Generalized LIQUAC Model for the Single- and Mixed-Solvent Strong Electrolyte Systems

Mi-Yi Li, Li-Sheng Wang, and Bo Jiang
Dept. of Chemical Engineering, School of Chemical Engineering and the Environment, Beijing Institute of Technology, 100081 Beijing, China

Jürgen Gmehling
Dept. of Industrial Chemistry, Institute for Pure and Applied Chemistry, Carl von Ossietzky University Oldenburg, D-26111 Oldenburg, Germany

DOI 10.1002/aic.12445

A generalized strong electrolyte LIQUAC model is presented to describe the vapor–liquid equilibria, osmotic coefficients, mean ion activity coefficients, and solid–liquid equilibria for the single- and mixed-solvent electrolyte systems over the entire concentration range from infinite dilution to saturated solutions. An appropriate reference state for the ions was first applied to test the capability of the model in simultaneously describing the mean ion activity coefficients and the solubility of a salt in a binary solvent mixture. The influence of salt on the vapor–liquid equilibrium behavior is predicted with the new correlated parameters. The generalized activity coefficient formulations are presented through the investigation of thermodynamic properties and phase phenomena in the single- and mixed-solvent electrolyte systems. This work is a continuous study for the LIQUAC activity coefficient model. A reliable representation of the single- and mixed-solvent salt solutions is obtained. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 2535–2546, 2011

Keywords: electrolyte system, phase equilibrium, activity coefficient, mixed solvent

Introduction

This work was performed following a major project dealing with experimental and theoretical investigations on the salt solubilities in single and mixed solvents. The main goal of that project was to predict salt solubilities using the LIQUAC model,[1] which is semiempirical, reliable, predictive, comprehensive, and engineering oriented. It is able to thermodynamically represent vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE), solid–liquid equilibria (SLE), gas–liquid equilibria (GLE), mean ion activity coefficient ($\gamma_{\pm}$), osmotic coefficients (ϕ), etc., and is suitable for chemical process simulation in industrial practice. A large number of experimental data for electrolyte systems obtained from published literatures were compiled and critically evaluated in the Dortmund Data Bank (DDB).[2] They were computed with the model to predict the equilibrium phase behavior of electrolyte systems, and they also provide a supporting for the further modeling.

In the last few decades, several semiempirical electrolyte models are presented. Pitzer[3] developed a series of semiempirical equations from the view of statistical thermodynamics to calculate the experimental results of aqueous electrolyte systems up to a high ionic strength. Chen et al.[4] combined the electrostatic function of the Pitzer model with an extension of the NRTL equation, which was called eNRTL. Sander et al.[5–7] introduced an extended UNIQUAC term of concentration-dependent parameters and a simplified Debye–Hückel[8] (DH) term to calculate the VLE, LLE, and SLE for the mixed-solvent electrolyte systems. Kikic et al.[9] substituted the UNIQUAC term with the UNIFAC group contribution model to describe the behavior of electrolyte systems. Polka et al.[10] and

---

Correspondence concerning this article should be addressed to L.-S. Wang at lishengwang@bit.edu.cn.

Table 1. The Reference State of Activity Coefficient Models for the Electrolyte Systems

References	Reference State	Equilibria
Pitzer and Simonson[15]	$\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$ $\gamma_j \rightarrow 1$ as $x_s \rightarrow 1$ or $\gamma_j \rightarrow 1$ as $x_s \rightarrow 0$ (aqueous)	SLE
Sander et al.[5-7]	$\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$ $\gamma_j \rightarrow 1$ as $\sum_j x_j \rightarrow 0$ (single or mixed solvent)	VLE, LLE, SLE
Zerres and Prausnitz[16]	$\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$ $\gamma_j \rightarrow 1$ as $x_j \rightarrow 0$ and $x_{\mathrm{water}} \rightarrow 1$ (single or mixed solvent)	VLE, LLE
Papaiconomou et al.[17]	$\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$ $\gamma_j \rightarrow 1$ as $x_s \rightarrow 1$ (single or mixed solvent)	ϕ, $\gamma_\pm$
Chen and Song[18]	$\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$ $\gamma_j \rightarrow 1$ as $x_{\mathrm{water}} \rightarrow 1$ (aqueous) $\gamma_j \rightarrow 1$ as $\sum_s x'_s \rightarrow 1$ (mixed solvent)	$\gamma_\pm$
Kamps[19]	$\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$ $\gamma_j \rightarrow 1$ as $x_s \rightarrow 1$ (single or mixed solvent)	SLE, GLE
Kiepe et al.[13]	$\gamma_s \rightarrow 1$ as $x_s \rightarrow 1$ $\gamma_j \rightarrow 1$ as $x_{\mathrm{water}} \rightarrow 1$ (single or mixed solvent)	VLE, LLE, ϕ

Yan et al.[11] used the LIQUAC model to calculate the phase equilibrium behavior of single- and mixed-solvent electrolyte systems. The model was also used to predict the salt solubilities consisting of various cations (Na^+, K^+, and NH_4^+) and anions (F^-, Cl^-, Br^-, I^-, and SO_4^{2-}) and their mixtures in aqueous solutions by Li et al.[12] The predicted average relative deviations for single salts are less than 4%, and those for mixed-salt solutions are less than 10%. Modified LIQUAC model was further developed for the reliable VLE and LLE by Kiepe et al.[13] in 2006. Huang et al.[14] deduced a series of theoretical formulas to calculate the salt solubilities not only in water but also in organic or mixed-solvent electrolyte systems. The results were in good agreement with measurements in the water–methanol electrolyte systems.

Furthermore, the LIQUAC model has often been applied for the calculation of salt solubilities, VLE behavior in the single or mixed solvents containing water. However, general equations for calculating the mean ion activity coefficients in the mixed solvents or organic solvents have not been presented simultaneously with salt solubilities yet. Thus, the model was summarized in this work to describe the mean ion activity coefficients, salt solubilities, as well as the influence of that salt on the VLE of the mixed-solvent electrolyte systems. Four salts (NaCl, KCl, NaBr, and KBr) and three solvents (water, methanol, and ethanol) were selected to check the capability of the newly derived equations and the new reference state for ions. The salt solubilities and mean ion activity coefficients were investigated over the whole range of concentration and solvent composition, i.e., from pure water to pure methanol or ethanol.

General Thermodynamic Relations

The prediction of phase equilibrium behavior in mixtures with strong electrolytes is of great industrial interest. The basic assumption for facilitating the calculations assumes that all electrolytes are completely dissociated in the solutions. Thus, the mole fraction of any species k is related to the mole numbers n by:

$$x_k = \frac{n_k}{\sum_i n_i}, \tag{1}$$

where x_k is the true mole fraction of species k, and n_i is the amount of compound i in the solution (including solvent and solute species). The solute-free mole fraction of solvent is defined as follows:

$$x'_s = \frac{n_s}{\sum_s n_s}, \tag{2}$$

where n_s is the mole number of the solvent s, and Σ means the summation over all solvents. The Gibbs energy of an electrolyte solution containing neutral solvents and ionic solutes can be normalized as two contributions:

$$G = G^{\mathrm{id}} + G^{\mathrm{E}}. \tag{3}$$

The superscript "id" indicates the ideal solution contribution and "E" is the excess contribution at the same conditions of temperature, pressure, and composition. The mole fraction scale was chosen here. For simplifying the following derivations, only single and binary solvent mixtures were considered, but all the expressions can be straightly extended to the multicomponent solvent mixture.

Ideal solution

For the solvent components s (water or organic), the chemical potential is normalized according to the Raoult's law. The reference state for the chemical potential of a solvent component s is the pure liquid state at equilibrium temperature and system pressure, which is designated as symmetrical convention. The chemical potential of the solute species is normalized according to Henry's law, which is designated as unsymmetrical convention. Thus, the reference state for the chemical potential of solute is the pure solute infinitely diluted in the solvent. The solvent can be a single solvent (pure water or organic) or binary mixture (water–organic). The discussion on the reference state for ions was performed in many articles as shown in Table 1. From the theoretical and practical view of electrolyte systems, the pure liquid as the reference state for the solvent is achieved in agreement in single- or mixed-solvent systems. The infinite dilution in a single or mixed solvent as the reference state for ionic species for the calculations of SLE and $\gamma_\pm$ is emphasized by Chen and Song,[18] Sander et al.,[5] and Kamps.[19] Based on this reference state for all the species in the solution, the Gibbs energy of the ideal solution is obtained:

$$G^{\mathrm{id}} = n_{aq}\mu^0_{\mathrm{aq}}(T,P) + n_{\mathrm{org}}\mu^0_{\mathrm{org}}(T,P) + \sum_{j \neq \mathrm{aq,org}} n_j \mu_j^{\nabla}(T,P,x'_s) + RT\left(n_{\mathrm{aq}}\ln x_{\mathrm{aq}} + n_{\mathrm{org}}\ln x_{\mathrm{org}} + \sum_{j \neq \mathrm{aq,org}} n_j \ln x_j\right), \tag{4}$$

where $\mu^0_{\mathrm{aq}}(T,P)$ and $\mu^0_{\mathrm{org}}(T,P)$ are the standard chemical potential of solvent components and $\mu_j^{\nabla}(T,P,x_s')$ is the standard chemical potential of ions in the solution based on the mole scale. Superscript 0 indicates the pure liquid state as the reference state, and superscript $\triangledown$ represents the infinite dilution of the solute species j in the solution as the reference state. It was also suggested by Sander et al.[5] and Kamps[19] that the standard Gibbs energy function of the ions as a function of salt-free solvent composition should be adjusted for the SLE, LLE, and $\gamma_\pm$ calculations in the mixed-solvent electrolyte systems. By combining Eq. 3 with Eq. 4, the chemical potential of all the species in the system is defined:

$$\mu_s = \mu_s^0(T,P) + RT\ln(x_s\gamma_s) \tag{5}$$

$$\mu_j = \mu_j^\triangledown(T,P,x'_s) + RT\ln(x_j\gamma_j^\triangledown), \tag{6}$$

where s represents the solvent component (aqueous or organic, respectively), and the reference states for the solvents are normalized at $\gamma_s \to 1$ as $x_s \to 1$ and for the solutes at $\gamma_j^\triangledown \to 1$ as $x_j \to 0$, respectively. Moreover, the usual concentration scale of the electrolyte solution is the molality scale ($m^0 = 1$ mol kg^{-1}), and the molality of ion j is given by:

$$m_j = \frac{n_j}{M_{mix}\sum_s n_s} \tag{7}$$

$$M_{mix} = \sum_s x'_s M_s, \tag{8}$$

where M_{mix} is the molar mass of the solvent mixture in kg mol^{-1}, and M_s is the molar mass of the each solvent. The chemical potential for the ion j must be the same for a given composition on either mole or molality basis. The following equation gives the conversion from the mole fraction basis to the molality scale retaining the infinitely dilute reference state:

$$\mu_j = \mu_j^\triangledown(T,P,x'_s) + RT\ln(x_j\gamma_j^\triangledown) = \mu_j^*(T,P,x'_s) + RT\ln(m_j\gamma_j^*) \tag{9}$$

$$\mu_j^\triangledown(T,P,x'_s) - \mu_j^*(T,P,x'_s) = RT\ln(M_{mix}) \tag{10}$$

$$\gamma_j^* = \gamma_j^\triangledown \Big/ \left(1 + M_{mix}\sum_j m_j\right). \tag{11}$$

The superscript * indicates the molality scale and infinite diluted reference state. By holding those conversions, the standard state for ions is normalized as the concentration of solute with unity molality at system temperature and pressure, where $\gamma_j \to 1$. In the ideal solution, for all the species, where $\gamma \to 1$. Nevertheless, in the real solution, $\gamma_s \to 1$ as $x_s \to 1$ and $\gamma_j{}^* \to 1$ as $m_j \to 0$.

G^E model

In this work, the LIQUAC activity coefficient model was used to present the phase equilibrium behavior for the single- or mixed-solvent electrolyte systems. The activity coefficient of the component is defined as the sum of three contributions:

$$\ln\gamma = \ln\gamma_{LR} + \ln\gamma_{MR} + \ln\gamma_{SR}. \tag{12}$$

The first term on the right side of the equation represents the long-range interaction contribution caused by the Coulomb electrostatic forces. The second term represents the dipole–dipole, dipole–induced dipoles, and dispersion interactions, which is named middle-range (MR) and originally proposed by Li et al.[1] The third term represents the short-range (SR) interactions. It can be calculated by using the UNIQUAC model. The specific formulas are given in Appendix B.

Vapor–liquid equilibrium

By assuming an ideal vapor-phase behavior and neglecting the Poynting correction, VLE can be calculated using the simplified equation:

$$x_s\gamma_s P_s^{sat} = y_s P, \tag{13}$$

where P^{sat} and P are the vapor pressure of the pure solvent s and the system pressure in kPa at system temperature. y_s is the vapor-phase mole fraction of solvent s.

Molal osmotic coefficients

In the single-solvent electrolyte system, the molal osmotic coefficient for the solvent s at system temperature and pressure is calculated from:

$$\phi = -\frac{\ln(x_s\gamma_s)}{M_s\sum_j m_j}, \tag{14}$$

where M_s is the molar mass of the solvent s (kg mol^{-1}). Subscript j indicates all the ions in the solution.

Mean ion activity coefficient

The mean ion activity coefficient ($\gamma_\pm$) is related to individual ion activity coefficients. A simple and illustrative example considering the completely dissociated salt of $M_{v+}X_{v-}$ into cation M and anion X:

$$M_{v_+}X_{v_-} \to v_+M + v_-X, \tag{15}$$

where v_+ and v_- are the stoichiometric coefficients. The single ion activity coefficient is obtained by using Eq. 11. Then, the rational mean ion activity coefficient is defined as follows:

$$\gamma_\pm = \left[\gamma_M^{*\,v+}\gamma_X^{*\,v-}\right]^{1/v} \tag{16}$$

$$v = v_+ + v_-\ , \tag{17}$$

where $\gamma_\pm$ is the molal mean ion activity coefficient. It retains the infinite dilution reference state from the individual ion activity coefficient, which is salt-free composition dependence as shown in Eq. 9.

Solid–liquid equilibria

The general equilibrium constant for the solubility of the solid electrolyte $M_{v+}X_{v-}\cdot nH_2O$ can be derived starting from the following reaction:

$$M_{v+}X_{v-}\cdot nH_2O(\text{solid}) \overset{\Delta G}{\rightleftharpoons} v_+M(\text{liquid}) + v_-X(\text{liquid}) + nH_2O(\text{liquid}) \tag{18}$$

where the condition of chemical equilibrium is given as follows:

$$\Delta G = v_+\mu_{M(\text{liqiud})} + v_-\mu_{X(\text{liquid})} + n\mu_{H_2O(\text{liquid})} - \mu_{M_{v+}X_{v-}\cdot nH_2O(\text{solid})} = 0. \tag{19}$$

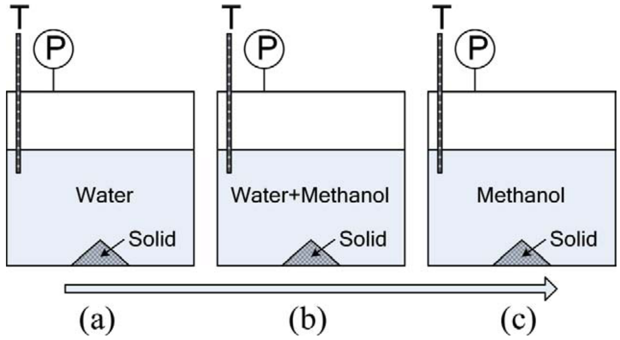

Figure 1. The schematic of transferring the standard state from aqueous system to the mixed-solvent and organic system.

(a) Water + salt; (b) water + methanol + salt; and (c) methanol + salt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The subscript liquid indicates the ions in the solutions and solid indicates the solid phase of the salt. n is the stoichiometric number of water in the hydrated crystal. By substituting Eqs. 5 and 9 into Eq. 19, the chemical potential of the salt is obtained:

$$\mu_{\mathrm{M}_{\nu+}\mathrm{X}_{\nu-}\cdot n\mathrm{H_2O(solid)}} = \mu^*_{\mathrm{M}_{\nu+}\mathrm{X}_{\nu-}\mathrm{(liquid)}} + RT\ln(m_\pm\gamma_\pm) + n\left[\mu^0_{\mathrm{H_2O}} + RT\ln(x_{\mathrm{H_2O}}\gamma_{\mathrm{H_2O}})\right] \quad (20)$$

$$m_\pm = \left(m_{\mathrm{M}}^{\nu+} m_{\mathrm{X}}^{\nu-}\right)^{1/\nu} \quad (21)$$

$$\mu^*_{\mathrm{M}_{\nu+}\mathrm{X}_{\nu-}} = \left(\nu_+\mu^*_{\mathrm{M}} + \nu_-\mu^*_{\mathrm{X}}\right)/\nu, \quad (22)$$

where $\mu^*_{M\nu+X\nu-}$ is the standard state for the anhydrate solute $\mathrm{M}_{\nu+}\mathrm{X}_{\nu-}$ in the liquid phase, which is also a function of temperature, pressure, and solvent composition retaining from Eq. 9. The solubility of the solute depends on the solubility product in the desired solvent. As the activity of solid phase is defined as unity, the solubility product is obtained:

$$K_{\mathrm{sp}} = (m_\pm\gamma_\pm)^\nu (x_{\mathrm{H_2O}}\gamma_{\mathrm{H_2O}})^n. \quad (23)$$

Using the Gibbs–Helmholtz equation, the temperature dependence of the solubility product K_{sp} can be expressed by:

$$\ln K_{\mathrm{sp}}(T) = -\frac{\Delta g^0(T_{\mathrm{ref}})}{RT_{\mathrm{ref}}} - \frac{\Delta h^0(T_{\mathrm{ref}})}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right) + \frac{1}{R}\int_{T_{\mathrm{ref}}}^{T}\left[\frac{\int_{T_{\mathrm{ref}}}^{T}\Delta c_{\mathrm{p}}^0(T)}{T^2}\right]dT \quad (24)$$

$$\Delta g^0(T_{\mathrm{ref}}) = \nu_+\Delta_f g^0_{\mathrm{M}}(T_{\mathrm{ref}}) + \nu_-\Delta_f g^0_{\mathrm{X}}(T_{\mathrm{ref}}) + n\Delta_f g^0_{\mathrm{H_2O}}(T_{\mathrm{ref}}) - \Delta_f g^0_{\mathrm{M}_{\nu+}\mathrm{X}_{\nu-}\cdot n\mathrm{H_2O}}(T_{\mathrm{ref}}) \quad (25)$$

Table 2. The New Correlated Parameters of the Model

i	j	$b_{i,j}$	$c_{i,j}$	$a_{i,j}$	$a_{j,i}$
Na^+	Cl^-	0.0999	0.6895	75.736	−330.205
Na^+	H_2O	−0.0189	−0.0095	−431.376	1232.89
Na^+	MeOH	0.0059	0.0041	−577.082	692.224
Na^+	EtOH	0.1138	0.0209	−55.694	611.76
Cl^-	H_2O	0.0123	0.0050	−296.43	766.38
Cl^-	MeOH	0.2690	0.0108	11036.7	100.882
Cl^-	EtOH	0.2561	0.0149	5581.19	1962.14
Na^+	Br^-	0.1547	−0.0692	−461.33	11036.7
Br^-	H_2O	−0.1375	0.0099	−131.457	17.672
Br^-	MeOH	0.0602	−0.0116	29.179	−580.147
Br^-	EtOH	−0.0872	−0.0222	4105.53	1013.93
K^+	Cl^-	0.1121	−0.1972	−61.702	1635.20
K^+	H_2O	0.0412	−0.0078	96.572	982.352
K^+	MeOH	0.1175	0.0000	4329.20	138.664
K^+	EtOH	0.1953	0.1669	−290.489	295.142
K^+	Br^-	0.0642	0.0880	−267.903	10480.0

$$\Delta h^0(T_{\mathrm{ref}}) = \nu_+\Delta_f h^0_{\mathrm{M}}(T_{\mathrm{ref}}) + \nu_-\Delta_f h^0_{\mathrm{X}}(T_{ref}) + n\Delta_f h^0_{\mathrm{H_2O}}(T_{\mathrm{ref}}) - \Delta_f h^0_{\mathrm{M}_{\nu+}\mathrm{X}_{\nu-}\cdot n\mathrm{H_2O}}(T_{\mathrm{ref}}) \quad (26)$$

$$\Delta c^0_p(T_{\mathrm{ref}}) = \nu_+ c^0_{p,\mathrm{M}}(T_{\mathrm{ref}}) + \nu_- c^0_{p,\mathrm{X}}(T_{\mathrm{ref}}) + n c^0_{p,\mathrm{H_2O}}(T_{\mathrm{ref}}) - c^0_{p,\mathrm{M}_{\nu+}\mathrm{X}_{\nu-}\cdot n\mathrm{H_2O}}(T_{\mathrm{ref}}) \quad (27)$$

In Eqs. 25–27, $\Delta_f\ g^0(T_{\mathrm{ref}})\Delta_f\ h^0(T_{\mathrm{ref}})$ and $c^0_{\mathrm{p}}(T_{\mathrm{ref}})$ are the standard Gibbs energies of formation, standard enthalpies of formation, and standard heat capacities, respectively. T_{ref} is the given reference temperature usually at 298.15 K. All these values of the standard state for ions in aqueous solution, crystalline salts, and water are available from references, e.g., Wagman et al.,[20] or can be found in data banks such as the DDB.[2] The salt solubility product in the aqueous system can be calculated directly using those equations and the published standard thermodynamic properties. For the calculation of salt solubilities in organic or mixed-solvent system, the values of the solubility product should be first transferred from aqueous solution to the desired solutions properly by the following procedures:

(i) The first rule is based on the assumption of Pitzer and Simonson[15] in discussing the binary and pseudo-binary ionic systems miscible from dilute solution in polar solvent to the fused salt. It is not convenient to select the infinite dilution as the reference state for the solute when encountering the electrolyte systems at high concentration. Based on the relationship between symmetric and asymmetric conventions, a "supercooled" liquid as the reference state for the solute may be useful for the system at the temperature well below the melting point of the solute. It presents a hypothetical pure liquid reference state for the solute, which obeys Raoult's law. Based on this assumption, the chemical potential of the solute in the solvent s (single or mixed solvent) using this pure liquid

Table 3. The Average Absolute Relative Deviation (AARD) of Binary and Ternary Systems

		AARD (%)			
System	Temperature Range (K)	Osmotic Coefficient	Salt Solubility	VLE	Mean Ion Activity Coefficient
Salt + water	273.15–373.15	0.8	1.2	0.6	0.7
Salt + organic	273.15–333.15	1.5	6.8	0.2	3.8
Salt + water + organic	273.15–353.15	–	3.8	4.2	2.7

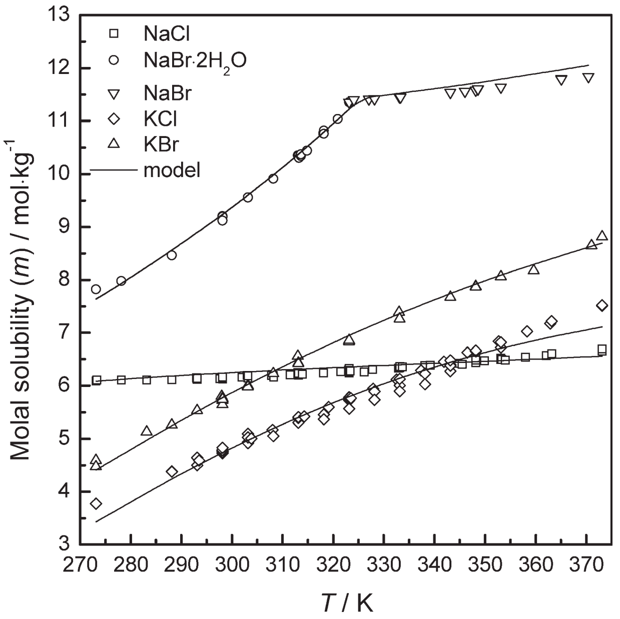

Figure 2. Salt solubilities in pure water.

The symbols denote the data stored in DDB,[22-29] and the solid lines represent the calculated results using the model.

reference state should be related to the infinite dilute reference state by taking the anhydrate solute $M_{v+}X_{v-}$ as an example:

$$\begin{aligned}\mu_{\mathrm{M}_{v+}\mathrm{X}_{v-}}(T,P,x'_{\mathrm{s}}) &= \mu^0_{\mathrm{M}_{v+}\mathrm{X}_{v-}}(T,P)\\ &\quad + RT\ln(x_{\mathrm{M}}^{v+}x_{\mathrm{X}}^{v-}\gamma_{\mathrm{M}}^{v+}\gamma_{\mathrm{X}}^{v-})\\ &= \mu^*_{\mathrm{M}_{v+}\mathrm{X}_{v-}}(T,P,x'_{\mathrm{s}})\\ &\quad + RT\ln(m_{\mathrm{M}}^{v+}m_{\mathrm{X}}^{v-}\gamma_{\mathrm{M}}^{*v+}\gamma_{\mathrm{X}}^{*v-})\end{aligned} \tag{28}$$

$$\mu^0_{\mathrm{M}_{v+}\mathrm{X}_{v-}}(T,P) = \mu^*_{\mathrm{M}_{v+}\mathrm{X}_{v-}}(T,P,x'_{\mathrm{s}}) + RT\ln\left[1/(M^v_{\mathrm{mix}}\gamma_{\mathrm{M}}^{\infty v+}\gamma_{\mathrm{X}}^{\infty v-})\right] \tag{29}$$

μ^0_{Mv+Xv-} is the standard chemical potential at pure liquid standard state of the solute. It is in according with the hypothetical "supercooled" liquid as the reference state as proposed by Pitzer. It is also the function of system temperature and pressure. The individual activity coefficient of ion is based on mole fraction and symmetric convention, which is normalized $\gamma \to 1$ as $x \to 1$. γ^* is the activity coefficient of ions based on molality scale using asymmetric convention. γ^∞ is the infinite dilution activity coefficient based on mole fraction, and it is obviously solvent composition dependence. Equation 29 presents the difference between pure liquid standard state in mole scale and infinite dilute standard state based on molality scale in the same electrolyte system, which is obtained by setting the limiting of solute species $\gamma^* \to 1$ as $m_j \to 0$ at each side of Eq. 28.

(ii) The second rule is constructed based on the SLE by investigating three different saturated systems as shown in Figure 1. In those three different solvent composition systems, the chemical potentials of the solute in the liquid phase equal to the pure solid phase at system temperature and pressure. Thus, the phase equilibrium expressions are obtained using Eq. 28 as follows:

$$\begin{aligned}\mu_{\mathrm{M}_{v+}\mathrm{X}_{v-}(\mathrm{solid})} &= \mu^*_{\mathrm{M}_{v+}\mathrm{X}_{v-}(\mathrm{aq})}\\ &\quad + RT\ln\left[m^{v+}_{\mathrm{M(aq)}}m_{\mathrm{X(aq)}}{}^{v-}\gamma^*_{\mathrm{M(aq)}}{}^{v+}\gamma^*_{\mathrm{X}(aq)}{}^{v-}\right]\\ &= \mu^*_{\mathrm{M}_{v+}\mathrm{X}_{v-}(\mathrm{aq+org})}\\ &\quad + RT\ln\left[m^{v+}_{\mathrm{M(aq+org)}}m^{v-}_{\mathrm{X}(aq+org)}\gamma^{*\,v+}_{\mathrm{M(aq+org)}}\gamma^{*\,v-}_{\mathrm{X(aq+org)}}\right]\\ &= \mu^*_{\mathrm{M}_{v+}\mathrm{X}_{v-}(\mathrm{org})}\\ &\quad + RT\ln\left[m^{v+}_{\mathrm{M(org)}}m^{v-}_{\mathrm{X(org)}}\gamma^{*v+}_{\mathrm{M(org)}}\gamma^{*v-}_{\mathrm{X(org)}}\right],\end{aligned} \tag{30}$$

where subscript "solid" indicates the solid phase, aq, aqorg, and org represent the aqueous, water organic, and organic electrolyte systems, respectively. By substituting Eq. 29 into Eq. 30, the general transferring equation is obtained:

$$\mu^*_{\mathrm{M}_{v+}\mathrm{X}_{v-}(\mathrm{aq+org})} = \mu^*_{\mathrm{M}_{v+}\mathrm{X}_{v-}(\mathrm{aq})} + RT\ln\left[\frac{\mathrm{M}^v_{\mathrm{aq+org}}\gamma^{\infty v+}_{\mathrm{M,aq+org}}\gamma^{\infty v-}_{\mathrm{X,aq+org}}}{\mathrm{M}^v_{\mathrm{aq}}\gamma^{\infty v+}_{\mathrm{M,aq}}\gamma^{\infty v-}_{\mathrm{X,aq}}}\right]. \tag{31}$$

This equation can be used to transfer the standard state retaining the infinite dilution reference state from pure aqueous system ($x'_{\mathrm{aq}} \to 1$) to the mixed solvent and even to the pure organic electrolyte systems ($x'_{\mathrm{org}} \to 1$). The infinite dilution activity coefficient (γ^∞) of ion in different solvent composition is estimated using LIQUAC model as shown in Appendix C. By substituting Eqs. 23 and 31 into Eq. 30, the solubility product of salt in aqueous systems can be transferred into water–organic mixtures even to the pure organic solutions as follows:

$$\ln K_{\mathrm{sp(aq+org)}} = \ln K_{\mathrm{sp(aq)}} - \ln\left[\frac{\mathrm{M}^v_{\mathrm{aq+org}}\gamma^{\infty v+}_{\mathrm{M,aq+org}}\gamma^{\infty v-}_{\mathrm{X,aq+org}}}{\mathrm{M}^v_{\mathrm{aq}}\gamma^{\infty v+}_{\mathrm{M,aq}}\gamma^{\infty v-}_{\mathrm{X,aq}}}\right]. \tag{32}$$

Results and Discussion

Improvements and new parameters for the model

Because the results obtained for the fitting of mean ion activity coefficients for salts in mixed or organic solvent using the variable reference state[1] have been rather bad, a different

Table 4. The Standard Thermodynamic Properties of the Species for the Correlations in This Work, T_{ref} = 298.15 K

	$\Delta_f g^0$ (kJ mol^{-1})	$\Delta_f h^0$ (kJ mol^{-1})	c_{p}^0 (kJ mol^{-1})
KCl	−409.34*	−437.783 −431.3*	51.3*
KBr	−380.917 −380.47*	−386.739 −397.798*	52.306*
NaCl	−384.024*	−410.49 −411.12*	50.503*
NaBr	−349.441 −349.267*	−358.297 −361.414*	51.893*
NaBr·2H$_2$O	−828.63 −828.29*	−945.086 −951.94*	133.958
H$_2$O (aq)	−237.141*	−285.83*	75.29*
K$^+$ (aq)	−283.27*	−252.38*	21.8*
Na$^+$ (aq)	−261.905*	−240.120*	176.7*
Cl$^-$ (aq)	−131.228*	−167.159*	−136.4*
Br$^-$ (aq)	−104.16*	−119.57*	−72.3*

The standard thermodynamic properties stored in DDB were not used when two values are given in the table.
*The values are taken from DDB.[3]

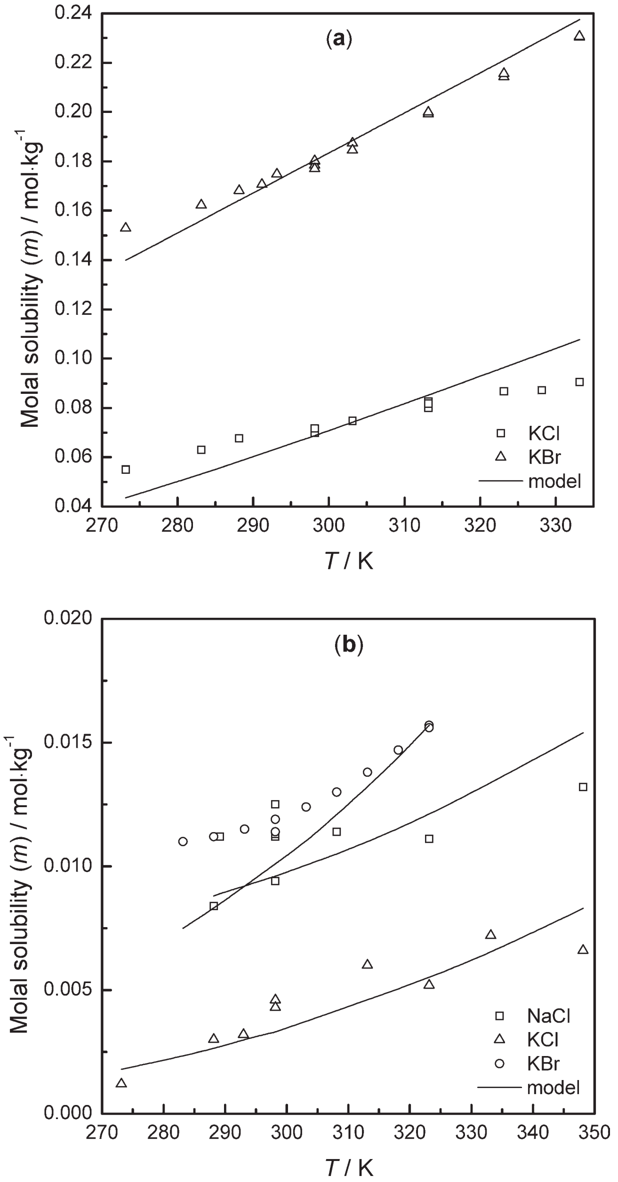

Figure 3. Salt solubilities in the pure organic solvents as a function of temperature.

(a) Salt in pure methanol and (b) salt in pure ethanol. The symbols denote the data stored in DDB,[24,26,27,29] and the solid lines represent the calculated results using the model.

reference state based on the definition of ideal solution was finally introduced for the ions in this work. As shown in Eqs. B17 and B18 in Appendix B, the reference state for ions is solvent composition dependent and at infinite dilution. Applying this new reference state, the cases of solubility and mean ion activity coefficient in mixed and organic solvents can be presented simultaneously.

In aqueous systems, standard thermodynamic properties for the ions are available as mentioned above. However, in the mixed- or organic solvent systems, the Gibbs energy of formation and the enthalpy of formation in Eqs. 25–27 are not available. An explicit and reasonable procedure was also introduced to enable the calculation of salt solubilities not only in aqueous but also in mixed solvents or pure organic solvents. Using Eq. 32, the correctness of solubility product can be ensured by transferring from aqueous system to the desired solvents.

Furthermore, for the representation of electrolyte systems, two sets of adjustable parameters are needed in the LIQUAC model. One set of parameters are the $B_{i,j}$ parameters for the contribution of the MR term, where the parameter d_{salt} is set to 0.125. Then, there are the UNIQUAC parameters $a_{i,j}$, $a_{j,i}$ representing the SR term contribution. Another improvement is carried out for the SR term by following the assumption of local like-charge repulsion and local electroneutrality by

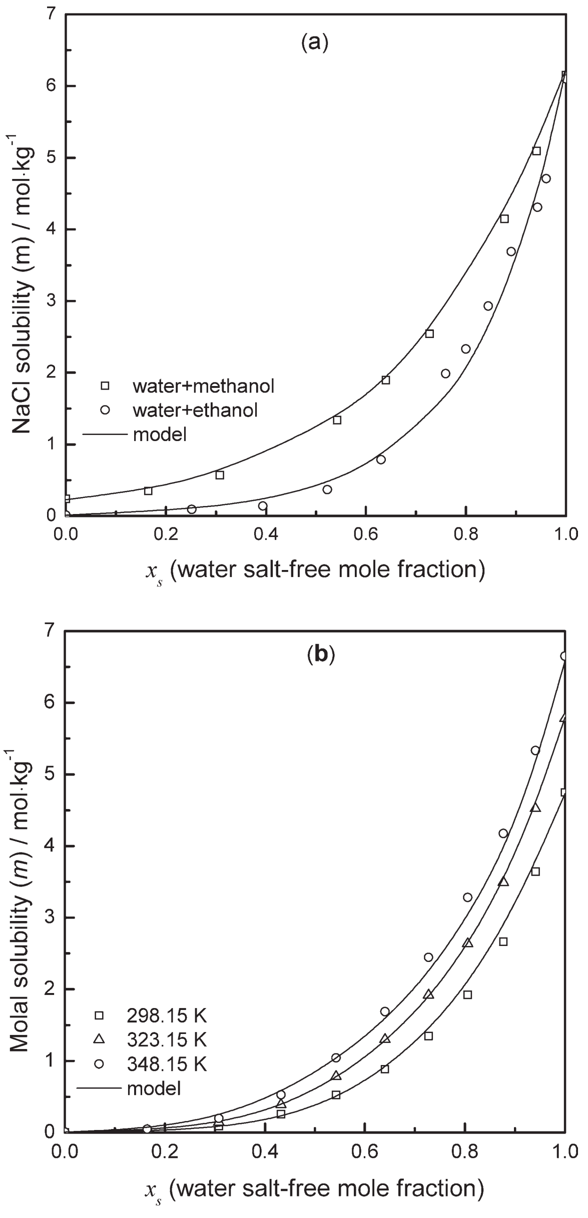

Figure 4. Experimental and calculated salt solubilities in the mixed solvent.

(a) NaCl solubility in water–methanol and water–ethanol mixtures at 298.15 K and (b) KCl solubility in the water–ethanol mixtures at different temperatures. The symbols denote the data stored in DDB,[24,27] and the solid lines represent the calculated results using the model.

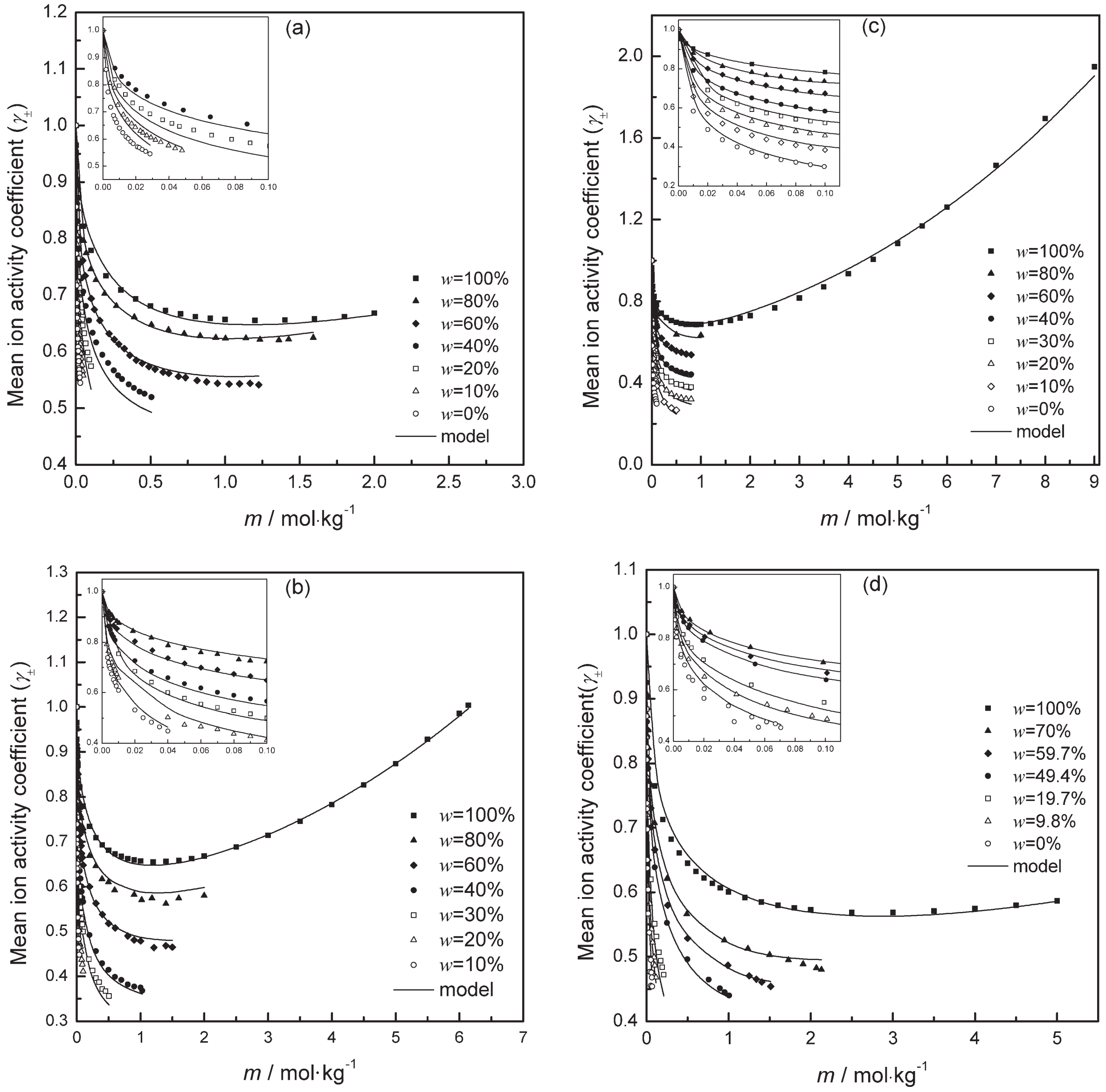

Figure 5. Experimental and calculated mean ion activity coefficients in water–organic mixtures at 298.15 K.

(a) NaCl + H_2O + MeOH[30]; (b) NaCl + H_2O + EtOH[31]; (c) NaBr + H_2O + EtOH[32]; and (d) KCl + H_2O + MeOH.[33]

Chen et al.[21] to describe the real local composition of the electrolyte solutions, which is equivalent to the assumption that UNIQUAC parameter $a_{i,i}$ of the like-charge ions is much greater than other interaction energies. Thus, there are no like-charge neighborhoods around the center of cations or anions. This assumption is applied in the residual part of the UNIQUAC equations and the combinatorial term is kept without changing. Within this study, Four salts (NaCl, KCl, NaBr, and KBr) and three solvents (water, methanol, and ethanol) were investigated to check the capability of the reference state for the LIQUAC model in describing the phase equilibrium behavior not only in aqueous systems but also in mixed- and pure organic solvent systems. The considered temperature range is from 273.15 to 373.15 K in aqueous systems and from 273.15 to 333.15 K in organic solvent systems and concentrations up to 10 mol kg^{-1}. The parameters were determined by minimization of the following objective function:

$$F(a_{i,j}, a_{j,i}, b_{i,j}, c_{i,j}) = \sum_{\text{np}} \sum_{\text{nt}} w_Q \left(\frac{Q_{\text{exp}} - Q_{\text{calc}}}{Q_{\text{exp}}} \cdot 100 \right)^2 = \text{min}, \tag{33}$$

where Q represents the respective value of ϕ, $\gamma_\pm$, T, P, m, and w_Q is a weighting factor of Q. np and nt refer to the number of data points and data types, respectively. The subscripts "exp" and "calc," respectively, refer to experimental and calculated values. The van der Waals volumes and surface areas for the ions were taken directly from Kiepe et al.[13] The SR interaction parameters and the volume and surface area parameters for the solvents were taken directly from the parameters of the UNIQUAC model. The new parameters, which take into

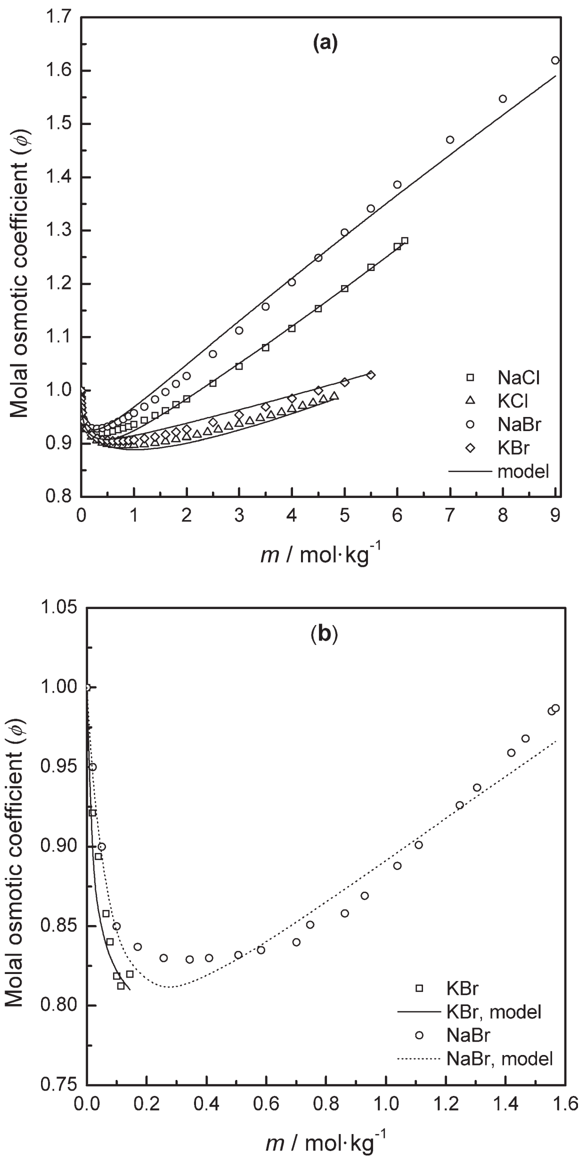

Figure 6. Correlation of molal osmotic coefficients of the solvents at 298.15 K.

(a) Aqueous electrolyte systems[34] and (b) pure methanol electrolyte systems.[35,36]

account of new reference state and all the related systems, are listed in Table 2. Table 3 summarizes the average absolute relative deviation (AARD) values obtained in this work by using the function:

$$\mathrm{AARD} = \frac{1}{np}\sum_{i=1}^{\mathrm{np}}\left|\frac{Q_i^{\mathrm{calc}} - Q_i^{\mathrm{exp}}}{Q_i^{\mathrm{exp}}}\cdot 100\right|. \qquad (34)$$

Salt solubilities

The salt solubilities in water can be calculated using Eq. 23 and the LIQUAC model. Using Eqs. 24–27, the solubility product of salt in water can be calculated directly with available thermodynamic properties. The Newton method was used to determine the concentration of the salt in Eq. 23, which presents the solubility in the aqueous solution. The results of those four salts in water are shown in Figure 2, and the considered temperature range is from 273 to 373 K. For the NaBr–water electrolyte system, the SLE diagram is determined by intersection of two curves representing anhydrate solid (NaBr) and hydrate crystal ($NaBr{\cdot}2H_2O$); the peritectic point for these two solids is 325.57 K at a concentration of 11.436 mol kg^{-1}. In the correlations, it was found that the calculated salt solubilities are sensitive to the solubility product, which is calculated by using Eqs. 24–27 and thermodynamic properties of the ions and pure solid salts. Thus, the values were slightly modified to obtain a good agreement with experimental results, which are given in Table 4.

The salt solubilities in the pure organic solvents as a function of temperature and in the mixed solvents with salt-free solvent composition dependence calculated with the LIQUAC model are shown in Figures 3 and 4 together with the experimental data. The same procedures were used as for aqueous solutions before transferring the solubility product from the aqueous system into organic or mixed-solvent systems by using Eq. 32. A good agreement is obtained in methanol for KCl and KBr as a function of temperature with an AARD less than 7%. However, greater deviations are observed for the calculated salt solubilities in ethanol when comparing with the experimental results. It can be recognized from Figure 3b that the large scatter and systematic deviations of the experimental data are observed, and the salt solubilities are very small. Comparing experimental data with the calculated values, the same tendency of increasing solubility with temperature is observed. For the mixed-solvent electrolyte systems, the solubilities of sodium chloride in water–methanol and water–ethanol mixtures were investigated at 298.15 K as shown in Figure 4a. With an increasing mole fraction of water a strongly increasing salt solubility is observed. The solubilities of potassium chloride in water–ethanol at 298.15, 323.15, and 348.15 K were also investigated. The results are shown in Figure 4b. The correlated results match well with the experimental results with an AARD less than 4%. It proves that the LIQUAC model has a good capability not only for describing the salt solubilities in aqueous systems but also in mixed and pure organic solvent as mentioned by Li et al.[12] and Huang et al.[14]

Mean ion activity coefficients in mixed-solvent mixtures

In this study, the polar organic solvents methanol and ethanol are used as organic additives. The polar natures of these alcohols allow mixing them with water at any mole fractions. Because of the available data of NaCl, NaBr, and KCl (Yan et al.,[22] Esteso et al.,[23,24] and Malahias et al.,[25]) in water–methanol and water–ethanol mixtures, the mean ion activity coefficients in those mixtures are correlated with LIQUAC model. Those data were reported covering entire solvent compositions using infinite dilution in the mixed solvents as the reference state. The reference state chosen for ions in this work is in coordinate with the experimental method. All the mean activity coefficient data are collected by covering 0–100% weight fraction of water in water–organic mixtures. The correlated results using the model are shown in Figure 5 together with the experimental data published. The quality of the fitting is influenced by the quality

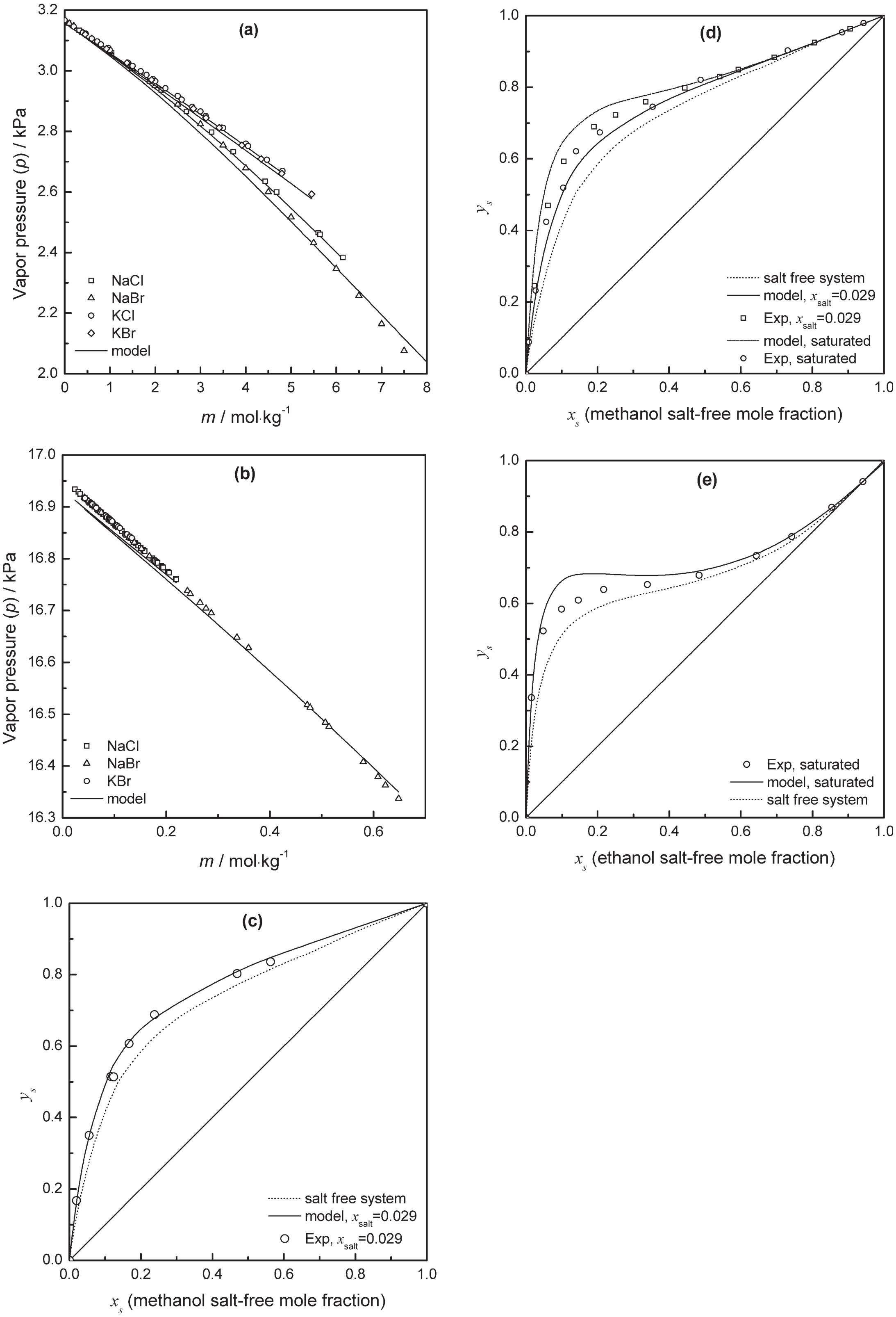

Figure 7. Experimental and calculated vapor–liquid equilibria using the LIQUAC model.[37,38]

(a) Vapor pressures of aqueous electrolyte systems; (b) vapor pressures of methanol electrolyte systems; (c) the VLE of NaCl + H_2O + MeOH system at 101.325 kPa; (d) the VLE of NaCl + H_2O + EtOH system at 101.325 kPa; and (e) the VLE of KCl + H_2O + EtOH system at 100.258 kPa.

of the data. The data at 90 and 80% water mass fraction of KCl–water–methanol system are not used in the regression, because they appear to be inconsistent with the data in pure aqueous solutions as mentioned by Kunz and coworkers.[17] From the figures, it can be seen that excellent correlations were obtained even for the pure organic solvents and at low concentration. The mean ion activity coefficients decrease strongly as the salt-free water composition decrease. For each salt-free solvent composition, the correlation covers the whole concentration range from infinite dilution to the saturated solutions. Overall, the AARD of the correlation is less than 3%.

Molal osmotic coefficients

The molal osmotic coefficients for water in the strong electrolyte solutions were investigated at 298.15 K, as the systems of methanol–salt were homogeneous as shown in Figure 6. The calculated results matched well with the experimental data from dilute region to the saturated solutions in aqueous and pure organic solvent electrolyte system. Otherwise, an acceptable tendency of concentration dependence was obtained for the methanol–salt system for the reason that the experimental data of organic electrolyte system are not satisfying or strongly scattering.

Vapor–liquid equilibria

The model was furthermore applied to represent the experimental VLE data of the binary and ternary systems in Figure 7. The system pressures of aqueous and organic binary electrolyte systems were quantitatively correlated with the model. In particular, as it can be seen from Figures 7c–e, with the increasing salt concentration in liquid solvent mixtures, the concentration of the volatile organic compound in the vapor phase increases. It indicates that organic components are ‘‘salted out,'' whereas water is ‘‘salted in.'' This behavior is predicted with the new interaction parameters.

Conclusion

In previous applying of the LIQUAC model,[1,10,12,13,14] the SLE, VLE, and LLE in aqueous and mixed solvents were well represented. Model parameters were systematically developed from reliable experimental information collected in DDB.[1] As a continuation of the study in electrolyte systems, the model is now extended to allow the description of salt solubilities and mean ion activity coefficients simultaneously in mixed-solvent electrolyte solutions. Choosing the pure liquid state as a reference state for the chemical potential of the solvent components and the infinite dilution as the reference state for the ions, which depends on the composition of the salt-free solvents or solvent mixtures, it results in a good consistency of representing the activity coefficients of solvents and solutes. The capability of the new reference state and parameters was successfully tested with the experimental data of SLE, VLE, mean ion activity coefficients, and osmotic coefficients. With an increasing number of available data for organic and mixed-solvent electrolyte systems, more reliable parameters will be determined to represent the phase equilibrium behavior of electrolyte systems for industrial applications.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft for financial support of the ongoing research project. They also thank DDBST GmbH (Oldenburg, Germany) for providing the latest version of the Dortmund Data Bank for the model development.

Literature Cited

1. Li J, Polka HM, Gmehling J. A gE model for single and mixed solvent electrolyte systems. I. Model and results for strong electrolytes. *Fluid Phase Equilib.* 1994;94:89–114.
2. DDBST Software and Separation Technology GmbH. *Dortmund Data Bank, Version 2008*. Oldenburg: DDBST Software and Separation Technology GmbH. Available at: www.ddbst.de. 2008.
3. Pitzer KS. Thermodynamics of electrolytes. I. Theoretical and general equations. *J Phys Chem.* 1973;77:268–277.
4. Chen CC, Britt HI, Evans LB. Local composition model for excess Gibbs energy of electrolyte systems. *AIChE J.* 1982;28:588–596.
5. Sander B, Fredenslund A, Rasmussen P. Calculation of vapor-liquid equilibria in mixed solvent salt systems using an extended UNIQUAC equation. *Chem Eng Sci.* 1986;41:1171–1183.
6. Sander B, Fredenslund A, Rasmussen P. Calculation of vapor-liquid equilibria in nitric acid-water-nitrate salt systems using an extended UNIQUAC equation. *Chem Eng Sci.* 1986;41:1185–1195.
7. Sander B, Fredenslund A, Rasmussen P. Calculation of solid-liquid equilibria in aqueous solutions of nitrate salts using an extended UNIQUAC equation. *Chem Eng Sci.* 1986;41:1197–1202.
8. Debye P, Hückel E. Zur Theorie der Elektrolyte. I. Gefrierpunkt-serniedrigung und verwandte Erscheinungen. *Phys Z.* 1923;24:185–206.
9. Kikic I, Fermeglia M, Rasmussen P. UNIFAC prediction of vapor-liquid equilibria in mixed-solvent-salt systems. *Chem Eng Sci.* 1991;46:2775–2780.
10. Polka HM, Li J, Gmehling J. A gE model for single and mixed solvent electrolyte systems. II. Results and comparison with other models. *Fluid Phase Equilib.* 1994;94:115–127.
11. Yan W, Topphoff M, Rose C, Gmehling J. Prediction of vapor-liquid equilibria in mixed-solvent electrolyte systems using the group contribution concept. *Fluid Phase Equilib.* 1999;162:97–113.
12. Li J, Lin Y, Gmehling J. g^E model for single and mixed solvent electrolyte systems. III. Prediction of salt solubilities in aqueous electrolyte systems. *Ind Eng Chem Res.* 2005;44:1602–1609.
13. Kiepe J, Noll O, Gmehling J. Modified LIQUAC and modified LIFAC—a further development of electrolyte models for the reliable prediction of phase equilibria with strong electrolytes. *Ind Eng Chem Res.* 2006;45:2361–2373.
14. Huang J, Li J, Gmehling J. Prediction of solubilities of salts, osmotic coefficients and vapor-liquid equilibria for single and mixed solvent electrolyte systems using the LIQUAC model. *Fluid Phase Equilib.* 2009;275:8–20.
15. Pitzer KS, Simonson JM. Thermodynamics of multicomponent, miscible, ionic systems: theory and equations. *J Phys Chem.* 1986;90:3005–3009.
16. Zerres H, Prausnitz JM. Thermodynamics of phase equilibria in aqueous-organic systems with salt. *AIChE J.* 1994;40:676–690.
17. Papaiconomou N, Simonin JP, Bernard O, Kunz W. MSA-NRTL model for the description of the thermodynamic properties of electrolyte solutions. *Phys Chem Chem Phys.* 2002;4:4435–4443.
18. Chen CC, Song Y. Generalized electrolyte-NRTL model for mixed-solvent electrolyte systems. *AIChE J.* 2004;50:1928–1941.
19. Kamps APS. Model for the Gibbs excess energy of mixed-solvent (chemical-reacting) electrolyte systems. *Ind Eng Chem Res.* 2005;44:201–225.
20. Wagman DD, Evans WH, Parker VB, Schumm RH, Bailey IHSM, Churney KL, Nuttall RL. The NBS tables of chemical thermodynamic properties: selected values for inorganic and C1 and C2 organic substances in SI units. *J Phys Chem Ref Data.* 1982;11(Suppl 2):1–389.
21. Chen CC, Britt HI, Boston JF, Evans B. Local composition model for excess Gibbs energy of electrolyte systems. *AIChE J.* 1982;28:588–596.
22. Farelo F, Vonbrachel G, Offermann H. Solid liquid equilibria in the ternary-system NaCl-KCl-H2O. *Can J Chem Eng.* 1993;7:141–146.

23. Trypuc M, Kielkowska U, Chalat M. Solubility investigations in the $NaCl + V_2O_5 + H_2O$ system from 293 K to 323 K. *J Chem Eng Data.* 2002;47:765–767.
24. Pinho SP, Macedo EA. Solubility of NaCl, NaBr, and KCl in water, methanol, ethanol, and their mixed solvents. *J Chem Eng Data.* 2005;50:29–32.
25. Zhang L, Gui Q, Lu X, Wang Y. Measurement of solid–liquid equilibria by a flow-cloud-point method. *J Chem Eng Data.* 1998;43:32–37.
26. Sousa P, Lopes AMC. Solubilities of potassium hydrogen tartrate and potassium chloride in water + ethanol mixtures. *J Chem Eng Data.* 2001;46:1362–1364.
27. Pinho SP, Macedo EA. Representation of salt solubility in mixed solvents: a comparison of thermodynamic models. *Fluid Phase Equilib.* 1996;116:209–216.
28. Wang Y, Sha Z, Wang F, Zheng Q. Solubility of KBr in binary solvents formed by acetone and water in the temperature range between (288.15 and 313.15) K. *J Chem Eng Data.* 2008;53:2547–2549.
29. Pinho SP, Macedo EA. Experimental measurement and modeling of KBr solubility in water, methanol, ethanol, and its binary mixed solvents at different temperatures. *J Chem Thermodyn.* 2002;34:337–360.
30. Yan WD, Xu YJ, Han SJ. Activity coefficients of sodium chloride in methanol-water mixed solvents at 298.15 K. *Acta Chim Sin.* 1994;52:937–946.
31. Esteso MA, Gonzalez DOM, Hernandez MLF. Activity coefficients for NaCl in ethanol-water mixtures at 25°C. *J Solution Chem.* 1989;18:277–288.
32. Gonzalez DOM, Fernandez ML, Hernandez MLF, Esteso MA. Activity coefficients for NaBr in ethanol-water mixtures at 25°C. *J Solution Chem.* 1995;24:551–563.
33. Malahias L, Popovych O. Activity coefficients and transfer free energies of potassium chloride in methanol-water solvents at 25°C. *J Chem Eng Data.* 1982;27:105–109.
34. Hamer WJ, Wu YC. Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25°C. *J Phys Chem Ref Data.* 1972;1:1047–1100.
35. Kolhapurkar RR, Patil PK, Dagade DH, Patil KJ. Studies of thermodynamic properties of binary and ternary methanolic solutions containing KBr and 18-Crown-6 at 298.15 K. *J Solution Chem.* 2006;35:1357–1376.
36. Nasirzadeh K, Salabat A. Isopiestic determination of osmotic coefficients and evaluation of vapor pressures for solutions of sodium bromide and sodium thiocyanate in methanol at 25 degrees C. *J Mol Liq.* 2003;106:1–14.
37. Berling D, Joensson B, Olofsson G. The use of isothermal heat-conduction calorimetry in direct measurements of solvent vapor pressure. *J Solution Chem.* 1999;28:693–710.
38. Barthel J, Neueder R, Lauermann G. Vapor-pressures of non-aqueous electrolyte-solutions. I. Alkali-metal salts in methanol. *J Solution Chem.* 1985;14:621–633.
39. Prausnitz JM, Lichtenthaler RN, Azevedo EG. *Molecular Thermodynamics of Fluid-Phase Equilibria, 3rd ed.* Prentice Hall PTR: Pearson Education, Inc., 1999.

Appendix A: Definition of the Reference State and the Standard State for Ions

As indicated earlier, the chemical potentials for the solvent and solute are given in Eqs. 5 and 6 in mole scale. By introducing the molal concentration, the chemical potential for the solute is related as Eq. 9. For the solute species, the activity against the molality is shown in Figure A1. The dashed line with a unity slope is defined as ideal solution, which represents the activity coefficient of the solute. It equals to unity covering all the concentration range. The point A, where $\gamma^* \rightarrow 1$ as $m_i \rightarrow 1$, implies that the chemical potential of the ideal solution is defined as the standard state for the real solution. In the real solution, the activity coefficient of the solute is decided by *CD*/*BD*. However, the real solution has the same properties with the ideal solution, where $\gamma^* \rightarrow 1$ as $m_i \rightarrow 0$ (origin of coordinate), which implies the infinite dilution reference state. The specific definition can be obtained in the book of Prausnitz et al.[39]

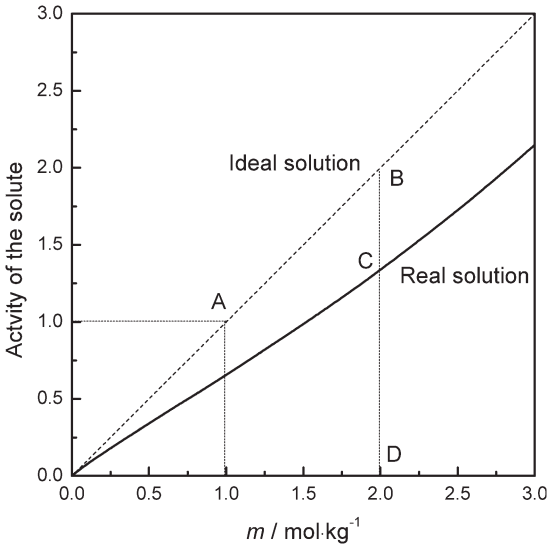

Figure A1. The activity of the solute in ideal and real solutions.

Appendix B: Expressions of the LIQUAC Model

For the solvent s, each part of the activity coefficients is calculated by:

$$\ln \gamma_{s,\mathrm{LR}} = \left(\frac{2AM_s d_m}{b^3 d_s}\right)\left[1+b\sqrt{I}-\left(1+b\sqrt{I}\right)^{-1}-2\ln\left(1+b\sqrt{I}\right)\right] \tag{B1}$$

$$d_m = \sum_s \varphi'_s d_s \tag{B2}$$

$$\varphi'_s = \frac{x'_s \overline{V}_s}{\sum_s x'_s \overline{V}_s} \tag{B3}$$

$$I = 0.5 \sum_{\mathrm{ion}} m_{\mathrm{ion}} z^2_{\mathrm{ion}} \tag{B4}$$

$$A = 1.327757 \times 10^5 d_m^{0.5}/(DT)^{1.5} \tag{B5}$$

$$b = 6.35969 d_m^{0.5}/(DT)^{0.5}, \tag{B6}$$

where $\overline{V}_s$ (m^3 mol^{-1}) is the molar volume of pure solvent s. *I* is the ionic strength of the solution and ion covers all the ionic species, and *z* is the charge number of ion. *T* is the absolute temperature and *D* represents the dielectric constant for the mixed solvents. For binary solvent mixtures, Oster's mixing rule is used:

$$D = D_1 + [(D_2 - 1)(2D_2 + 1)/2D_2 - (D_1 - 1)]\varphi'_2. \tag{B7}$$

For a multicomponent mixture, *D* can be estimated by:

$$D = \sum_s \varphi'_s D_s \tag{B8}$$

$$\begin{aligned}\ln\gamma_{s,\mathrm{MR}} &= \sum_{\mathrm{ion}} B_{\mathrm{s,ion}}(I)m_{\mathrm{ion}} \\ &- \left(\frac{M_{\mathrm{s}}}{M_{\mathrm{mix}}}\right)\sum_{\mathrm{s}}\sum_{\mathrm{ion}}\left[B_{\mathrm{s,ion}}(I)+IB'_{\mathrm{s,ion}}(I)\right]x'_{\mathrm{s}}m_{\mathrm{ion}} \\ &- M_{\mathrm{s}}\sum_{\mathrm{c}}\sum_{\mathrm{a}}\left[B_{\mathrm{ca}}(I)+IB'_{\mathrm{ca}}(I)\right]m_{\mathrm{c}}m_{\mathrm{a}}\end{aligned} \tag{B9}$$

$$B_{\mathrm{s,ion}}(I) = b_{\mathrm{s,ion}} + c_{\mathrm{s,ion}}\exp(-1.2I^{1/2}+2d_{\mathrm{salt}}I) \tag{B10}$$

$$B_{\mathrm{c,a}}(I) = b_{\mathrm{c,a}} + c_{\mathrm{c,a}}\exp(-I^{1/2}+d_{\mathrm{salt}}I), \tag{B11}$$

where d_{salt}, $b_{\mathrm{s,ion}}$, and $c_{\mathrm{s,ion}}$ are the MR interaction parameters between solvents s and ionic species ion. $b_{\mathrm{c,a}}$, $c_{\mathrm{c,a}}$, and d_{salt} are the parameters between cations c and anions a. $B'(I)$ equals to $dB(I)/dI$.

$$\begin{aligned}\ln\gamma_{\mathrm{s,SR}} &= 1 - V_{\mathrm{s}} + \ln V_{\mathrm{s}} - 5q_{\mathrm{s}}\left[1-\frac{V_{\mathrm{s}}}{F_{\mathrm{s}}}+\ln\left(\frac{V_{\mathrm{s}}}{F_{\mathrm{s}}}\right)\right] \\ &+ q_{\mathrm{s}}\left\{1-\ln\left(\frac{\sum_i q_{\mathrm{i}}x_{\mathrm{i}}\psi_{\mathrm{i,s}}}{\sum_{\mathrm{i}} q_{\mathrm{i}}x_{\mathrm{i}}}\right)-\sum_i\left[\frac{q_{\mathrm{i}}x_{\mathrm{i}}\psi_{\mathrm{s,i}}}{\left(\sum_{\mathrm{k}} q_{\mathrm{k}}x_{\mathrm{k}}\psi_{\mathrm{k,i}}\right)}\right]\right\}\end{aligned} \tag{B12}$$

$$V_{\mathrm{s}} = r_{\mathrm{s}}\bigg/\sum_i r_ix_i \tag{B13}$$

$$F_{\mathrm{s}} = q_{\mathrm{s}}\bigg/\sum_i q_ix_i \tag{B14}$$

$$\psi_{i,j} = \exp(-a_{i,j}/T), \tag{B15}$$

where r_i and q_i are the van der Waals volumes and surface areas, and $a_{i,j}$ represents the UNIQUAC interaction parameters, whereby $a_{i,j}$ is different from $a_{j,i}$. x_i is the mole fraction of species i in the solution. In these equations, i and j cover all solvents and ions.

For the ion j, each part of the activity coefficient is given based on the unsymmetrical convention on molality scale.

$$\ln\gamma^{\nabla}_{j,\mathrm{LR}} = -\frac{z_j^2A\sqrt{I}}{1+b\sqrt{I}} \tag{B16}$$

$$\begin{aligned}\ln\gamma^{\nabla}_{j,\mathrm{MR}} &= (M_{\mathrm{mix}})^{-1}\sum_{\mathrm{s}} B_{\mathrm{j,s}}(I)x'_{\mathrm{s}} \\ &+ \left[\frac{z_j^2}{2M_{\mathrm{mix}}}\right]\sum_{\mathrm{s}}\sum_{\mathrm{ion}} B'_{\mathrm{s,ion}}(I)x_{\mathrm{s}}m_{\mathrm{ion}} \\ &+ \sum_{\mathrm{ion}} B_{\mathrm{j,ion}}(I)m_{\mathrm{ion}} \\ &+ \left(\frac{z_j^2}{2}\right)\sum_{\mathrm{c}}\sum_{\mathrm{a}} B'_{\mathrm{ca}}(I)m_{\mathrm{c}}m_{\mathrm{a}} - \frac{\sum_{\mathrm{s}} B_{\mathrm{j,s}}(I=0)x'_{\mathrm{s}}}{M_{\mathrm{mix}}}\end{aligned} \tag{B17}$$

$$\ln\gamma^{\nabla}_{j,\mathrm{SR}} = \ln\gamma_{j,\mathrm{SR}} - \ln\gamma_{j,\mathrm{SR}}(I=0), \tag{B18}$$

where the superscript ∇ indicates the unsymmetrical convention for ions based on the mole fraction scale and $\ln\gamma_{j,\mathrm{SR}}$ can be written as Eq. B12. The terms $\sum B_{j,\mathrm{s}}(I=0)x'_{\mathrm{s}}/M_{\mathrm{mix}}$ in Eqs. B17 and B18 represent the reference state for ion j at infinite dilution based on the mole fraction scale. Based on molality scale, the expression for ion j is obtained:

$$\begin{aligned}\ln\gamma^{*}_{j} &= \left(\ln\gamma^{\nabla}_{j,\mathrm{LR}} + \ln\gamma^{\nabla}_{j,\mathrm{MR}} + \ln\gamma^{\nabla}_{j,\mathrm{SR}}\right) \\ &- \ln\left(1 + M_{\mathrm{mix}}\sum_{\mathrm{ion}} m_{\mathrm{ion}}\right).\end{aligned} \tag{B19}$$

Appendix C: The Infinite Dilution Activity Coefficients of Ions Using the LIQUAC Model

For transferring the salt solubility product from aqueous system to the mixed-solvent or organic systems, the infinite dilution activity coefficients of ions are predicted using the model as follows:

$$\begin{aligned}\ln\gamma^{\infty}_{j} &= \sum_{s}\frac{B_{j,\mathrm{s}}(I=0)x'_{\mathrm{s}}}{M_{\mathrm{mix}}} + 1 - \frac{r_j}{r_{\mathrm{mix}}} + \ln\left(\frac{r_j}{r_{\mathrm{mix}}}\right) \\ &- 5q_j\left[1-\frac{r_jq_{\mathrm{mix}}}{r_{\mathrm{mix}}q_j}+\ln\left(\frac{r_jq_{\mathrm{mix}}}{r_{\mathrm{mix}}q_j}\right)\right] \\ &+ q_j\left(1-\psi_{j,\mathrm{mix}}-\ln\psi_{\mathrm{mix},j}\right)\end{aligned} \tag{C1}$$

$$B_{j,\mathrm{s}}(I=0) = b_{j,\mathrm{s}} + c_{j,\mathrm{s}} \tag{C2}$$

$$r_{\mathrm{mix}} = \sum_{\mathrm{s}} x'_{\mathrm{s}}r_{\mathrm{s}} \tag{C3}$$

$$q_{\mathrm{mix}} = \sum_{\mathrm{s}} x'_{\mathrm{s}}q_{\mathrm{s}} \tag{C4}$$

$$\psi_{\mathrm{mix},j} = \frac{\sum\limits_{\mathrm{s}} q_{\mathrm{s}}x'_{\mathrm{s}}\psi_{\mathrm{s},j}}{\sum\limits_{\mathrm{s}} q_{\mathrm{s}}x'_{\mathrm{s}}} \tag{C5}$$

$$\psi_{j,\mathrm{mix}} = \sum_{k=1}^{\mathrm{s}}\frac{q_kx'_k\psi_{j,k}}{\sum\limits_{l=1}^{\mathrm{s}} q_lx'_l\psi_{l,k}}. \tag{C6}$$

By substituting those equations into Eq. 32 and using the thermodynamic properties in aqueous solutions, the solubility product in the mixed-solvent or organic solutions can be predicted properly.

Manuscript received May 12, 2010, and revision received Sept. 16, 2010.