

VAPOR-LIQUID EQUILIBRIA OF SOLVENTS IN MIXED STRONG 1 : 1 ELECTROLYTES-SOLVENT SYSTEM

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Abstract—Phase equilibrium calculation of electrolyte-mixed solvent systems is important in separation processes including extractive distillation. Although methods for equilibrium calculations are available in the literature, they are specific to each application and no general methods have been proposed. In the present work we extended the semiempirical method applicable to the solute properties of mixed electrolyte-mixed solvent systems to the calculation of solvent properties. In the present method excess Gibbs function was represented as the sum of Debye-Hückel term, Born term and NRTL term. Experimental data for mixed 1 : 1 strong electrolytes-mixed solvent systems showed close agreements with calculated values.

INTRODUCTION

Vapor-liquid equilibria of electrolyte-solvent systems are important in electrochemical applications or in separation processes. Since the pioneering researches of Debye-Hückel for dilute electrolyte solutions, investigators reported results for concentrated solutions and mixtures. Most of researches on mixtures are concerned with the behaviors of single electrolyte or mixed electrolytes [1, 2] in a single solvent. In recent work of Evans and Chen [3], results have been reported for the vapor liquid equilibria of single salt-mixed solvent systems based on the NRTL model and the local electric neutrality condition. So far no single model has been successful in calculating the behavior of electrolytes and solvents in the mixed electrolyte-mixed solvent systems.

In most of works for concentrated electrolyte solutions the excess Gibbs function of the system is represented by adding a short range interaction term to the long range Debye-Hückel contribution. The short range effect is often modelled by the NRTL term. Cruz and Renon [4] added the Born term to the Debye-Hückel term and the NRTL term to account for change of dielectric constants of systems due to the addition of electrolytes. This term is seldom used by other investigators. Due to cancellation a short range interaction term is often sufficient to represent the combined effect of the Born term and the short range interaction. In using the Born term, however, the evaluation of dielectric constant in concentrated electro-

lyte solutions presents a difficult problem.

Recently we have reported a model for mixed electrolyte-mixed solvent systems and applied it to the calculation of electrolyte behaviors and solubilities [5-8]. In this model the excess Gibbs function is modelled as the sum of Debye-Hückel term, Born term and NRTL term as Cruz and Renon did for single electrolyte-single solvent systems. In this paper we applied the model to the vapor-liquid equilibria of mixed electrolyte-mixed solvent systems as a step to the solution of more general problems.

EXCESS GIBBS FUNCTION MODEL

In the semiempirical approach, we consider three contributions to the excess Gibbs function as did Cruz and Renon [4] for single electrolyte-single solvent systems. The Debye-Hückel term is written for an infinite dilution reference state as given by the Guggenheim representation,

$$G_{DH}^{E*} = -\frac{kTV}{4\pi a^3 N_o} \left[\frac{(Ka)^2}{2} - (Ka) + \ln(1 + Ka) \right] \quad (1)$$

where

$$K = \left(\frac{8\pi e^2 N_o I}{D^* kT} \right)^{1/2} \quad (2)$$

$$I = \frac{1}{2} \sum_m N_m z_m^2 / 2V \quad (3)$$

and the following mixing rule for 'a' was assumed,

$$a = \sum_i^E N_i a_i / (\sum_i^E N_i) \quad (4)$$

Here I and E in the summation indicate that the sums are over all ions and electrolytes respectively.

The Born model contribution is represented by the wellknown expression for the infinite dilution reference state,

$$G_B^E = \frac{e^2 N_o}{2} \left(\frac{1}{D} - \frac{1}{D_s} \right) \sum_m^I \frac{N_m Z_m^2}{r_m} \quad (5)$$

where D is the solution dielectric constant.

The NRTL contribution to the excess Gibbs function is expressed by the NRTL model assuming that no ions are present around ions due to solvation. Then we have,

$$G_{NRTL}^E = \sum_i^s N_i (N_{Zi} + \sum_k^{CI} N_k Z_{k+ki}) / (N_{Gi} + \sum_k^{CI} N_k G_{k+ki}) \\ + \sum_i^I N_i (\sum_k^s N_k Z_{ki}) / (\sum_k^s N_k G_{ki}) \quad (6)$$

where

$$N_{Gi} = \sum_{m \neq i}^s N_m G_{mi} + N_i \quad (7)$$

$$N_{Zi} = \sum_{m \neq i}^s N_m Z_{mi} \quad (8)$$

and s and CI in the summation indicate that the sums are over all solvents and cations respectively. Note that this contribution is given for the pure component reference state unlike the Debye-Hückel or the Born contributions.

Kim and Lee [5] derived the activity coefficient expression for solutes which is given by the sum of the three contributions as,

$$\ln \gamma_i^* = \ln \gamma_{DH}^* + \ln \gamma_B^* + \ln \gamma_{NRTL}^* \quad (9)$$

where the first two terms on the right hand side are the partial molar properties of the quantities given by Eqs. (1) and (5). However, the third term is obtained from the well-known relation [9],

$$\ln \gamma_{NRTL,i}^* = \ln \gamma_{NRTL,i} - \lim_{ion \rightarrow 0} \ln \gamma_{NRTL,i} \quad (10)$$

where the quantity on the right hand side is the partial molar property of Eq. (6).

The activity coefficient for solvent is calculated similarly,

$$\ln \gamma_i = \ln \gamma_{DH} + \ln \gamma_B + \ln \gamma_{NRTL} \quad (11)$$

where the first two terms on the right hand side are

obtained using the relation [9],

$$\ln \gamma_i = \ln \gamma_i^* - \lim_{x_i \rightarrow 1} \ln \gamma_i^* \quad (12)$$

The Debye-Hückel contribution for the solute activity coefficient was derived assuming the system volume is equal to the solvent volume. Based on the same assumption we can calculate the solvent activity coefficient of pure solvent system. Cardoso and O'Connell argued that the volume be fixed in taking the partial derivatives for the mixed solvent system [10]. Taking the partial molar properties at the fixed volume and applying Eq. (12) we have,

$$\ln \gamma_{DH} = - \frac{v_i}{4\pi a^3 N_o} \left(- \frac{(Ka)}{2} + \ln(1 + Ka) - \frac{Ka}{2(1 + Ka)} \right) \quad (13)$$

The Born contribution is obtained as,

$$\ln \gamma_B = - \frac{e^2}{2kT} \left[\frac{1}{D^2} \frac{\partial D}{\partial N_i} - \frac{1}{D_s^2} \frac{\partial D_s}{\partial N_i} \right. \\ \left. \left(\frac{2}{3} + \frac{1}{3} \frac{D_s}{D} \right) \right] \sum_m^I \frac{N_m}{r_m} \quad (14)$$

The NRTL contribution to the activity coefficient is calculated from the corresponding excess Gibbs function [Eq. (6)] by taking the partial molar properties and is given by the following expression,

$$\ln \gamma_{NRTL,i} = \frac{1}{RT} \left(\frac{N_{Zi} + \sum_k^{CI} N_k Z_{k+ki}}{N_{Gi} + \sum_k^{CI} N_k G_{k+ki}} \right. \\ + \sum_{m \neq i}^s \frac{N_m Z_{mi}}{N_{Gi} + \sum_k^{CI} N_k G_{k+ki}} \left. \right) \\ - \sum_i^s \frac{N_m G_{im}}{RT} \left(\frac{N_{Zm} + \sum_k^{CI} N_k Z_{k+km}}{(N_{Gi} + \sum_k^{CI} N_k G_{k+ki})} \right) \\ + \sum_i^I \frac{N_i}{RT} \left(\frac{Z_{i1}}{\sum_j N_j G_{j1}} - \frac{G_{i1} \sum_k N_k Z_{k+1}}{(\sum_k N_k G_{k1})^2} \right) \quad (15)$$

There are four NRTL parameters for each ion-solvent pair in the last term which are not present in other terms. This term vanishes for pure solvent systems. Due to cancellation of terms these parameters do not appear in the solute activity coefficients. Four new parameters for each ion-solvent pair appear to be too complicated to characterize the interaction. Therefore instead of the last term, we assume a similar but less complicated relation,

$$\sum_i^{CI} \frac{N_i}{RT} \left(\frac{Z_{i+1}}{\sum_j N_j G_{j+1}} - \frac{G_{i+1} \sum_k N_k Z_{k+1}}{(\sum_k N_k G_{k+1})^2} \right) \quad (16)$$

where the summation is over all cations instead of ions and ion-solvent interaction parameters are replac-

ed by solute-solvent parameters. We further assume that solute-solvent interaction parameters are related by the following relation which is usually assumed in the NRTL model,

$$Z_{k+1} = Z_{i,1k} \frac{G_{k+1} \ln G_{k+1}}{G_{i,1k} \ln G_{i,1k}} \quad (17)$$

In this way we need only one more parameter G_{k+1} for a solvent(k)-solute(1) pair to calculate solvent activity coefficient in mixed solvent systems.

EQUILIBRIUM CALCULATION

The Vapor liquid equilibrium is calculated using the relation.

$$f_i^V = f_i^L \quad (18)$$

Since we have the activity coefficient of solvent species, the liquid phase fugacity is readily calculated.

$$f_i^L = x_i \gamma_i^* f_i^0 \quad (19)$$

where the reference fugacity f_i^0 is obtained from the relation.

$$f_i^0 = P_i^{sat} \phi_i^{sat} \exp \left(\int_{P^0}^P \frac{v_i}{RT} dP \right) \quad (20)$$

The gas phase fugacity is calculated by the following relation.

$$f_i^V = P y_i \phi_i \quad (21)$$

where P is the pressure. The fugacity coefficient ϕ_i can be calculated using the virial equation of state.

$$\ln \phi_i = \left[2 \sum_{j=1}^m y_j B_{ij} - B_{mix} \right] \frac{P}{RT} \quad (22)$$

where

$$B_{mix} = \sum_{i=1}^m \sum_{j=1}^m y_i y_j B_{ij} \quad (23)$$

The equilibrium calculation is carried out by an iteration method at a fixed temperature with initial values of the gas phase composition.

$$P = f_1^L / \phi_1 + f_2^L / \phi_2 \quad (24)$$

Then the gas phase composition is refined.

$$y_1 = (f_1^L / \phi_1) / (f_1^L / \phi_1 + f_2^L / \phi_2) \quad (25)$$

Since the gas phase is nearly ideal the convergent solution is readily obtained.

PROPERTIES NEEDED FOR CALCULATION

The NRTL term requires three NRTL parameters (only three of G_{ij} , G_{ji} , Z_{ij} and Z_{ji} are independent) for each solvent-solvent pair and three NRTL parameters ($Z_{i,k1}$, $G_{i,k1}$ and $G_{i,-k}$) for each solvent-electrolyte pair. Only the first two of solvent-electrolyte parameters are required for all properties of single solvent systems and for electrolyte properties of mixed solvent systems.

For the evaluation of the Debye-Hückel term an electrolyte size parameter 'a' and data for the solvent dielectric constant, D_s , and for the solvent volume V are required. For the Born term we need an ion size parameter r_i and the solution dielectric constant D and the partial molar volume v_i of the solvents in solvent mixture. Of these 'a' and NRTL parameters are adjustable parameters. r_i is calculated by the following equation,

$$r_i = 3.0989 \times 10^{-12} (|\delta_s| / D_s) \quad (26)$$

where δ_s is the Hasted depression coefficient. We use experimental data for D_s , V and y_i . The partial molar volume of a solvent in solvent mixtures are obtained, for example, from Sandler [11].

For the water-methanol system D_s is given as a function of the methanol mass fraction by Conway [12].

$$D_s = -0.45W + 78.71 \quad (27)$$

Solution dielectric constants for concentrated electrolyte solutions are known difficult to experimentally determine and only limited sets of data are available for mixed solvents in the literature. Following empirical formula was proposed [5] by modifying the Ball's expression.

$$D = D_0 + (D_s - D_0) \left(\frac{1 + Y'}{1 + Y'/2} - \frac{(1 - Y')^2}{2TV} \sum \frac{E_i N_i}{r_i'} \right) \quad (28)$$

where

$$Y' = (4/3) \pi N_0 \sum_j N_j r_j'^3 / V \quad (29)$$

$$Y'' = (4/3) \pi N_0 \sum_k N_k r_k'^3 / V \quad (30)$$

D_0 is the dielectric constant in vacuum and E_i is a constant which is $1.0 \times 10^{-11} \text{ K m}^4 \text{ mol}^{-1}$ for cations and zero for anions. r_i' is calculated from following definition,

$$r_i' = \sum_j N_j r_{ij}' / \sum_j N_j \quad (31)$$

where r_{ij}' is the r' value of ion i in pure solvent j . r_i'' is assumed independent of solvent species. They

Table 1. Ionic properties

	H ⁺	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻
$r_{iw}/10^{-10}\text{m}$	0.263	2.40	1.84	1.30	1.81	1.95
$r_{ia}/10^{-10}\text{m}$	—	3.79	3.28	2.79	1.81	1.95
$r_{ij}^*/10^{-10}\text{m}$	2.26	3.05	2.66	2.54	0.0	0.0
$\delta_i/10^{-3}\text{m}^3\text{mol}^{-1}$	-16.4	-9.8	-8.0	-6.6	-3.6	-4.1

The subscript W or A designates water or methanol, respectively.

are fitting parameters to dielectric constants.

The derivative of dielectric constant with respect to a solvent component is given by

$$\frac{\partial D}{\partial N_i} = \left(\frac{3Y'}{2(1+Y'/2)^2} + \frac{1-4Y''+3Y''^2}{2TV} \sum_j \frac{E_j N_j}{r_{ij}''} \right) \frac{V_i}{V} (D_s - D_0) - \left(\frac{9}{2(1+Y'/2)^2} - \frac{4\pi N_0}{3V} \sum_j N_j \left(\frac{r_{ij}'}{r_j'} - 1 \right) r_{ij}^{*3} / \sum_m N_m \right) (D_s - D_0) + \left(\frac{\partial D_s}{\partial N_i} \right) \left[\frac{1+Y'}{1+Y'/2} - \frac{(1-Y'')^2}{2TV} \sum_j \frac{E_j N_j}{r_{ij}''} \right] \quad (32)$$

where $\partial D_s / \partial N_i$ is calculated from Eq. (27).

The second virial coefficients for water (1)-methanol (2) mixtures are calculated by the Tsonopoulos's method [13] which is applicable to polar substances. At 298.15 K calculated values of B_{11} , B_{22} and B_{12} are $-2997.075 \text{ cm}^3/\text{mol}$, $-2056.06 \text{ cm}^3/\text{mol}$ and $-1274.02 \text{ cm}^3/\text{mol}$, respectively. Vapor pressure values P_1^0 and P_2^0 are 23.756 mmHg and 125.027 mmHg at the same temperature.

The ionic parameters are listed in Table 1. These values are the same as those used of electrolyte property calculations [8]. Electrolyte parameters are listed in Table 2. Except for the NRTL parameters between solvents, they are identical to those given in the reference [8].

RESULTS AND DISCUSSION

Fig. 1 and 2 respectively compare the calculated va-

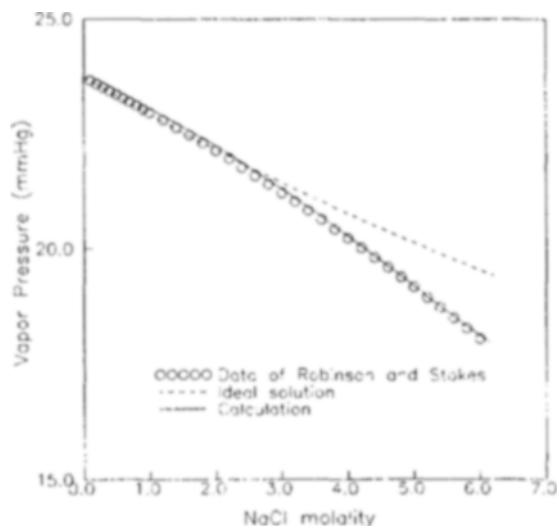


Fig. 1. Vapor pressure of NaCl-water system at 298.15 K.

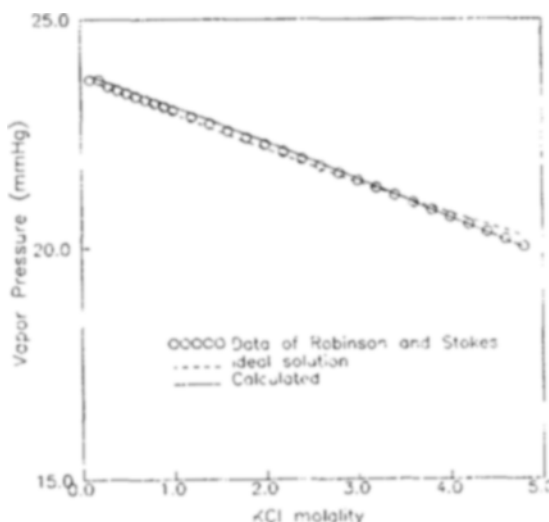


Fig. 2. Vapor pressure of KCl-water system at 298.15 K.

Table 2. Binary parameters

	HCl	LiCl	NaCl	KCl	NaBr	KBr
$a/10^{-10}\text{m}$	6.1	5.6	4.80	4.10	5.1	4.6
$Z_{\pm W}/\text{kJmol}^{-1}$	82.946	99.37	120.0	83.57	83.985	98.704
$G_{\pm W}$.0500	.2419	.2992	.4200	.04112	.04192
$Z_{\pm A}/\text{kJmol}^{-1}$	—	130.0	160.7	128.0	—	—
$G_{\pm A}$	—	.8020	.3080	.4200	—	—

The subscript W or A designates water or methanol, respectively. The NRTL parameter for solvents are $Z_{H_2O} = 0.62718 \text{ kJ/mol}$, $Z_{H_2O} = 0.74253 \text{ kJ/mol}$, $G_{H_2O} = 0.9226$ and $G_{H_2O} = 0.9076$.

Table 3. Comparison of calculated water activities with experimental values at 298.15 K

Systems	Properties	Max. conc. molality	No. of data points	Rel. Avg. deviation ^a	Data ref.
NaCl-H ₂ O	P	6.0	35	0.337	[22]
KCl-H ₂ O	P	4.8	29	0.244	[22]
LiCl-H ₂ O	α_w	7.0	24	0.057	[22]
HCl-H ₂ O	α_w	7.0	24	0.382	[22]
NaBr-H ₂ O	α_w	4.0	19	0.144	[22]
KBr-H ₂ O	α_w	5.0	21	0.091	[22]
LiCl-CH ₃ OH	P	2.0	3	1.54	[16]

^a: $\Sigma |P_{exp} - P_{cal}| / P_{exp} \times 100 / \text{No. of data}$, α_w : converted from osmotic coefficient

Table 4. Comparison of error^a of the present method with other models^b at 298.15 K

Systems	Max. conc. molality	Chen & Evans	Pitzer & Kim	Cruz & Renon	Ananth & Ramachandran	Present method
NaCl-H ₂ O	6.0	1.20	0.30	1.30	0.62	0.78
KCl-H ₂ O	4.5	0.20	0.10	0.10	0.09	1.49
LiCl-H ₂ O	6.0	2.40	0.80	1.20	0.96	0.66
HCl-H ₂ O	6.0	1.90	0.20	0.80	0.36	1.60
NaBr-H ₂ O	4.0	0.60	0.10	0.70	0.38	1.44
KBr-H ₂ O	5.5	0.30	0.30	0.10	0.10	1.53

^a: error = $\{\Sigma [(\Phi_{exp} - \Phi_{cal}) / \Phi_{exp}]^2 / \text{no. of data points}\}^{1/2} \times 100$

Table 5. Comparison of calculated results with the experimental values at 298.15 K

Systems	Properties	Total salts conc.	No. of data points	Average deviation ^a	Data ref.
NaCl-KCl-H ₂ O	P	3.4284-3.6564	4	0.23	[23]
NaCl-KBr-H ₂ O	P	4.1664-4.4833	4	0.23	[23]
		3.0112-3.1736	4	0.08	[23]
NaCl-NaBr-H ₂ O	P	4.1958-4.3446	4	0.25	[23]
		2.8495-2.9340	4	0.14	[23]
KCl-NaBr-H ₂ O	P	3.7469-4.1631	4	0.78	[23]
		3.0292-3.3155	4	0.38	[23]
		1.9281-2.0549	4	0.06	[23]
KCl-KBr-H ₂ O	P	4.3175-4.3456	4	0.45	[23]
		3.0147-3.0421	4	0.08	[23]
		2.0386-2.0562	4	0.03	[23]
NaBr-KBr-H ₂ O	P	3.9034-4.3173	4	0.69	[23]
		1.9269-2.0485	4	0.08	[23]
		1.1032-1.1459	4	0.04	[23]
LiCl-KCl-H ₂ O	P	2.9360-3.0328	2	0.44	[6]
HCl-NaCl-H ₂ O ^b	α_w	0.9418-3.6740	10	1.04	[12]

^a: $\Sigma |P_{exp} - P_{cal}| / P_{exp} \times 100 / \text{no. of data}$

por pressure of aqueous NaCl solutions and aqueous KCl solutions with experimental data. The deviation from the ideal solution behavior is apparent only for the salt concentration above 4 molal. In Table 3 results of comparison of calculated values with experimental solvent properties for single electrolyte-single solvent

systems are summarized. The solubilities of LiCl in methanol solutions are more than five molal, but the comparison was made up to the 2 molal solution beyond which the error increases. We suspect the prediction of solution dielectric constant is probably in error. In Table 4 the results for aqueous systems are

Table 6. Comparison of errors^a of the present method with other models' at 298.15 K

Systems	Max. conc. molality	Chen & Evans	Pitzer & Kim	Present method
NaCl-KCl-H ₂ O	Φ^*	1.9	0.1	1.8
NaCl-NaBr-H ₂ O	Φ	0.9	0.1	1.4
NaCl-LiCl-H ₂ O	Φ	1.7	0.1	—
KCl-KBr-H ₂ O	Φ	0.61	0.2	1.7
NaBr-KBr-H ₂ O	Φ	0.3	0.3	2.7

^a: error = $\{\sum[(\Phi_{exp} - \Phi_{cal})/\Phi_{exp}]^2/\text{no. of data points}\}^{1/2} \times 100$

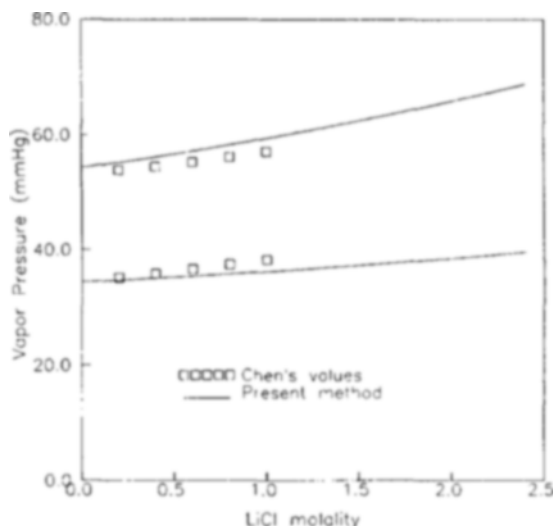
compared with other investigators' results from Ananth and Ramachandran [14]. In this comparison the methods of Cruz and Renon [4] and Ananth and Ramachandran are applicable only to single electrolyte-single solvent systems. Since solvent activity coefficients are directly related to solute activity coefficients by the Gibbs-Duhem equation for single solute-single solvent systems, this comparison is expected similar to that of solute activity coefficients [5]. It is seen that the present method is somewhat inferior to the method of Pitzer and Kim [1], but similar to the method of Chen and Evans [2]. It is to be noted that these methods are applicable only to single solvent systems. The comparison is made in the osmotic coefficient Φ which is related to the solvent activity coefficient in a dilute solution by

$$\Phi = -\ln x_1 \gamma_1 / (\sum_i N_i / N_{\text{solvent}}) \quad (33)$$

and it is more sensitive to nonideality.

In Table 5 the calculated values are compared with experimental activity coefficient data for mixed electrolyte-single solvent systems and Table 6 shows the comparison of the present results with other investigators'. When applied to mixed electrolyte systems the method of Pitzer and Kim requires two binary parameters without which it gives less good results, whereas no binary parameters required in the present method. The method of Chen and Evans also requires a binary parameter between electrolytes in general although it can be set to zero in many cases. Present method gives comparable errors with the method of Chen and Evans while the method of Pitzer and Kim fits data probably within experimental errors.

Evans and Chen [3] gave the comparisons of the calculated total pressure and the vapor phase composition values with experimental data for mixed solvent systems. Among the system they analyzed, only LiCl-water-methanol parameters are presently available in our method. Therefore we applied the present method to the system. The original data reference is not avail-

**Fig. 3. Vapor pressure of LiCl-methanol-water at 298.15 K.**

able and we used the calculated values by their correlation of which the error is 0.1 mmHg. To calculate the solvent activity coefficient in mixed solvent systems, we need parameters G_{w+LiCl} and G_{A+LiCl} in addition to the NRTL parameters between solvents [14] and those already available in Tables 1 and 2. Setting $G_{w+LiCl} = .50$ arbitrarily, we found that $G_{A+LiCl} = 0.77$ gives close agreements with data as shown by Fig. 3. For selected data points up to 3 molal salt concentration the relative average error of total pressure and vapor phase composition is about 1 percent.

It should be noted that the method of Pitzer and Kim is not applicable to mixed solvent systems, whereas the Gibbs function model employed in this study is applicable to the calculation of solute activity coefficient and the transfer Gibbs free energy [8] in mixed electrolyte-mixed solvent systems as well as to the solvent activity coefficients in mixed electrolyte-solvent systems. The NRTL parameters of Evans and Chen are specific to the vapor-liquid equilibrium calculation. On the other hand the present method and parameters are general.

The inclusion of the Born term appears conceptually sound. This term does not have any adjustable parameters, but the calculation of the solution dielectric constant is not quite reliable. Since the combined effect of the Born term and the NRTL term can be approximately represented by the NRTL term, further examination is needed to see if the Born term is really needed. As stated in the introduction, models without the Born term works well in limited cases.

CONCLUSION

A semi-empirical excess Gibbs function model for mixed electrolytes-mixed solvent systems was extended to the calculation of vapor-liquid equilibrium. For the calculation of solvent properties in a mixed solvent system, a new NRTL parameter was introduced. When applied to 1 : 1 strong electrolytes-water-methanol systems, the model was found to give good results for the properties of solutes and solvents.

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NOMENCLATURE

a	: distance of the closest approach between oppositely charged ions [m]
B	: second virial coefficient [cm^3/mol]
D	: dielectric constant of electrolyte solution [$\text{J}^{-1}\text{C}^2\text{m}^{-1}$]
D_v	: dielectric constant in vacuum [$1.113 \times 10^{-10} \text{ J}^{-1}\text{C}^2\text{m}^{-1}$]
D_s	: dielectric constant of solvent [$\text{J}^{-1}\text{C}^2\text{m}^{-1}$]
e	: charge of an electron [$1.602 \times 10^{-19} \text{ C}$]
f_i	: fugacity of i component
G^E	: excess Gibbs energy of solution [Jmol^{-1}]
G	: NRTL parameter [—]
I	: ionic strength [mol dm^{-3}]
k	: Boltzmann constant [$1.381 \times 10^{-23} \text{ J}^\circ\text{K}^{-1}$]
K	: reciprocal of Debye length [m^{-1}]
N_j	: no. of moles of component j per kg solvent [mol/kg solvent]
N_A	: Avogadro's no. [$6.022 \times 10^{23} \text{ mol}^{-1}$]
N_{vi}	: defined by Eq. (14) [mol]
N_{zi}	: defined by Eq. (14) [mol]
P	: pressure [mmHg]
r_i	: saturated cavity radius [m]
r_i'	: Stokes radius for cation and Pauling radius for anion [m]
r_h''	: parameter in Eq. (18) [m]
R	: gas constant [$8.314 \text{ JK}^{-1}\text{mol}^{-1}$]
T	: absolute temperature [K]
v_i	: partial molar volume of component i [dm^3/mol]
V	: volume per kg solvent [dm^3]
x_i	: mol fraction in liquid phase
y_i	: mol fraction in gas phase
Y, Y'	: volume fraction defined Eq. (17) and Eq. (18) [—]

Z	: NRTL parameter [Jmol^{-1}]
ϕ_i	: fugacity coefficient
δ_i	: Hasted depression [$\text{m}^3\text{mol}^{-1}$]
γ_i	: activity coefficient of solvent i

Superscripts

sat	: saturation
*	: infinite dilution reference state
o	: reference state
E	: excess properties
L	: liquid phase
V	: vapor phase

Subscripts

k	: cation of electrolytes
i	: chemical species
ij	: interaction between solvent i and j
$\pm ki, i \pm k$: interaction between an electrolyte whose cation is k and solvent i

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