

Thermodynamic behavior of electrolyte solutions

Part II. Prediction of vapor–liquid equilibria for mixed-solvent electrolyte systems

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ABSTRACT

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A predictive model for vapor–liquid equilibria of ternary systems, composed of two solvents and one electrolyte, is developed. The parameters for ternary systems are calculated from those for the constituent pairs of binary systems with simple mixing rules. Two isothermal and three isobaric sets of experimental data obtained from the literature and from our laboratory are compared with those calculated by this proposed model. The results are quite satisfactory, with average absolute error of vapor phase mole fractions of less than 0.0193.

Keywords: theory, application, methods of calculation, vapor–liquid equilibria, mixing rules, activity coefficient, osmotic coefficient, electrolytes, mixtures, water.

INTRODUCTION

Distillation is one of the most important separation processes in the chemical industry. A good design of distillation tower is highly dependent

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on complete, accurate vapor–liquid equilibrium (VLE) data. However, it is not possible to provide VLE data solely by experimental work. Theoretical models or empirical correlations are often needed to predict the VLE data. Several models, based on the local composition concept, have been developed for non-electrolyte solutions. These models, such as the Wilson model (Wilson, 1964), the NRTL model (Renon and Prausnitz, 1968) and the UNIQUAC model (Abrams and Prausnitz, 1975), have been verified and are successful in predicting the vapor–liquid equilibrium of non-electrolyte solutions. Unfortunately, all these models cannot be applied to electrolyte solutions without some modifications. Thus the development of a satisfactory model for the vapor–liquid equilibrium of electrolyte solutions has become an active research area in the field of fluid phase equilibria.

Unlike non-electrolyte solutions, there exists not only solvent molecules but also ions, dissociated from the salt or electrolyte, in the electrolyte solutions. These charged anions/cations will interact with each other, and also with solvent molecules and will significantly influence the thermodynamic properties such as activity coefficients, relative volatilities, etc. Discussions of the salt effect on the VLE can be found in the excellent review papers by Furter and Cook, 1967 and Furter, 1977.

The earliest model representing the salt effect on vapor–liquid equilibria of electrolyte solutions is probably the one proposed by Johnson and Furter (1960),

$$\ln(\alpha_s/\alpha_0) = Kx_3 \quad (1)$$

where α_s and α_0 are relative volatilities of solvent in the electrolyte solution and in the salt-free non-electrolyte solution respectively. x_3 is the mole fraction of salt and K is a salt effect parameter. This model is very simple, but in practical applications, it is found that parameter K is strongly dependent on the compositions of salt and solvent, and therefore seriously limits its applicability.

In subsequent research, the concepts of solvation and pseudo-component are adopted by many researchers to describe the salt effect on vapor–liquid equilibria of electrolyte solutions. Ohe and co-workers (1971, 1976) assumed that in a two-solvent one-salt system, the salt preferentially forms solvate with one of the solvents, then the solvated solvent molecules become inactive, i.e. only free solvent molecules play a role in the calculation of the vapor–liquid equilibrium. This model requires the estimation of solvation number to calculate the number of solvated solvent molecules. However, the solvation number, just like the salt effect parameter, is highly dependent on the compositions of salt and solvent, and is therefore the main drawback of this model. Jaques and Furter (1972) proposed a model to describe the vapor–liquid equilibrium of electrolyte solutions with saturated salt concen-

tration. Based on the concept of pseudo-component, this model assumed that there are only two components in the electrolyte solution, component 1 being solvent 1 saturated with salt, and component 2 being solvent 2 saturated with salt. It is these two pseudo-components that actually participate in vapor–liquid equilibrium. Rousseau and co-workers (1972, 1978) also adopted the pseudo-component approach. They assumed that the solvate, which was formed preferentially by one of the mixed solvents with the salt, was the pseudo-component. It was this pseudo-component, not the original pure solvent, that participated in the VLE. These models, with the pseudo-component approach, are satisfactory for some systems, but they are not thermodynamically consistent (Sander et al., 1986).

Schmitt and Vogelpohl (1982) proposed that for a system with one salt and two solvents, each of the two solvents will form a complex with the salt, and the distribution factor K_z , which is the mole ratio of these two complexes, is proportional to the ratio of solubilities of the salt in each solvent. This model can predict well for a few alcohol–water–salt systems except at low salt concentrations where the deviations of the predicted values from the experimental data become large. Lee et al. (1991) modified the Schmitt and Vogelpohl model by introducing a new distribution factor which takes into consideration the solubilities of salt in each constituent component. This modification can yield better accuracy in predictions at low salt concentrations.

All the aforementioned models are based on the concepts of solvation and pseudo-components, and one of the local composition models was employed in the calculation of vapor–liquid equilibria of electrolyte solutions. Starting from the expression of excess Gibbs function, new models were developed based on the modification of local-composition models, such as Wilson, NRTL, and UNIQUAC. Bekerman and Tassios (1976) tried to modify the NRTL equation and nine binary parameters were required to predict the vapor–liquid equilibrium of a ternary system. Håla (1983) considered that the excess Gibbs function was composed of two parts; one due to the solvent–solvent interaction which could be expressed by the Margules equation, the other due to the solvent–salt interaction which was expressed by an empirical function of $x_s^{3/2}$, where x_s is the mole fraction of salt. This model fitted well the vapor–liquid equilibrium data of the MeOH–H₂O–LiCl system at 60°C. Mock et al. (1986) proposed a VLE representation for mixed-solvent electrolyte systems. In their calculations, the solvent–solvent interaction was expressed by the NRTL model, and the solvent–salt interaction was calculated with the electrolyte NRTL model developed by Chen and co-workers (1982, 1986). In their model, the solvent–solvent and solvent–salt binary parameters were determined independently, and three more additional parameters were determined for

two-solvent electrolyte systems. For a non-aqueous two-solvent electrolyte system, e.g. propanol–isopropanol– CaCl_2 , six more parameters are needed for the model.

Sander et al. (1986) combined a modified Debye–Hückel term and a modified UNIQUAC model to describe the vapor–liquid equilibrium of ternary systems. This model gives reasonable agreement for a few alcohol– H_2O –salt systems. A model was developed by Tan (1987) with the same concept as Wilson. It contained two groups of parameters, one of which was the same as that of the Wilson equation for salt-free solutions. The other one was used to describe the interaction between solvent and salt. This model was tested satisfactorily with 57 alcohol– H_2O –salt systems. Tan and Ti (1989) further extended this model to organic mixtures and aqueous organic acid solutions. All the aforementioned models can be correlated to experimental data of solvent electrolyte systems quite satisfactorily by adjusting some parameters. The number of adjustable parameters range from two to six. In order to have a model with prediction ability, Kikic et al. (1991) modified the work of Sander et al. (1986) by replacing the UNIQUAC model with the UNIFAC model, which is a predictive group-contribution method. For 19 mixed-solvent electrolyte systems, the absolute deviations between calculated and experimental data are approximately 9% in pressure and 0.042 in vapor phase mole fractions.

In the present study, the nonideality of the mixtures is expressed in terms of excess Gibbs function. The solvent–solvent interaction was calculated by the Wilson model, the ion–ion interaction was calculated by solving the Poisson–Boltzmann equation, and the ion–molecule interaction was calculated by considering the solvation effect. The development of the model and the estimation of the binary parameters of single-solvent electrolyte systems were described in Part I of this paper (Lin et al., 1993a). Since the parameters involved in the model for single-solvent electrolyte solutions have clear physical meanings, it is possible to extend this model to predict the VLE of mixed-solvent electrolyte systems by using simple mixing rules and the binary parameters of single-solvent electrolyte systems which have been determined independently. The details of the model formulation and the prediction of VLE for mixed-solvent electrolyte solutions are discussed here as Part II.

DEVELOPMENT OF THE MODEL

Activity coefficient of electrolytes in a binary system

Consider a solution of a strong electrolyte dissociated completely into v_+ cations with electric charge number z , and v_- anions with electric charge

number w . The potential of a charged cation in a uniform electric field, Φ_c , can be obtained by solving the Poisson–Boltzmann equation, as described in the Part I (Lin et al., 1993a):

$$y^4 \frac{d^2 \Phi_c}{dy^2} = \frac{\exp(w\Phi_c) - \exp(-z\Phi_c)}{w + z} \quad (2)$$

with boundary conditions:

$$\text{B.C.1: } y = 0, \quad \Phi_c = 0$$

$$\text{B.C.2: } y = 1/\kappa\tilde{a}, \quad \frac{d\Phi_c}{dy} = z\kappa\lambda$$

where,

$$\Phi_c = e\psi_c/kT$$

$$y = 1/\kappa r$$

$$\kappa = \{4\pi(v_+ z^2 + v_- w^2)\lambda C\}^{1/2}$$

$$C = A_v d_s m$$

$$\lambda = e^2/4\pi\epsilon_0 \bar{D}_e kT$$

The potential Φ_c can be considered as the contributions of the surrounding ions, Φ_{cr} , and of the ion itself. It can be shown that

$$\Phi_{cr} = \Phi_c - z\lambda/\tilde{a} \quad (3)$$

Similarly, the potentials Φ_a , Φ_{ar} can be evaluated by the same forms of eqns. (2) and (3).

In Part I of this paper (Lin et al., 1993a), a model has been developed to calculate the mean activity coefficient of electrolyte.

$$(v_+ + v_-) \ln \gamma_{\pm} = v_+ \int_0^z \Phi_{cr} dz + v_- \int_0^w \Phi_{ar} dw + S \cdot m^{2n} \quad (4)$$

where m is the molal concentration, n is a geometric parameter, and S is the solvation parameter.

In eqn. (4), four parameters n , \bar{D}_e , \tilde{a} , and S are involved. These parameters can be determined by fitting eqn. (4) to the available experimental data by means of a nonlinear regression technique. The parameter n was designated to be a constant of 0.645, since during our calculations it did not change significantly even for different systems. This saved a lot of computation time. The remaining three parameters were determined for 144 aqueous electrolyte solution and 16 non-aqueous electrolyte solutions, as reported in Part I of this paper (Lin et al., 1993a).

Activity coefficient of electrolytes in a ternary system

Consider a mixed solvent electrolyte system with mole fractions for solvents 1 and 2 and the electrolytes being x_1 , x_2 , and x_3 . Based on the same considerations as in Part I, eqn. (4) is modified in the following way for calculating the mean activity coefficient of the electrolyte in a mixed-solvent ternary mixture.

Here, we propose that the solvation parameter S for the mixed-solvent electrolyte system is a linear combination of the solvation parameter S_1 for the electrolyte in solvent 1, and the solvation parameter S_2 for the electrolyte in solvent 2. We further assume the solvation parameter S is calculated by the mixing rule:

$$S = x'_1 \cdot S_1 + x'_2 \cdot S_2 \quad (5)$$

where x'_1 is the electrolyte-free composition, and can be expressed as

$$x'_1 = \frac{x_1}{x_1 + x_2} \quad (6)$$

and

$$x'_2 = \frac{x_2}{x_1 + x_2} \quad (7)$$

Substitution of eqn. (5) into eqn. (4) gives

$$(v_+ + v_-) \ln \gamma_{\pm} = v_+ \int_0^z \Phi_{cr} dz + v_- \int_0^w \Phi_{ar} dw + (x'_1 \cdot S_1 + x'_2 \cdot S_2)m^{2n} \quad (8)$$

Similar to the mathematical manipulation in Part I, prior to the evaluation of Φ_{cr} and Φ_{ar} , the equivalent dielectric constant, \bar{D}_e , for the mixed-solvent electrolyte system must be determined. We assume that \bar{D}_e can be calculated from the equivalent dielectric constant for the solvent 1–electrolyte system, \bar{D}_{e1} , and that for the solvent 2–electrolyte system, \bar{D}_{e2} , by the following mixing rule:

$$\frac{1}{\bar{D}_e} = \frac{x'_1}{\bar{D}_{e1}} + \frac{x'_2}{\bar{D}_{e2}} \quad (9)$$

Relationship between activities of the mixed solvents

The relationship between the activity of solvent 1, a_1 , and that of solvent 2, a_2 , can be derived from the Gibbs–Duhem equation. For a ternary system at constant temperature and pressure, the Gibbs–Duhem equation

can be expressed as,

$$N_1 d\bar{G}_1 + N_2 d\bar{G}_2 + N_3 d\bar{G}_3 = 0 \quad (10)$$

where the partial molar Gibbs free energies are related to activities of solvents and solute as

$$d\bar{G}_1 = RT d \ln(a_1) \quad (11)$$

$$d\bar{G}_2 = RT d \ln(a_2) \quad (12)$$

$$d\bar{G}_3 = \nu RT d \ln(m\gamma_{\pm}) \quad (13)$$

The molality of the solution can be expressed as

$$m = \frac{N_3}{N_1 M_1 + N_2 M_2} \times 1000 \quad (14)$$

Expressing N_3 in terms of m , and substituting into eqn. (10),

$$\frac{-1000}{\nu m} \frac{1}{N_1 M_1 + N_2 M_2} [N_1 d \ln(a_1) + N_2 d \ln(a_2)] = d \ln(m\gamma_{\pm}) \quad (15)$$

We define

$$\bar{\phi}_1 = \frac{-1000}{\nu m M_1} \ln(a_1) \quad (16)$$

where the osmotic coefficient of solvent 1 is related to its activity in the solution. Similarly,

$$\bar{\phi}_2 = \frac{-1000}{\nu m M_2} \ln(a_2) \quad (17)$$

The derivatives of eqn. (16) and eqn. (17) are

$$m d\bar{\phi}_1 + \bar{\phi}_1 dm = (-1000/\nu M_1) d \ln(a_1) \quad (18)$$

and,

$$m d\bar{\phi}_2 + \bar{\phi}_2 dm = (-1000/\nu M_2) d \ln(a_2) \quad (19)$$

Substituting eqns. (18) and (19) into eqn. (15) yields

$$\begin{aligned} & \frac{1}{N_1 M_1 + N_2 M_2} [N_1 M_1 (m d\bar{\phi}_1 + \bar{\phi}_1 dm) + N_2 M_2 (m d\bar{\phi}_2 + \bar{\phi}_2 dm)] \\ & = m d \ln(m\gamma_{\pm}) \\ & = dm + m d \ln \gamma_{\pm} \end{aligned} \quad (20)$$

Let

$$\alpha = \frac{N_1 M_1}{N_1 M_1 + N_2 M_2} = \frac{1}{1 + (x_2/x_1)(M_2/M_1)} \quad (21)$$

Substituting eqn. (21) into eqn. (20),

$$\alpha m \, d\bar{\phi}_1 + (1 - \alpha)m \, d\bar{\phi}_2 + [\alpha\bar{\phi}_1 + (1 - \alpha)\bar{\phi}_2] \, dm = dm + m \, d \ln \gamma_{\pm} \quad (22)$$

If x_2/x_1 is kept constant, then α is constant. Eqn. (22) can be simplified into

$$d\{m[\alpha\bar{\phi}_1 + (1 - \alpha)\bar{\phi}_2 - 1]\} = m \, d \ln \gamma_{\pm} \quad (23)$$

Integration of eqn. (23) yields

$$\{m[\alpha\bar{\phi}_1 + (1 - \alpha)\bar{\phi}_2 - 1]\} \Big|_{m=0}^{m=m} = \int_{m=0}^{m=m} m \, d \ln \gamma_{\pm} \quad (24)$$

Since $m = 0$ is for the case where the solution is electrolyte-free, it can be shown that

$$\{m[\alpha\bar{\phi}_1 + (1 - \alpha)\bar{\phi}_2 - 1]\}_{m=0} = \frac{-1000}{v} \left[\frac{\alpha}{M_1} \ln(x_1 \gamma_1^\circ) + \frac{(1 - \alpha)}{M_2} \ln(x_2 \gamma_2^\circ) \right] \quad (25)$$

where γ_1° and γ_2° are the activity coefficients of solvent 1 and solvent 2 in an electrolyte-free solution respectively, and it is clear that α is the same as that of the electrolyte solution. The activity coefficients γ_1° and γ_2° can be evaluated by local-composition models, such as Wilson, NRTL or UNIQUAC. In the present study, the Wilson model is adopted, and the parameters, $\lambda_{12} - \lambda_{11}$ and $\lambda_{21} - \lambda_{22}$ can be found elsewhere (Gmehling et al., 1980).

Vapor–liquid equilibrium of a ternary system

At low pressure, the relation of vapor–liquid equilibrium can be stated as,

$$x_1 \gamma_1 P_1^s = y_1 P \quad (26)$$

$$x_2 \gamma_2 P_2^s = y_2 P \quad (27)$$

Since $y_1 + y_2 = 1$, eqns. (26) and (27) can be combined and rearranged into,

$$\frac{x_1 \gamma_1 P_1^s}{P} + \frac{x_2 \gamma_2 P_2^s}{P} = 1 \quad (28)$$

The vapor phase compositions y_1 and y_2 can then be calculated by the following steps.

(1) γ_{\pm} is calculated with eqn. (4), where the parameters S and \bar{D}_e are evaluated by the mixing rules, eqns. (5) and (9), and the binary parameters \tilde{a} , \bar{D}_{e1} , S_1 for solvent 1–electrolyte mixtures and \tilde{a} , \bar{D}_{e2} , S_2 for solvent 2–electrolyte mixtures. Note that the closest distance of approach \tilde{a} shares the same value for two binary systems containing identical electrolytes. The values of these parameters for 160 systems have been tabulated in Part I of this paper (Lin et al., 1993a).

(2) γ_1° and γ_2° are calculated for solvent 1–solvent 2 mixtures by using the Wilson equation with the parameters obtainable from the literature (Gmehling et al., 1980).

(3) An equation relating $\bar{\phi}_1$ and $\bar{\phi}_2$ (thus γ_1 and γ_2) can be obtained from eqn. (24) by carrying out an integration of the right-hand side of eqn. (24). This equation can be solved with eqn. (28) simultaneously to obtain γ_1 and γ_2 at a specific temperature, pressure and constant α for a constant mole ratio of solvent 1 to solvent 2 while varying the molal concentration of the electrolyte.

(4) The vapor pressures P_1^S and P_2^S are calculated at the system temperature for pure solvent 1 and pure solvent 2 respectively by employing the Antoine equation.

(5) γ_1 and γ_2 are calculated from eqns. (26) and (27) respectively.

RESULTS AND DISCUSSION

In order to test the applicability of the proposed model, three mixed-solvent electrolyte solutions, MeOH–H₂O–LiCl, IPA–H₂O–LiCl and IPA–H₂O–LiBr are considered. For isothermal systems, the VLE data of these solutions are obtained from the literature (Broul et al., 1969; Sada et al., 1975). The binary parameters for the calculation of vapor phase compositions are listed in Tables 1 and 2. The predicted results are listed in Tables

TABLE 1

Binary parameter values of single-solvent electrolyte systems

System	Temp. (°C)	\tilde{a}	\bar{D}_e	S	Data source
MeOH–LiCl	60	4.000	14.126	0.607	Broul et al., 1969
H ₂ O–LiCl	60	4.000	31.445	0.320	Broul et al., 1969
IPA–LiCl	75.1	4.000	9.960	1.462	Sada and Morisue, 1975
H ₂ O–LiCl	75.1	4.000	22.903	0.320	Sada and Morisue, 1975
IPA–LiBr	75.0	3.988	8.764	0.922	Sada and Morisue, 1975
H ₂ O–LiBr	75.0	3.988	43.827	0.403	Sada and Morisue, 1975

TABLE 2
Binary parameters of the Wilson equation for mixed-solvent systems at 60°C

System	$\lambda_{12} - \lambda_{11}$	$\lambda_{21} - \lambda_{22}$	Data source
MeOH–H ₂ O	–184.8143	653.4817	Gmehling et al., 1980
IPA–H ₂ O	437.9789	1238.9966	Gmehling et al., 1980

TABLE 3
Prediction of vapor–liquid equilibrium of MeOH–H₂O–LiCl system at 60°C

<i>P</i> (mmHg)	<i>x</i> ₃	<i>x</i> ₁	<i>y</i> ₁ ^{exp}	<i>y</i> ₁ ^{pred}	<i>y</i> ₁ ^{pred} – <i>y</i> ₁ ^{exp}
144.70	0.0296	0.0074	0.0418	0.0285	0.0133
151.08	0.0331	0.0119	0.1026	0.0899	0.0127
159.75	0.0348	0.0189	0.1555	0.1424	0.0131
171.76	0.0036	0.0236	0.1565	0.1418	0.0147
174.11	0.0377	0.0299	0.2430	0.2323	0.0107
167.06	0.0949	0.0516	0.4139	0.4931	0.0792
211.19	0.0058	0.0637	0.3396	0.3326	0.0070
198.33	0.0872	0.0757	0.4990	0.5421	0.0431
195.64	0.0360	0.0555	0.3405	0.3289	0.0116
222.11	0.0341	0.0815	0.4317	0.4229	0.0088
245.10	0.0325	0.1077	0.4989	0.4891	0.0098
235.88	0.0827	0.1137	0.5880	0.6165	0.0285
258.82	0.0062	0.1178	0.4896	0.4847	0.0049
275.43	0.0332	0.1428	0.5712	0.5652	0.0060
277.41	0.0813	0.1712	0.6726	0.6949	0.0223
297.82	0.0339	0.1720	0.6162	0.6127	0.0035
454.68	0.0634	0.6400	0.8953	0.8951	0.0002
476.88	0.0147	0.5951	0.8465	0.8372	0.0093
422.48	0.0733	0.5661	0.8759	0.8820	0.0061
434.90	0.0527	0.5297	0.8503	0.8459	0.0044
410.72	0.0495	0.4428	0.8105	0.8098	0.0007
399.48	0.0571	0.4210	0.8078	0.8101	0.0023
401.47	0.0134	0.3822	0.7522	0.7480	0.0042
378.71	0.0439	0.3423	0.7607	0.7583	0.0024
359.64	0.0697	0.3316	0.7761	0.7865	0.0104
340.35	0.0410	0.2501	0.7088	0.6979	0.0109
319.84	0.0748	0.2420	0.7295	0.7427	0.0132
313.95	0.0337	0.1984	0.6457	0.6425	0.0212

$\sigma y_1 = 0.0127$. Experimental data are taken from Broul et al., 1969. $\sigma y_1 = \Sigma |y_1^{\text{pred}} - y_1^{\text{exp}}|/n_p$.

TABLE 4

Prediction of vapor–liquid equilibrium of IPA–H₂O–LiCl system at 75.1°C

P (mmHg)	x_3	x_1	y_1^{exp}	y_1^{pred}	$ y_1^{\text{pred}} - y_1^{\text{exp}} $
591.8	0.0300	0.2803	0.6070	0.5913	0.0157
589.1	0.0500	0.2746	0.6490	0.6210	0.0280
577.8	0.0700	0.2678	0.6880	0.6657	0.0223
542.7	0.1000	0.2592	0.7520	0.7618	0.0098
595.5	0.0300	0.3773	0.6300	0.5988	0.0312
588.1	0.0500	0.3696	0.6730	0.6519	0.0211
573.9	0.0700	0.3608	0.7140	0.7322	0.0182
531.2	0.1000	0.3492	0.7760	0.7925	0.0165
598.6	0.0300	0.5015	0.6740	0.6495	0.0245
583.3	0.0500	0.4902	0.7160	0.6739	0.0421
560.2	0.0700	0.4799	0.7570	0.7740	0.0170
510.7	0.1000	0.4635	0.8150	0.7862	0.0288
401.2	0.1500	0.4369	0.8840	0.8953	0.0113
587.7	0.0300	0.7178	0.7920	0.8131	0.0211
566.0	0.0500	0.7021	0.8290	0.7915	0.0375
537.6	0.0700	0.6863	0.8620	0.8345	0.0275
479.8	0.1010	0.6635	0.8950	0.9061	0.0111
370.6	0.1500	0.6265	0.9330	0.9651	0.0321

$\sigma y_1 = 0.0231$. Experimental data are taken from Sada and Morisue, 1975. $\sigma y_1 = \sum |y_1^{\text{pred}} - y_1^{\text{exp}}|/n_p$.

3 to 5. It can be seen that the deviations between the predicted and experimental values of the vapor phase compositions are quite small. The average errors, σy_1 , for these three systems are 0.0127, 0.0231 and 0.0192 respectively. It should be emphasized that in our calculation, only binary parameters of the single-solvent electrolyte solutions are needed; there are no additional parameters, as required by other approaches.

For the prediction of VLE of isobaric systems, the temperature effect on the parameters \tilde{a} , S and \bar{D}_e should be considered. It has been pointed out in Part I (Lin et al., 1993a), that \tilde{a} and S are nearly temperature independent. For instance, the values of \tilde{a} and S at temperatures of 60°C are identical to those at 75.1°C for the H₂O–LiCl system. However, the third parameter \bar{D}_e depends strongly on temperature. As can be seen from Table 1, for the H₂O–LiCl system, the value of \bar{D}_e changes from 32.136 at 60°C to 24.156 at 75.1°C. The effect of \bar{D}_e on the VLE calculation is through its effect on γ_{\pm} . The experimental data of γ_{\pm} as a function of temperature were reported by Robinson and Stokes (1959) for KBr and NaCl aqueous solutions as plotted in Fig. 1. It can be seen that γ_{\pm} does not vary significantly with

TABLE 5
Prediction of vapor–liquid equilibrium of IPA–H₂O–LiBr system at 75°C

<i>P</i> (mmHg)	<i>x</i> ₃	<i>x</i> ₁	<i>y</i> ₁ ^{exp}	<i>y</i> ₁ ^{pred}	<i>y</i> ₁ ^{pred} – <i>y</i> ₁ ^{exp}
567.2	0.0100	0.1970	0.5370	0.5267	0.0103
572.2	0.0300	0.1930	0.5760	0.5468	0.0292
575.0	0.0500	0.1881	0.6120	0.6007	0.0113
565.8	0.0700	0.1841	0.6490	0.6610	0.0120
544.6	0.1000	0.1782	0.7040	0.7316	0.0276
481.5	0.1500	0.1675	0.7920	0.7664	0.0256
601.5	0.0100	0.4762	0.6150	0.5895	0.0255
591.7	0.0300	0.4666	0.6580	0.6834	0.0254
569.7	0.0500	0.4560	0.6950	0.6685	0.0265
537.2	0.0700	0.4455	0.7300	0.6967	0.0333
461.5	0.1000	0.4311	0.7800	0.7896	0.0096
269.7	0.1500	0.4063	0.8510	0.8711	0.0201
602.9	0.0100	0.7346	0.7470	0.7266	0.0204
582.1	0.0300	0.7188	0.7900	0.7714	0.0186
555.5	0.0500	0.7030	0.8270	0.7969	0.0301
523.5	0.0700	0.6882	0.8550	0.8326	0.0224
442.5	0.1000	0.6651	0.8840	0.8939	0.0099
245.5	0.1500	0.6273	0.9190	0.9446	0.0256

$\sigma y_1 = 0.0192$. Experimental data are taken from Sada and Morisue, 1975. $\sigma y_1 = \Sigma |y_1^{pred} - y_1^{exp}| / n_p$.

temperature. To verify this consideration, the isobaric experimental data for IPA–H₂O–LiCl and IPA–H₂O–LiBr solutions, measured in our laboratory (Lin et al., 1993b) are compared with those calculated with the

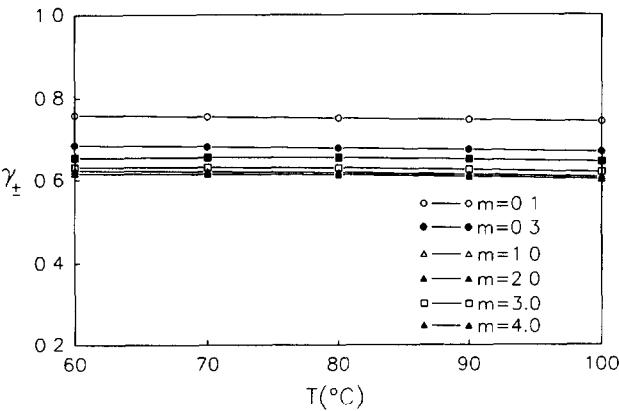


Fig. 1. Mean activity coefficients of KBr in aqueous KBr solutions at various temperatures.

parameters listed in Table 1. The value of \bar{D}_e listed in Table 1 for IPA and H₂O systems were evaluated from the vapor pressure data reported by Sada and Morisue (1975) at 75.1 and 75.0°C. Although the values of \bar{D}_e at 75.1/75.0°C were used to predict the isobaric VLE where the equilibrium temperatures ranged from 80.2 to 84.6°C, the predicted results for IPA–H₂O–LiCl and IPA–H₂O–LiBr agreed well with the experimental data, as shown in Tables 6 and 7. The average errors of vapor composition, σy_1 , are 0.0180 and 0.0201 respectively.

To visualize the predictability of the proposed model, the calculated values (y_1^{pred}) and the experimental data (y_1^{exp}) reported in Tables 3 to 7 are

TABLE 6

Prediction of vapor–liquid equilibrium of IPA–H₂O–LiCl system at 760 mmHg

T (°C)	x_3	x_1	y_1^{exp}	y_1^{pred}	$ y_1^{\text{pred}} - y_1^{\text{exp}} $
84.1	0.0082	0.0952	0.5112	0.4882	0.0230
84.6	0.0252	0.0864	0.5203	0.4987	0.0216
82.5	0.0410	0.0680	0.5564	0.5653	0.0089
82.6	0.0811	0.0521	0.6750	0.6527	0.0223
83.1	0.1200	0.0350	0.7412	0.7739	0.0327
81.7	0.0110	0.1745	0.5482	0.5556	0.0074
81.8	0.0200	0.1652	0.5898	0.5643	0.0255
82.0	0.0451	0.1421	0.6110	0.5952	0.0158
80.9	0.0652	0.1320	0.6448	0.6564	0.0116
81.8	0.1101	0.1208	0.7532	0.7990	0.0458
81.5	0.0092	0.3120	0.5713	0.5645	0.0068
81.3	0.0281	0.2911	0.5980	0.6047	0.0067
80.8	0.0520	0.2560	0.6327	0.6561	0.0234
80.4	0.0701	0.2465	0.6833	0.7011	0.0178
81.1	0.0102	0.4003	0.6089	0.5832	0.0257
80.8	0.0276	0.3903	0.6223	0.6371	0.0148
80.8	0.0530	0.3454	0.6644	0.6812	0.0168
82.0	0.0901	0.3387	0.7324	0.7530	0.0206
81.0	0.0111	0.5214	0.6541	0.6346	0.0195
80.6	0.0350	0.5021	0.6804	0.6971	0.0167
81.8	0.0650	0.4972	0.7412	0.7374	0.0038
80.6	0.0121	0.5897	0.6373	0.5999	0.0186
80.8	0.0220	0.5712	0.6522	0.6559	0.0037
80.7	0.0360	0.5630	0.7510	0.7402	0.0108
80.9	0.0130	0.7360	0.7723	0.7629	0.0094
81.2	0.0071	0.8210	0.8444	0.8324	0.0120
81.3	0.0030	0.9060	0.9210	0.8911	0.0299

$\sigma y_1 = 0.0180$. Experimental data from Lin et al., 1993b. $\sigma y_1 = \Sigma |y_1^{\text{pred}} - y_1^{\text{exp}}| / n_p$.

TABLE 7

Prediction of vapor–liquid equilibrium of IPA–H₂O–LiBr system at 760 mmHg

T (°C)	x_3	x_1	y_1^{exp}	y_1^{pred}	$ y_1^{\text{pred}} - y_1^{\text{exp}} $
84.2	0.0102	0.0732	0.5232	0.4873	0.0359
84.1	0.0250	0.0621	0.5343	0.5076	0.0264
84.0	0.0430	0.0534	0.5640	0.5369	0.0271
82.7	0.0730	0.0444	0.5933	0.6330	0.0397
82.6	0.1030	0.0383	0.7234	0.7777	0.0543
81.8	0.0111	0.1703	0.5448	0.5528	0.0080
82.0	0.0340	0.1497	0.5712	0.5774	0.0062
81.1	0.0503	0.1400	0.6021	0.6210	0.0189
81.0	0.0689	0.1343	0.6423	0.6585	0.0162
81.3	0.0903	0.1203	0.6844	0.7134	0.0290
81.6	0.0099	0.3073	0.5712	0.5619	0.0093
81.8	0.0230	0.2902	0.5930	0.5784	0.0146
80.8	0.0503	0.2687	0.6220	0.6521	0.0301
80.4	0.0703	0.2586	0.6643	0.6560	0.0083
82.2	0.0856	0.2521	0.6911	0.6940	0.0029
81.1	0.0101	0.4012	0.6020	0.5827	0.0193
80.8	0.0303	0.3812	0.6334	0.6399	0.0065
82.1	0.0820	0.3410	0.6889	0.7056	0.0167
81.1	0.0121	0.5222	0.6231	0.6300	0.0069
80.6	0.0460	0.4998	0.6956	0.7235	0.0279
81.7	0.0702	0.4811	0.7223	0.7373	0.0150
80.5	0.0102	0.6133	0.6633	0.6251	0.0382
80.9	0.0255	0.6003	0.6983	0.6690	0.0293
80.8	0.0388	0.5921	0.7244	0.7417	0.0173
80.5	0.0188	0.7132	0.7443	0.6962	0.0481
80.6	0.0085	0.8012	0.8021	0.8153	0.0132
81.4	0.0021	0.9013	0.8902	0.8830	0.0072

$\sigma_{y_1} = 0.0201$. Experimental data from Lin et al., 1993b. $\sigma_{y_1} = \Sigma |y_1^{\text{pred}} - y_1^{\text{exp}}| / n_p$.

all plotted in Fig. 2. It can be seen that most of the data either fall on or near the diagonal line, which is a good indication of the predictability of the proposed model.

CONCLUSION

A model to predict the VLE of mixed-solvent electrolyte ternary systems has been developed. The only data required in the prediction are the Wilson parameters, and the characteristic parameters of the constituent single-solvent electrolyte binary systems. These parameters of binary systems can be

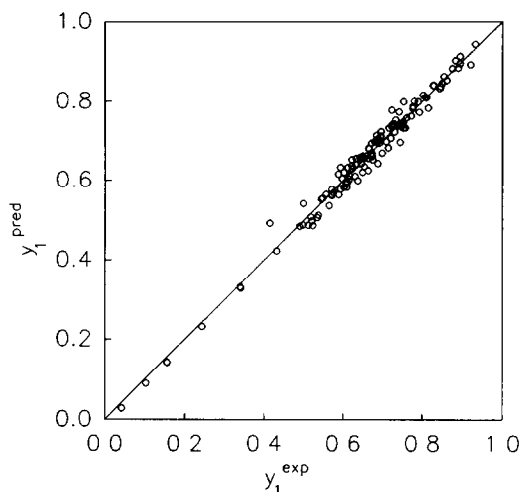


Fig. 2. Comparison of predicted values of the mole fraction of the volatile component in the vapor phase with experimental values.

determined independently from activity coefficient or osmotic coefficient data. The match of the calculated vapor phase compositions and the 117 experimental data for MeOH–H₂O–LiCl, IPA–H₂O–LiCl and IPA–H₂O–LiBr solutions is quite satisfactory.

More experiments are needed to test the applicability of the present model to other mixed-solvent electrolyte systems.

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LIST OF SYMBOLS

A_v	Avogadro's constant
a	activity of solvent
\tilde{a}	closest distance of approach (Å)
C	number of electrolytes per unit volume (particles/m ³ of solution)
\bar{D}_e	equivalent dielectric constant
d_s	density of solvent (kg/m ³)
e	electron charge

\bar{G}	partial Gibbs energy
IPA	iso-propyl alcohol (2-propanol)
k	Boltzmann's constant
M	molecular weight (g/g mol)
m	molality (g mol/kg of solvent)
N	number of moles
n	power of m
n_p	number of data points
P	pressure of system
r	radius of a spherical shell
S	solvation parameter
T	temperature of solution
w	absolute value of anionic charge
x	mole fraction of component in liquid phase
x'	salt-free mole fraction of component in liquid phase
y	mole fraction of component in vapor phase
z	absolute value of cationic charge

Greek letters

α	defined in eqn. (21)
α_s	relative volatility in salt-containing mixture
α_0	relative volatility in salt-free mixture
γ	activity coefficient of solvent
γ_{\pm}	mean activity coefficient of electrolyte
v_+	stoichiometric number of cations in an electrolyte
v_-	stoichiometric number of anions in an electrolyte
v	$v_+ + v_-$
λ	$e^2/4\pi\epsilon kT$
$\lambda_{12} - \lambda_{11}, \lambda_{21} - \lambda_{22}$	Wilson parameters
ϵ_0	electrical permittivity in vacuum
ψ	electrical potential of an ion within an electric field
κ	$[4\pi(v_+ z^2 + v_- w^2)\lambda C]^{1/2}$
ϕ	osmotic coefficient of solution
$\bar{\phi}$	partial osmotic coefficient
Φ	dimensionless electrical potential, $= e\psi/kT$
σ	mean absolute deviation

Subscripts

1, 2	solvent 1, 2 in electrolyte solution
3	electrolyte in electrolyte solution
a	anion

c	cation
r	surrounding ion
s	solvent

Superscripts

°	salt-free state
s	saturation
exp	experimental value
pred	predicted value

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