+water+KCl system at 298.15 K.

Evaluation of the Standard Gibbs Energy of Transfer Based on the Data in the Literature

EMF measurement data of Malahias and Popovych for the methanol + water + KCl system at 298.15 K

Malahias and Popovych (1982) measured the mean activity coefficients and solubility data of KCl in the methanol+water mixture using the EMF method. The standard Gibbs energy for transferring KCl from water to the solvent mixture was also reported. It is well known that the ionic reference state in the EMF measurement is the infinite dilution in the solvent mixture. Since the solubilities of KCl in methanol (100 wt. %) and in the methanol (90 wt. %)+water (10 wt. %) mixture are low (mol fractions are 0.0023 and 0.0034, respectively), the DH model applied by Zerres and Prausnitz (1994) is adequate. The short-range term can be neglected. Figure 1 compares the measured data of the molar mean activity coefficients of KCl by Malahias and Popovych (open circles and squares) with the predictions using the DH model (solid lines). It can be seen that the predictions using the DH model are in good agreement with the measured data.

On the other hand, these mean ionic activity coefficients can be converted to those at the reference state of the infinite dilution in pure water by Eq. 17 through the standard Gibbs energy for transferring KCl from water to the mixed solvent (or pure methanol). The converted molar mean activity coefficients of KCl are also depicted in Figure 1. The solid squares and circles are the experimental mean activity coefficients converted through the experimental standard Gibbs energy of transfer. The dashed curves stand for the mean activity coefficients calculated by the DH model and converted through the experimental standard Gibbs energy of transfer. The converted values (referred to water) are much higher than those referred to the mixed solvent, especially in pure methanol.

Liu and Watanasiri (1996) used the Born term to convert mean ionic activity coefficients from one reference state to another. In that case, the Born term is written as

$$\left(\frac{g^E}{RT}\right)_{\text{BORN}} = \frac{Ne^2}{4\pi\epsilon_0 RT}\left(\frac{1}{D_{\text{mix}}} - \frac{1}{D_{\text{wat}}}\right)\sum_i \frac{x_i Z_i^2}{\sigma_i^*}. \quad (18)$$

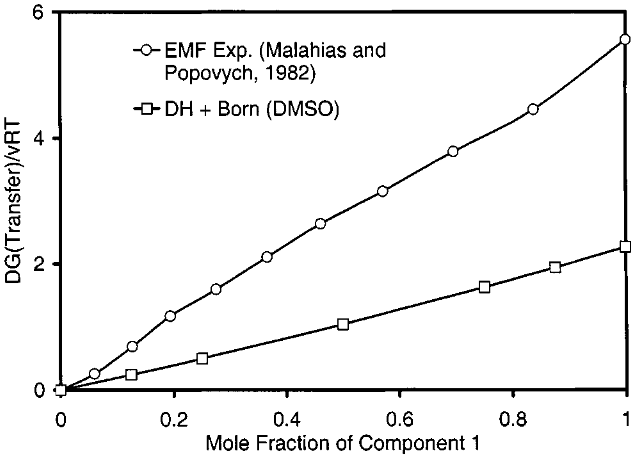

Figure 2. Standard molar Gibbs energy of transfer ($\Delta G^0_{E,\mathrm{tr}}/\nu RT$) in methanol (1)+water (2)+KCl (3) and DMF (1)+DMSO (2)+KCl (3) systems at 298.15 K.

The molar mean activity coefficients of KCl (referred to water) calculated by the DH model combined with the Born term are also depicted in Figure 1 (dotted curves). The ionic diameters (σ_i^*) are adjusted to fit the activity coefficient data in pure methanol, since the Born term is sensitive to the parameters. It can be seen that mean activity coefficients are underpredicted by the DH model combined with the Born term in 90.2 wt. % methanol.

The standard molar Gibbs energy for transferring KCl from water to the solvent mixture is depicted in Figure 2 (open circle–solid line). The experimental data are taken from Malahias and Popovych (1982). According to Eq. 17, $\gamma_\pm^{(\mathrm{tr})}(\mathrm{wat} \rightarrow \mathrm{mix})$ or the difference of mean activity coefficients between both reference states increases with methanol concentrations.

LLE measurement data of De Santis et al. for the 1-butanol + water + NaCl system at 298.15 K

De Santis et al. (1976b) measured the LLE data of the 1-butanol + water + NaCl system at 298.15 K. In the aqueous phase (′) of this system, the mol fraction of 1-butanol is very low ($x'_{\mathrm{butanol}} = 0.002$–$0.02$ on the salt-free basis). Therefore, the mean ionic activity coefficients ($\gamma'_\pm$) in the aqueous phase are similar to those in binary aqueous NaCl solutions. Since experimental ionic mol fractions in both equilibrium liquid phases are known and $\gamma'_\pm$ in the aqueous phase can be obtained from the experimental data of binary aqueous NaCl solutions or calculated by the extended AEEOS, $\gamma''_\pm$ in the organic phase (″) can be obtained from the LLE criterion: $\gamma''_\pm = x'^{\mathrm{exp}}_\pm \gamma'^{\mathrm{cal}}_\pm / x''^{\mathrm{exp}}_\pm$. Here, superscript exp denotes the experimental value. As $\gamma'_\pm$ is based on the ionic reference state of the infinite dilution in pure water, $\gamma''_\pm$ must also be based on the same reference state. Figure 3 shows molar mean ionic activity coefficients at this reference state. The dot-dashed curve is the mean ionic activity coefficient in the aqueous phase (very close to the x-axis), and the open circles denote those in the organic phase. The mean activity coefficients ($\gamma'_\pm$) in the aqueous phase are in between 0.0 and 1.4, while those ($\gamma''_\pm$) in the organic phase are in between 14 and 68, which are much greater than the values estimated by the DH model or the MSA term (in between 0 and 1).

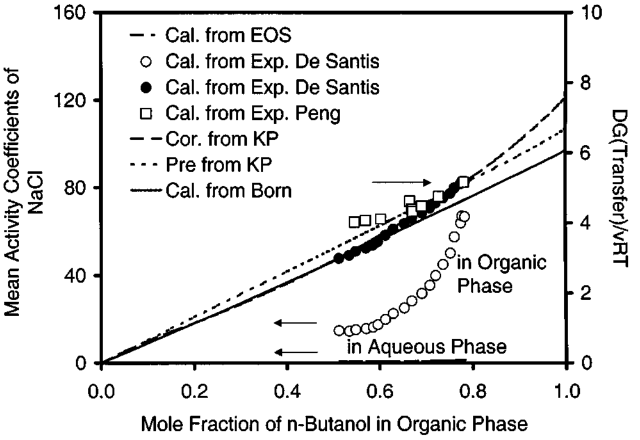

Figure 3. Molar mean activity coefficients and standard molar Gibbs energy of transfer ($\Delta G^0_{E,\mathrm{tr}}/\nu RT$) in the water + 1-butanol + NaCl system at 298.15 K.

In the organic phase of this system, the mol fraction of NaCl is extremely low ($x''_{\mathrm{NaCl}} = 0.0002$–$0.002$, $x''_{\mathrm{butanol}} = 0.5$–$0.8$). Hence, the MSA term (or the DH model) is adequate to describe mean activity coefficients and the contribution of the short-range term can be ignored. As we know, the mean activity coefficients ($\gamma''_\pm$) estimated by the MSA term (or the DH model) are usually between 0 and 1 ($0 < \gamma''_\pm < 1$) and close to unity at such low NaCl concentrations. Accordingly, ($\ln \gamma_\pm^{(\mathrm{wat})} - \ln \gamma_\pm^{(\mathrm{mix})}$) can be obtained, which is related to the standard molar Gibbs energy of transfer from Eq. 16. Figure 3 also shows the standard molar Gibbs energy of transfer divided by νRT. The solid circles and open squares are calculated from the experimental data of De Santis et al. (1976b) and Li et al. (1994b), respectively. Hence, if the reference state of ions in the long-range (MSA or DH) term is not converted, it can lead to a serious problem in the computation of LLE.

Salt solubility measurement data of Labban and Marcus for the DFM + DMSO + KCl system at 298.15 K

Labban and Marcus (1991) measured KCl solubility in *N*, *N*-dimethylformamide (DFM) + dimethylsulfoxide (DMSO) mixtures at 298.15 K. As pointed out by Labban and Marcus (1997), the DH (or MSA) model is adequate for calculating the mean activity coefficients of this system. The calculated molar mean activity coefficients are shown in Figure 4. The open diamond dot-dashed curve is calculated only using the DH model that is based on the reference state of the infinite dilution in the solvent mixture. The values are around 0.7–1 because the difference of dielectric constants between DMSO and DFM is not significant (46.68 and 36.71). The open square-dashed curve is calculated using the DH model and the Born term at the reference state of the infinite dilution in pure DMSO. Here, ionic diameters in the Born term are adjusted to fit the measured solubility data in both binary DMSO + KCl and DMF + KCl systems. The mean activity co-

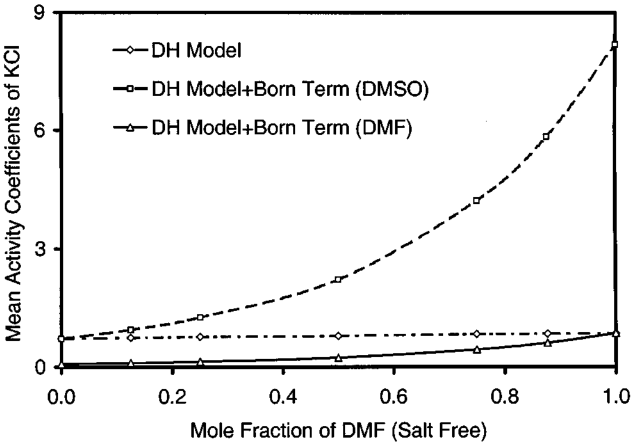

Figure 4. Molar mean activity coefficients in the DMF (1)+DMSO (2)+KCl (3) system at 298.15 K.

efficients are greater than those estimated by the DH model only. The difference becomes larger when the solvent approaches to pure DMF. The open triangle-solid curve is calculated using the DH model and the Born term at the reference state of the infinite dilution in pure DMF. The values remarkably decrease as DMF concentrations decrease.

The solubility data are shown in Figure 5. The solid curve is calculated using the DH model and the Born term at the reference state of the infinite dilution in pure DMSO or DMF. The calculated results are in good agreement with the measured data (open circles). The dashed curve is calculated using the DH model with the solubility product at the reference state of the infinite dilution in pure DMSO. The solubility is significantly overpredicted. Similarly, the dotted curve is calculated using the DH model with the solubility product at the reference state of the infinite dilution in pure DMF. The solubility is significantly underpredicted. The standard molar Gibbs energy for transferring KCl from DMSO to DMF is also shown in Figure 2 (square-solid curve). Therefore, if the ionic reference state in the DH or MSA term is not converted, it results in a serous problem in the calculation of salt solubility in the mixed solvent.

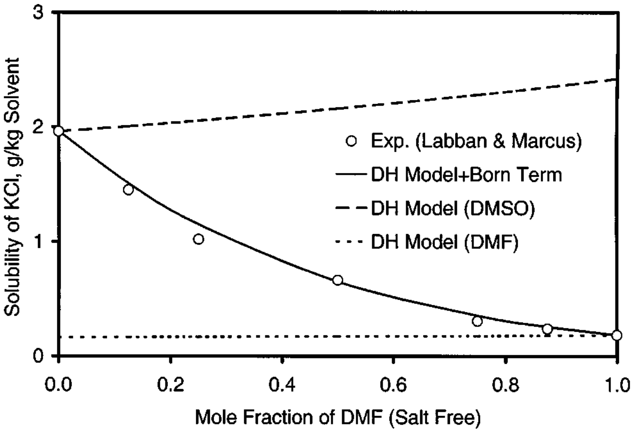

Figure 5. KCl solubility in the DMF (1)+DMSO (2)+KCl (3) system at 298.15 K.

As shown in Figures 2 and 3, the standard molar Gibbs energy for transferring a salt from a pure solvent 1 to solvent mixtures has similar trends. They more or less deviate from the linear line of the mol fraction of a solvent 2 multiplied by the standard molar Gibbs energy for transferring the salt from the pure solvent 1 to the pure solvent 2.

From the numerical point of view, the short-range term may compensate for the just-mentioned discrepancy regarding the ionic reference state. However, more parameters are required to fit the experimental LLE and salt solubility data and the same sets of parameters may not be suitable for the computation of VLE, LLE, mean ionic activity coefficient, and salt solubility simultaneously. For instance, Zerres and Prausnitz (1994) added a very important three-body interaction parameter (b) to obtain a reasonable representation of mean activity coefficients in the organic phase where the salt concentrations are extremely low and the DH model is adequate (dominant). Without this parameter, the model might have given a poor representation of LLE, although the model parameters for binary salt−organic solvent pairs were adjusted by fitting the experimental ternary LLE data.

As a result, it seems there are two ways of solving the problem mentioned earlier. One way is to apply the Born term to convert the ionic reference state in the long-range (MSA or DH) term. The other is to use the infinite dilution in the mixed solvent as the ionic reference state in the short-range and long-range terms. The mean activity coefficients at this reference state are then converted to those at the reference state of the infinite dilution in pure water through the ionic standard molar Gibbs energy of transfer. These two methods have been applied in this work to calculate LLE for mixed-solvent electrolyte systems.

Liquid−Liquid Equilibria in Mixed-Solvent Electrolyte Systems

Representation of LLE directly using the extended AEEOS

In the EOS approach, the liquid−liquid equilibrium criterion for all the species at a given temperature and pressure is given by

$$\phi_i' x_i' = \phi_i'' x_i'', \tag{19}$$

where ′ (prime) and ″ (double prime) denote both liquid phases; and ϕ and x are the fugacity coefficient and the mol fraction, respectively. For ions, the mean fugacity coefficient ($\phi_\pm$) and the mean mol fraction ($x_\pm$) must be used in Eq. 19. The validity of Eq. 19 requires that each species must have the same standard (or reference) state in both liquid phases. This method is referred to as Method I.

As pointed out by Rashin and Honing (1985), it is appropriate to use the diameter of the cavity that an ion forms in the solvent in Born's equation. That means the ionic diameters are solvent dependent. Harvey and Prausnitz (1989) modified the Born term slightly in their aqueous electrolyte EOS. They applied different cationic diameters in the Born and other terms of the EOS. Therefore, for simplicity, ionic diameters used in the Born term are assumed to be proportional to the ionic size parameters calculated by Eq. (10):

$$\sigma_i^* = f\sigma_i, \tag{20}$$

Table 5. Deviations of the Predicted LLE Using Method I

System	T, K	Max. wt. % Salt	Δz, %	Source of Data
Water + 1-butanol + NaCl	298.15	26	0.38	De Santis et al. (1976a)
Water + 2-butanol + NaCl	298.15	26	0.30	De Santis et al. (1976a)
Water + 2-propanol + NaCl	298.15	26	1.93	De Santis et al. (1976a)
Water + 1-propanol + NaCl	298.15	26	1.39	De Santis et al. (1976a)
Water + 2-butanone + KBr	298.15	37	0.49	Li et al. (1994)
Water + 2-butanone + NaCl	298.15	25	0.79	Li et al. (1994)
Water + 2-butanone + KCl	298.15	24	0.83	Li et al. (1994)
Water + 1-butanol + KBr	298.15	40	1.20	Al-Sahhaf and Kapetanovic (1997)
Water + 1-butanol + KCl	293.15–313.15	28	0.68	Li et al. (1994b)
Water + 1-butanol + KBr	298.15	39	0.96	Li et al. (1994b)
Water + 1-butanol + NaCl	298.15	26	0.38	Li et al. (1994b)
Water + 1-butanol + NaCl	293.15–313.15	26	0.63	De Santis et al. (1976b)
Water + 2-butanol + NaCl	298.15	26	0.68	De Santis et al. (1976a)

where the coefficient f is solvent dependent and determined by fitting the experimental solubility data of binary nonaqueous electrolyte systems (Seidell and Linke, 1958, 1965; De Santis et al., 1976a). The obtained coefficients (f) are 1.32 and 1.4 for binary propanol + salt systems and for binary butanol/butanone + salt systems, respectively. For binary water + salt systems it is assumed that f is equal to unity. For a ternary system, the arithmetical mean of the coefficient f is used. Therefore, $f = 1.16$ for water + propanol + salt systems and $f = 1.23$ for water + butanol/butanone + salt systems.

The LLE for 10 ternary water + organic solvent + salt systems have been predicted using the extended AEEOS. The predicted results are given in Table 5. The accuracy of the calculated results is represented by the average deviation, Δz, as defined by Sørensen and Arlt (1980):

$$\Delta z = \sqrt{\frac{\sum_{l}^{J} \sum_{r}^{M} \left[\left(z_{l,k}^{\prime(\mathrm{exp})} - z_{l,k}^{\prime(\mathrm{cal})} \right)^2 + \left(z_{l,k}^{\prime\prime(\mathrm{exp})} - z_{l,k}^{\prime\prime(\mathrm{cal})} \right)^2 \right]}{2JM}}, \qquad (21)$$

where J and M are the number of experimental data and the number of components in the system, respectively, and z is the apparent mol fraction.

A comparison of the extended AEEOS with the model of Zerres and Prausnitz (1994) and the electrolyte NRTL model used by Liu and Watanasiri (1996) for four ternary systems is given in Table 6. The extended AEEOS is comparable with the Zerres and Prausnitz model. For systems containing propanol, the extended AEEOS gives larger deviations than the model of Zerras and Prausnitz (1994) and the electrolyte NRTL model. This is because the extended AEEOS gives vapor-density roots (instead of liquid-density roots) in the organic phase at lower NaCl concentrations. Considering that the extended AEEOS, the model of Zerres and Prausnitz, and the electrolyte NRTL model have none, two and five parameters, which are adjusted by fitting the experimental ternary LLE data, respectively, the results predicted by the AEEOS are satisfactory.

Table 6. Extended AEEOS vs. Zerres and Prausnitz Model and Electrolyte NRTL Model Used by Liu and Watanasiri

	Δz, %		
System	ZP Model	NRTL	Extended AEEOS
Water + 1-butanol + NaCl	0.7	0.5	0.38
Water + 2-butanol + NaCl	1.3	0.4	0.30
Water + 2-propanol + NaCl	1.7	0.5	1.93
Water + 1-propanol + NaCl	1.0	0.6	1.39

Figure 6 shows the predicted LLE results of the water + 1-butanol + NaCl system at 298.15 K. The solid and open circles are experimental weight fractions of water and of 1-butanol in the aqueous phase (AP) and the organic phase (OP) measured by De Santis et al. (1976a,b). The solid and open squares are experimental weight fractions of water and of 1-butanol in the aqueous phase and the organic phase measured by Li et al. (1994b). The predictions (the solid and dashed curves) using Method I are in good agreement with experimental data.

Representation of LLE using ionic standard Gibbs energy of transfer

As mentioned previously, ionic activity coefficients can be calculated using the extended AEEOS at the reference state of the infinite dilution in the mixed solvent at the system temperature and pressure. Therefore, the ionic activity coefficients can be converted to those at the reference state of the infinite dilution in pure water through the standard molar Gibbs energy for transferring salts from water to the mixed solvent. The standard molar Gibbs energy of transfer can be

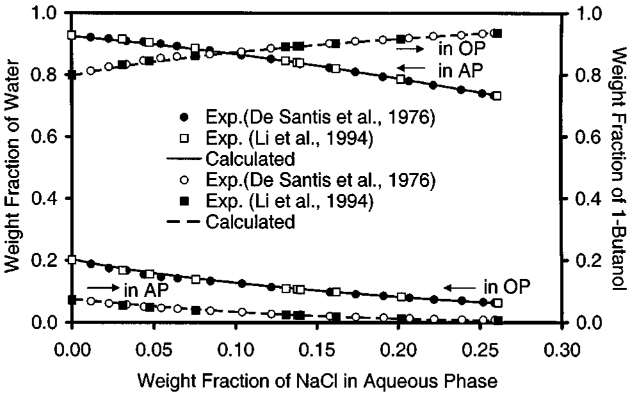

Figure 6. Composition of LLE of the water + 1-butanol + NaCl system at 298.15 K.

estimated using the model proposed by Kolker and de Pablo (1996). This method is referred to as Method II. In this case, the Born term vanishes.

At a given temperature and pressure, the LLE criterion for ionic species is written as

$$x'_{\pm}\gamma'^{(\mathrm{wat})}_{\pm} = x''_{\pm}\gamma''^{(\mathrm{wat})}_{\pm}, \tag{22}$$

where mean ionic activity coefficients are converted using Eq. 17. For molecular components, Eq. 19 is still applicable.

Since there are a few data of the standard molar Gibbs energy for transferring electrolyte E in the literature, a method is required to estimate such data. Kolker and de Pablo (1996) made some assumptions and proposed a method to estimate the chemical potential of electrolyte E at the standard state that is the ideal dilute solution in the mixed solvent at unit concentration (mol fraction):

$$\frac{\mu_E^{0(\mathrm{mix})}}{\nu RT} = \frac{x_1^0\,\mu_{E1}^{0(\mathrm{wat})} + x_2^0\,\mu_{E2}^{0(\mathrm{org})}}{\nu RT} + x_1^0\frac{\bar{\nu}_{E1}^{\infty}}{\nu_1^0}\ln a_1 + x_2^0\frac{\bar{\nu}_{E2}^{\infty}}{\nu_2^0}\ln a_2, \tag{23}$$

where 1 and 2 represent water and an organic solvent, respectively; a_i is the activity of solvent i in the salt-free solvent mixture, which is calculated by the extended AEEOS; μ_{Ei}^0 denotes the chemical potential of electrolyte E at the standard state of the ideal dilution in pure single solvent i at unit concentration; x_i^0 is the salt-free mol fraction of solvent i; $\bar{\nu}_{Ei}^{\infty}$ and ν_i^0 are the partial molar volume of electrolyte E at infinite dilution in pure single solvent i and the molar volume of pure solvent i, respectively, which have been related to the molecular weight (M) and density (ρ) by Kolker and de Pablo (1996):

$$\frac{\bar{\nu}_{Ei}^{\infty}}{\nu_i^0} = \frac{M_E}{M_i} - \frac{1}{\rho_i^0}\left(\frac{\partial \rho_{Ei}}{\partial x_E}\right)_{x_E=0}, \tag{24}$$

where M_E, M_i, ρ_i^0 are the molecular weights of electrolyte E and solvent i and the density of solvent i, respectively.

Hence, the standard molar Gibbs energy for transferring electrolyte E from water to the mixed solvent is estimated by:

$$\frac{\Delta G_{E,\mathrm{tr}}^0(\mathrm{wat}\rightarrow\mathrm{mix})}{\nu RT} = \frac{x_2^0\left(\mu_{E2}^{0(\mathrm{org})} - \mu_{E1}^{0(\mathrm{wat})}\right)}{\nu RT} + x_1^0\frac{\bar{\nu}_{E1}^{\infty}}{\nu_1^0}\ln a_1 + x_2^0\frac{\bar{\nu}_{E2}^{\infty}}{\nu_2^0}\ln a_2, \tag{25}$$

where $\Delta G_{E,\mathrm{tr}}^0(\mathrm{wat}\rightarrow\mathrm{org}) = \mu_{E2}^0 - \mu_{E1}^0$, that is, the standard molar Gibbs energy for transferring electrolyte E from water to a pure organic solvent. The first term of Eq. 25 is a linear contribution of the solvent mol fraction multiplied by the standard molar Gibbs energy for transferring electrolyte E from water to the pure organic solvent, and the last two terms can be considered to be a *corrective* contribution.

$\Delta G_{E,\mathrm{tr}}^0(\mathrm{wat}\rightarrow\mathrm{org})$ can be estimated by fitting the experimental salt solubility data in binary nonaqueous electrolyte solutions, as pointed out by Labban and Marcus (1991, 1997). According to the solid–liquid equilibrium criterion, the standard molar Gibbs energy of a binary solvent + electrolyte E solution at saturation is expressed as

$$\begin{aligned}\Delta G_{E,\mathrm{sat}}^0(\mathrm{solution}) &= \nu_a\,\mu_a^0 + \nu_c\,\mu_c^0 - \mu_E^0(\mathrm{solid}) \\ &= -\,\nu RT\ln x_{\pm,\mathrm{sat}}\gamma_{\pm,\mathrm{sat}} = -\,RT\ln K_{SP},\end{aligned} \tag{26}$$

where K_{SP} is the solubility product.

The standard molar Gibbs energy for transferring electrolyte E from water to a pure organic solvent, $\Delta G_{E,\mathrm{tr}}^0(\mathrm{wat}\rightarrow\mathrm{org})$, is then expressed as

$$\Delta G_{E,\mathrm{tr}}^0(\mathrm{wat}\rightarrow\mathrm{org}) = \Delta G_{E,\mathrm{sat}}^{0(\mathrm{org})}(\mathrm{solution}) - \Delta G_{E,\mathrm{sat}}^{0(\mathrm{wat})}(\mathrm{solution}), \tag{27}$$

where $\Delta G_{E,\mathrm{sat}}^{0(\mathrm{wat})}$(solution) in aqueous solutions can be obtained from handbooks of physical chemistry (Lide, 1996; Weast, 1971), while $\Delta G_{E,\mathrm{sat}}^{0(\mathrm{org})}$(solution) in organic solutions can be estimated from binary salt solubility data (Seidell and Linke, 1958, 1965; De Santis et al., 1976a) and mean activity coefficients at saturation using Eq. 26. In this work, since salt solubility in single organic solvents is very low, the mean activity coefficients are predicted using the extended AEEOS. Because the salt concentration is very low, the long-range (MSA) term is dominant and adequate for estimating mean activity coefficients. The values of $\Delta G_{E,\mathrm{tr}}^0(\mathrm{wat}\rightarrow\mathrm{org})/\nu RT$ on the mol fraction scale are listed in Table 7 (column 4). The ionic standard chemical potential given in handbooks of physical chemistry is usually based on the molality scale. The conversion among different concentration scales is given in Appendix B.

The ratio of $\bar{\nu}_{E1}^{\infty}/\bar{\nu}_1^0$ for binary aqueous electrolyte solutions is estimated by Eq. 24. Density data in aqueous electrolyte solutions are obtained from Novotny and Söhnel (1988). Those values are listed in Table 7 (column 3). The ratio of $\bar{\nu}_{E2}^{\infty}/\bar{\nu}_2^0$ for binary nonaqueous electrolyte solutions is empirically set to 0.5, which is obtained by numerical estimation of the ratios for some systems using the extended AEEOS. This makes the model predictive because no ternary data are required to determine model parameters.

The liquid–liquid equilibria for the same 10 ternary water + organic solvent + salt systems as given in Table 5 have been predicted using this method. The predicted results are given in Table 7. The predictions using Method II are comparable to those using Method I.

Figure 7 compares the experimental and predicted NaCl concentrations in both liquid phases. The solid and dashed curves are predicted by Methods I and II, respectively. The concentration of NaCl in the organic phase is very low and sensitive to any small calculation errors in water and 1-butanol concentrations. Since the difference between the experimental data measured by De Santis et al. (1976b) and by Li et al. (1994b) is appreciable, the predicted concentration of NaCl in the organic phase is acceptable.

The dotted curve is calculated by Method II but two parameters ($\Delta G_{E,\mathrm{tr}}^0(\mathrm{wat}\rightarrow\mathrm{org})/\nu RT = 7.6$ and $\bar{\nu}_{E2}^{\infty}/\upsilon_2^0 = 5.4$)

Table 7. Deviations of the Predicted LLE Using Method II

System	T, K	$\bar{v}^{\infty}_{E1}/v^0_1$	$\Delta G^0_{E,\mathrm{tr}}(\mathrm{wat} \rightarrow \mathrm{org})/\nu RT$	Δz, %
Water + 2-butanol + NaCl	298.15	0.8675	6.7	0.38
Water + 2-butanol + NaCl	298.15	0.8675	6.5	0.29
Water + 2-propanol + NaCl	298.15	0.8675	6.6	1.74
Water + 1-propanol + NaCl	298.15	0.8675	6.6	1.38
Water + 2-butanone + KBr	298.15	1.7910	6.6	0.49
Water + 2-butanone + NaCl	298.15	0.8675	6.8	0.82
Water + 2-butanone + KCl	298.15	1.4570	6.8	0.83
Water + 1-butanol + KBr	298.15	1.7910	5.6	0.96
Water + 1-butanol + KCl	293.15–313.15	1.4570	6.0	0.64
Water + 1-butanol + KBr	298.15	1.7910	5.6	0.69
Water + 1-butanol + NaCl	298.15	0.8675	6.7	0.38
Water + 1-butanol + NaCl	293.15–313.15	0.8675	6.7	0.68
Water + 2-butanol + NaCl	298.15	0.8675	7.0	0.66

have been determined by fitting the ternary LLE data of De Santis et al. (1976a). The calculated results are in good agreement with the experimental data. That is, the terms of $\Delta G^0_{E,\mathrm{tr}}(\mathrm{wat} \rightarrow \mathrm{org})/\nu RT$ and $\bar{v}^{\infty}_{E2}/v^0_2$ can be treated as adjustable parameters in order to obtain a good representation of LLE.

For comparison, the standard molar Gibbs energy for transferring NaCl from water to the mixed solvent is calculated by the Born term (Method I, solid curve) and the method of Kolker and de Pablo (Method II) without tuning (dotted curve) and with tuning (dashed curve). The results are shown in Figure 3. If the terms of $\Delta G^0_{E,\mathrm{tr}}(\mathrm{wat} \rightarrow \mathrm{org})/\nu RT$ and $\bar{v}^{\infty}_{E2}/v^0_2$ are not adjusted, the results do not match well with the experimental data of De Santis et al. (1976a,b). If the terms of $\Delta G^0_{E,\mathrm{tr}}(\mathrm{wat} \rightarrow \mathrm{org})/\nu RT$ and $\bar{v}^{\infty}_{E2}/v^0_2$ are adjusted to match the LLE data of De Santis et al. (1976a,b), very good agreement is reached between the calculated and experimental standard molar Gibbs energy of transfer, which is calculated from the LLE data of De Santis et al. (1976a,b).

The standard molar Gibbs energy of transfer from water to the mixed solvent can also estimated in terms of the quasi-lattice, quasi-chemical theory proposed by Marcus (1985). The method needs the following data: (1) the standard molar Gibbs energy for transferring electrolyte E from water to a pure organic solvent; (2) the Gibbs energy of mixing of the solvents for the equimolar mixture; and (3) a lattice adjustable parameter. Due to lack of data, that method is not tested in this work.

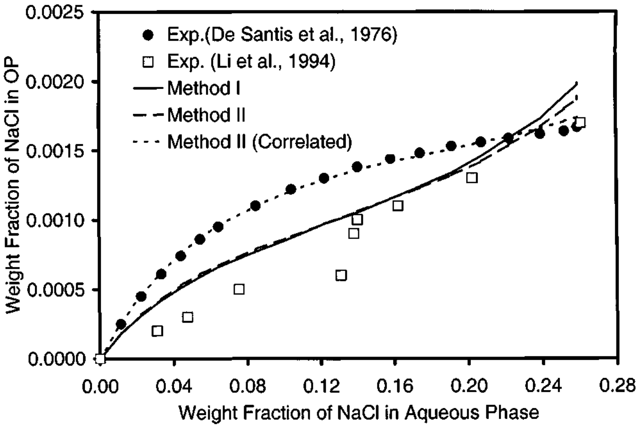

Figure 7. Concentrations of NaCl in two liquid phases of LLE of the water + 1-butanol + NaCl system at 298.15 K.

Up to now, experimental data of the standard molar Gibbs energy for transferring electrolytes from water (or noaqeuous solvents) to the mixed solvent are scarce in the open literature. Such experimental data are required in order to have a better understanding of ionic preferential solvation and to derive a more precise electrolyte model.

Conclusion

The electrolyte EOS of Fürst and Renon (1993) has been extended to represent LLE in mixed-solvent electrolyte systems. Two methods have been tested. The predicted results using the two methods are in good agreement with experimental data without any parameters adjusted from ternary data.

The thermodynamic framework proposed in this work provides a useful tool for the calculations of LLE in mixed-solvent electrolyte systems.

Notation

a = molar Helmholtz free energy
a_i = activity of solvent i
a^{SR} = energy parameter of molecular components
b = covolume
c = volume translation parameter
D = dielectric constant of a solution
D_s = dielectric constant of a solvent mixture
e = protonic charge
N = Avogadro number
P = pressure
R = gas constant
T = temperature
v = molar volume
W = interaction parameter
x = mol fraction
Z = ionic charge
$\gamma_{\pm}$ = mean ionic activity coefficient
ϵ_0 = electric permittivity of free space
λ = correlation coefficient of interaction parameter
μ = chemical potential
ν = stoichiometric coefficient
ρ = density
σ = diameter or size parameter
τ = binary interaction parameter
ϕ = fugacity coefficient
ω = acentric factor

Superscripts and subscripts

cal = calculated
exp = experimental
mix = infinite dilute solution in the mixed solvent
P = Pauling diameter
S = Stokes diameter
wat = infinite dilute solution in pure water
0 = standard state or property in salt-free solvents
1 = water
2 = alcohol
∞ = property at infinite dilution
a = anionic properties
BORN = Born's term
c = cationic properties
E = electrolyte or salt
i, j = species i or j
LR = long-range term
RF = replusive forces
s = solvent properties
sat = saturated properties
$SR1$ = nonelectrolyte short-range term
$SR2$ = ionic short-range term
$\pm$ = mean ionic properties

Literature Cited

Achard, C., C. G. Dussap, and J. B. Gros, "Representation of Vapor-Liquid Equilibria in Water-Alcohol-Electrolyte Mixtures with a Modified UNIFAC Group-Contribution Method," *Fluid Phase Equilibria*, **98**, 71 (1994).

Al-Sahhaf, T. A., and E. Kapetanovic, "Salt Effect of Lithium Chloride, Sodium Bromide, or Potassium Iodide on Liquid-Liquid Equilibrium in the System Water + 1-Butanol," *J. Chem. Eng. Data*, **42**, 74 (1997).

Ball, F.-X., H. Planche, W. Fürst, and H. Renon, "Representation of Deviation from Ideality in Concentrated Aqueous Solutions of Electrolytes Using a Mean Spherical Approximation Molecular Model," *AIChE J.*, **31**, 1233 (1985).

Boublik, T., V. Fried, and E. Hala, *The Vapor Pressures of Pure Substances*, Elsevier, Amsterdam (1973).

Cardoso, M. J. E. de M., and J. P. O'Connell, "Activity Coefficients in Mixed Solvent Electrolyte Solutions," *Fluid Phase Equilibria*, **33**, 315 (1987).

De Santis, R., L. Marrelli, and N. Muscetta, "Liquid-Liquid Equilibrium in Water-Aliphatic Alcohol Systems in the Presence of Sodium Chloride," *Chem. Eng. J.*, **11**, 207 (1976a).

De Santis, R., L. Marrelli, and N. Muscetta, "Influence of Temperature on the Liquid-Liquid Equilibrium of the Water-*n*-Butyl Alcohol-Sodium Chloride System," *J. Chem. Eng. Data*, **21**, 234 (1976b).

Fürst, W., and H. Renon, "Representation of Excess Properties of Electrolyte Solutions Using a New Equation of State," *AIChE J.*, **39**, 335 (1993).

Gmehling, J., and U. Onken, "Vapor-Liquid Equilibrium—Data Collection," *Chemistry Data Ser.*, Vol. 1, Part 1, DECHEMA, Frankfurt (1977).

Harvey, A. H., and J. M. Prausnitz, "Thermodynamics of High Pressure Aqueous Systems Containing Gases and Salts," *AIChE J.*, **35**, 635 (1989).

Kikic, I., M. Fermeglia, and P. Rasmussen, "UNIFAC Prediction of Vapor-Liquid Equilibria in Mixed Solvent-Salt Systems," *Chem. Eng. Sci.*, **46**, 2775 (1991).

Kolker, A., and J. J. de Pablo, "Thermodynamic Modeling of the Solubility of Salts in Mixed Aqueous-Organic Solvents," *Ind. Eng. Chem. Res.*, **35**, 228 (1996).

Labban, A. K. S., and Y. Marcus, "The Solubility and Solvation of Salts in Mixed Nonaqueous Solvents. 1. Potassium Halides in Mixed Aprotic Solvents," *J. Solution Chem.*, **20**, 211 (1991).

Labban, A. K. S., and Y. Marcus, "The Solubility and Solvation of Salts in Mixed Nonaqueous Solvents. 2. Potassium Halides in Mixed Protic Solvents," *J. Solution Chem.*, **26**, 1 (1997).

Li, J., H.-M. Polka, and J. Gmehling, "A g^E Model for Single and Mixed Solvent Electrolyte Systems. 1. Model and Results for Strong Electrolytes," *Fluid Phase Equilibria*, **94**, 89 (1994a).

Li, Z., Y. Tang, Y. Liu, and Y. Li, "Salting Effect in Partially Miscible Systems of *n*-Butanol-Water and Butanone-Water, 1. Determination and Correlation of Liquid-Liquid Equilibrium Data," *Fluid Phase Equilibria*, **103**, 153 (1994b).

Lide, D. R., *Handbook of Chemistry and Physics*, 77th ed., CRC Press, Cleveland, OH (1996).

Liu, Y., and S. Watanasiri, "Representation of Liquid-Liquid Equilibria of Mixed-Solvent Electrolyte Systems Using the Extended Electrolyte NRTL Model," *Fluid Phase Equilibria*, **116**, 193 (1996).

Macedo, E. A., V. Skovborg, and P. Rasmussen, "Calculation of Phase Equilibria for Solutions of Strong Electrolytes in Solvent-Water Mixtures," *Chem. Eng. Sci.*, **45**, 875 (1990).

Malahlas, L., and O. Popovych, "Activity Coefficients and Transfer Free Energies of Potassium Chloride in Methanol-Water Solvents at 25°C," *J. Chem. Eng. Data*, **27**, 105 (1982).

Marcus, Y., *Ion Solvation*, Wiley, Chichester, England (1985).

Meissner, H. P., and C. A. Stokes, "Solvent Dehydration by Salting out," *Ind. Eng. Chem.*, **36**, 816 (1944).

Novotny, P., and O. Söhnel, "Densities of Binary Aqueous Solutions of 306 Inorganic Substances," *J. Chem. Eng. Data*, **33**, 49 (1988).

Peng, Q., Z. Li, and Y. Li, "Application of Regular Solution Theory to Calculation of Liquid-Liquid Equilibria for Water-Containing Systems," *Fluid Phase Equilibria*, **97**, 67 (1994).

Rashin, A., and B. Honing, "Reevaluation of the Born Model of Ion Hydration," *J. Phys. Chem.*, **89**, 5588 (1985).

Reid, R., J. M. Prausnitz, and B. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987).

Sander, B., Aa. Fredenslund, and P. Rasmussen, "Calculation of Vapor-Liquid Equilibria in Mixed Solvent/Salt Systems Using an Extended UNIQUAC Equation," *Chem. Eng. Sci.*, **41**, 1171 (1986).

Schwartzentruber, J., H. Renon, and S. Watanasiri, "Development of a New Equilibria of State for Phase Equilibria Calculations," *Fluid Phase Equilibria*, **52**, 127 (1989).

Seidell, A., and W. F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds*, Vol. I, van Nostrand, Princeton, NJ (1958).

Seidell, A., and W F Linke, *Solubilities of Inorganic and Metal-Organic Compounds*, Vol. II, van Nostrand, Princeton, NJ (1965).

Sørensen, J. M., and W. Arlt, "Liquid-Liquid Equilibria—Data Collection," *Chemistry Data Ser.*, DECHEMA, Frankfurt/Main (1980).

Weast, R. E., *Handbook of Chemistry and Physics*, 52nd ed., CRC Press., Cleveland, OH (1971).

Wong, D. S., and S. I. Sandler, "Theoretically Correct New Mixing Rule for Cubic Equations of State," *AIChE J.*, **38**, 671 (1992).

Zerres, H., and J. M. Prausnitz, "Thermodynamics of Phase Equilibria in Aqueous-Organic Systems with Salt," *AIChE J.*, **40**, 676 (1994).

Zuo, Y.-X., and W. Fürst, "Prediction of Vapor Pressure for Nonaqueous Electrolyte Solutions Using an Electrolyte Equation of State," *Fluid Phase Equilibria*, **138**, 87 (1997).

Zuo, Y.-X., and W. Fürst, "Use of an Electrolyte Equation of State for the Calculation of Vapor-Liquid Equilibria and Mean Activity Coefficients in Mixed-Solvent Electrolyte Systems," *Fluid Phase Equilibria*, **150–151**, 267 (1998).

Appendix A: Evaluation of the EOS Parameters of Molecular Components

The energy parameter and the covolume of a pure molecular component (i) are calculated by

$$a_i^{SR} = \frac{1}{9(2^{1/3}-1)} \frac{(RT_{ci})^2}{P_{ci}} \Big[1 + m_i(\omega_i)\big(1-\sqrt{T_{ri}}\big) - p_1(1-T_{ri})\big(1+P_2 T_{ri} + p_3 T_{ri}^2\big)\Big]^2 \quad \text{(A1)}$$

$$m_i(\omega_i) = 0.48508 + 1.55171\,\omega_i - 0.15613\,\omega_i^2 \quad \text{(A2)}$$

$$b_i = \frac{2^{1/3}-1}{3}\frac{RT_{ci}}{P_{ci}} - c_i, \tag{A3}$$

where p_1, p_2, and p_3 are three polar parameters; ω, T_c, T_r, and P_c are the acentric factor, the critical temperature, the reduced temperature and the critical pressure, respectively.

In order to apply the Wong-Sandler mixing rule in the AEEOS, the contributions of molecular and ionic species are treated separately. The following mixing rules are derived for estimating parameters a^{SR} and b of mixtures:

$$\frac{a^{SR}}{RT} = \frac{Q_m D_m}{1-D_m} = D_m(b_m + c_m) \tag{A4}$$

$$b = b_m + b_{ion}, \tag{A5}$$

where subscripts m and ion stand for the molecular and ionic contributions, respectively. The covolumes and volume translation parameters are expressed as

$$b_m = \frac{Q_m}{1-D_m} - c_m \quad \text{and} \quad b_{\text{ion}} = \sum_i^{\text{ion}} x_i b_i. \tag{A6}$$

$$c_m = \sum_j^m x_i c_i \tag{A7}$$

Parameters (Q_m) and (D_m) are given by

$$Q_m = \sum_i^m \sum_j^m x_i x_j \left(\frac{b_i + c_i + b_j + c_j}{2} - \frac{\sqrt{a_i^{SR} a_i^{SR}}}{RT}(1-k_{ij}) \right) \tag{A8}$$

$$D_m = \sum_i^m x_i \frac{a_i^{SR}}{RT(b_i + c_i)} - \frac{g^E}{RT \ln 2}. \tag{A9}$$

The modified UNIQUAC model is used to estimate g^E. In order to reduce the model to the expression of Fürst and Renon (1993) for aqueous electrolyte solutions, the UNIQUAC model needs to be modified slightly. In the case of aqueous (single-solvent) electrolyte solution, $g^E = 0$. Since only the contribution of molecular species is taken into account in the g^E model, the summation runs over molecular species in the following expressions.

The combinatorial term is given by

$$\frac{g_C^E}{RT} = \sum_{i=1}^m x_i \ln\left(\frac{\Phi_i}{x_i^{(0)}}\right) + \frac{Z}{2}\sum_{i=1}^m x_i q_i \ln\left(\frac{\theta_i}{\Phi_i}\right), \tag{A10}$$

where $x_i^{(0)}$ is the salt-free mol fraction of solvent i rather than the mol fraction (x_i) in the original UNIQUAC model.

The molar excess Gibbs energy of the residual term is given by

$$\frac{g_R^E}{RT} = -\sum_{i=1}^m x_i q_i \ln\left(\sum_{j=1}^m \theta_j \lambda_{ji}\right), \tag{A11}$$

where λ_{ji} is treated as a function of compositions:

$$\lambda_{ji} = \exp\left[-\left(\tau_{ji}^{(0)} + \theta_j \theta_i \tau_{ji}^{(1)}\right)\right]. \tag{A12}$$

In this equation $\tau_{ji}^{(0)}$ and $\tau_{ji}^{(1)}$ are unsymmetrical and symmetrical parameters, respectively. For a binary system, there are three adjustable parameters: $\tau_{12}^{(0)}$, $\tau_{21}^{(0)}$, and $\tau_{12}^{(1)} = \tau_{21}^{(1)}$. Parameters $(k_{12} = k_{21})$ are set to zero.

Appendix B: Conversion of Ionic Properties among Concentration Scales

The mean ionic activity coefficients among different concentration scales are converted by

$$\gamma_\pm^{\text{mol fraction}} = \gamma_\pm^{\text{molality}}(1 + 0.001\nu \text{mM}_{\text{solv}}) \tag{B1}$$

$$\gamma_\pm^{\text{molality}} = \gamma_\pm^{\text{molarity}} \frac{c}{m\rho_{\text{solv}}} = \gamma_\pm^{\text{molarity}}\left(\frac{\rho_{\text{soln}} - 0.001cM_E}{\rho_{\text{solv}}}\right), \tag{B2}$$

where m, c, M_{solv}, M_E, ρ_{solv}, and ρ_{soln} are the molality, the molarity, the molecular weights (g/mol) of the solvent and electrolyte E, and the densities (g/cm^3) of the solvent and the solution, respectively.

The standard Gibbs energy of transfer among different concentration scales is converted by

$$\Delta G_{E,\text{tr}}^0(\text{wat} \rightarrow \text{mix})^{\text{mol fraction}} = \Delta G_{E,\text{tr}}^0(\text{wat} \rightarrow \text{mix})^{\text{molality}} + \nu RT \ln\left(\frac{M_{\text{solv}}^{(\text{wat})}}{M_{\text{solv}}^{(\text{mix})}}\right) \tag{B3}$$

$$\Delta G_{E,\text{tr}}^0(\text{wat} \rightarrow \text{mix})^{\text{molality}} = \Delta G_{E,\text{tr}}^0(\text{wat} \rightarrow \text{mix})^{\text{molarity}} + \nu RT \ln\left(\frac{\rho_{\text{solv}}^{(\text{wat})}}{\rho_{\text{solv}}^{(\text{mix})}}\right) \tag{B4}$$

The conversion of the standard Gibbs energy of the solution at solid–liquid equilibria on different concentration scales are given by

$$\Delta G_{E,\text{sat}}^0(\text{solution})^{\text{mol fraction}} = \Delta G_{E,\text{sat}}^0(\text{solution})^{\text{molality}} + \nu RT \ln\left(\frac{1{,}000}{M_{\text{solv}}}\right) \tag{B5}$$

$$\Delta G_{E,\text{sat}}^0(\text{solution})^{\text{molality}} = \Delta G_{E,\text{sat}}^0(\text{solution})^{\text{molarity}} - \nu RT \ln(\rho_{\text{solv}}). \tag{B6}$$

Manuscript received Nov. 9, 1999, and revision received May 8, 2000.