

# Measurement and correlation of excess enthalpies for water+ethanol+1-buthyl 3-methylimidazolium tetrafluoroborate system

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**Abstract**—It is difficult to find physical properties data for systems containing ionic liquids, excess molar enthalpies, binary interaction parameter, etc. In this study, the excess molar enthalpies were measured for water+ethanol+ionic liquid system using a isothermal microcalorimeter at 298.15 K. The ionic liquid used was 1-butyl 3-methyl imidazolium tetrafluoroborate, [BMIM][BF<sub>4</sub>]. The isothermal microcalorimeter (IMC) is a flow-type calorimeter that measures the heat of mixing directly, using specific mixing cell. By employing NRTL, electrolyte-NRTL and UNIQUAC models, binary interaction parameters were determined and investigated for the correlation with vapor liquid equilibrium (VLE). The e-NRTL model with the partial dissociation was employed to correlate the ionic liquid system. The binary data of VLE system were used from literatures. Specifically, UNIQUAC volume and surface area parameters were determined using Bondi radius.

**Keywords:** Isothermal Microcalorimeter (IMC), Ionic Liquids, NRTL, Electrolyte NRTL, UNIQUAC, Partial Dissociation, Bondi Radius

## INTRODUCTION

Ionic liquids (ILs) have received great interest from various industries, including gas capture and storage, catalysts, electrolyte solutions [1–7]. ILs are organic salts in the liquid state below 373.15 K and composed entirely of ions that determine the unique characteristics. By varying ion compounds, ILs have certain characteristics such as tunable electrochemical properties, including negligible vapor pressure and high thermal stability. Due to these properties, ILs are attracting much attention as green solvents. As an alternative solvent, several ionic liquids are attracting great attention in synthesis and electrical deposition of nanomaterials [8]. Researchers have investigated the use of ionic liquids for the recovery system of solutes [9,10]. Recent work has shown that ionic liquids are used in liquid-liquid separation [3,4]. Also, they can serve as solvents for biocatalysts [9]. In these processes, it is important to know the thermodynamic data of the mixture containing ionic liquids, to choose effective ionic liquids for separation [12].

But physical properties data of ionic liquids composed of various combinations are still lacking. Furthermore, an improved thermodynamic modeling is required for ionic liquid mixtures, because ionic liquids have negligible vapor pressure, high viscosity, and strong solvation property.

In this study, we used an isothermal microcalorimeter (IMC) for direct measurement of excess enthalpies at constant temperature. Using IMC, the excess enthalpy for the following ternary systems was measured: water, ethanol and 1-butyl-3-methylimidazolium

tetrafluoroborate ([BMIM][BF<sub>4</sub>]). Also, liquid activity coefficient models, such as NRTL, electrolyte NRTL (e-NRTL) and UNIQUAC, were used [13–17]. Binary interaction parameters of these models were determined by correlating with the VLE and with infinite activity coefficients. Partial dissociation that Simoni et al. [16] discussed was applied in e-NRTL model. As UNIQUAC parameters related to volume and surface area were not defined well in ionic liquid system, Bondi radius of each element was used to estimate the parameters in this study, particularly.

## EXPERIMENTAL

### 1. Materials

1-Methyl imidazole (purity: 99%), water (>99.8%), ethanol (99.9%), and acetonitrile (98%) were purchased from Aldrich Chemical Co. Deionized water was purchased from Fisher. All the chemicals were used as received without further purification. The ionic liquid, [BMIM][BF<sub>4</sub>], which was proposed by previous literature, was applied to synthesis, respectively, at room temperature. The mass fraction purities of these chemicals are over 99%, and their residual chloride and water contents are below 100 ppm by gas chromatography (GC).

### 2. Experimental Apparatus

The heat of mixing of ethanol and aqueous ionic liquid such as [BMIM][BF<sub>4</sub>] system was measured using the isothermal microcalorimeter (IMC). Fig. 1 and Fig. 2 show a schematic diagram of the experimental apparatus, and the flow mixing cell and mixing tee for measuring the heat of mixing, respectively. For this work, we used a modified version of the experimental apparatus used in our previous work [18]. The core of the system is the mixing cell. The main feature of using the mixing cell apparatus is that the

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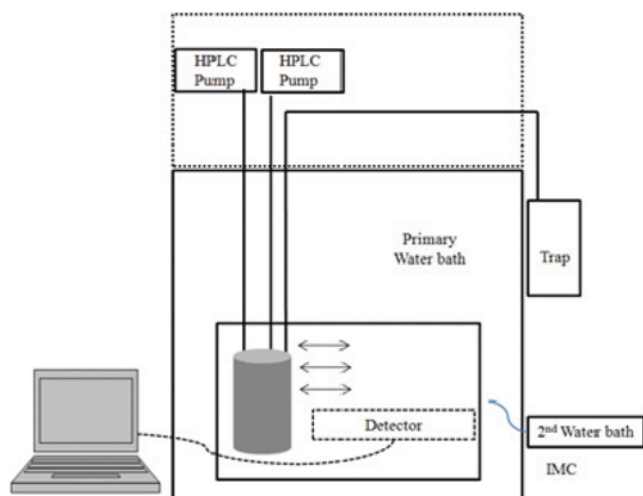


Fig. 1. Schematic diagram of experimental apparatus to measure the excess enthalpy of mixture.

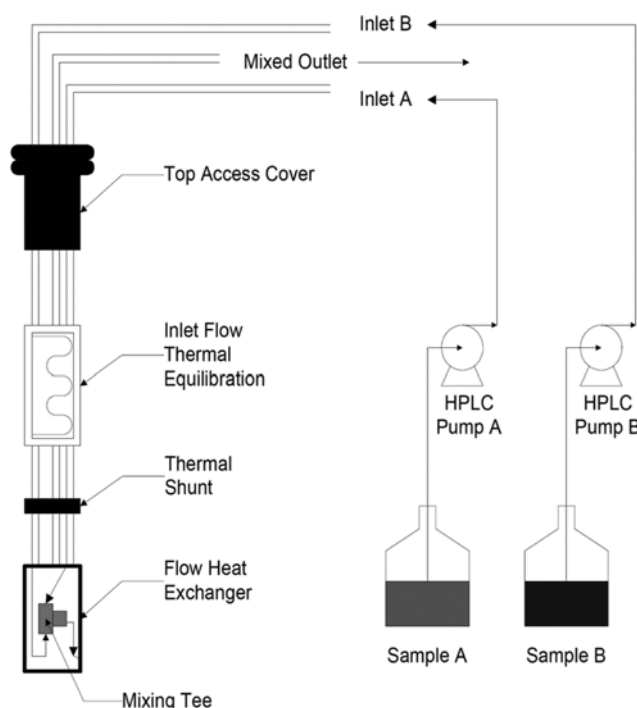


Fig. 2. Schematic diagram of the flow mixing cell and mixing tee for measuring the heat of mixing.

overall composition of the system is kept constant during the experiment, which is important since a change of composition in the cell causes a change of the heat flux. A detector (below  $0.1 \mu\text{W}$  precision) is inserted in the container at constant temperature.

The system pressure was measured with a high-precision pressure gauge (Dresser Heise model with 0.05 MPa accuracy placed in the system. The system temperature was fixed to stay within 0.01 K by an RTD temperature probe inserted into the interior of the container. A temperature-controlled forced-convection air bath was used to keep the temperature of the system's exterior constant.

### 3. Experimental Procedure

The isothermal microcalorimeter (IMC) was placed at a fixed temperature for several days. It yielded stable results when the heat of mixing occurred. The total flow rate passing through the mixing cell was kept below 0.3 ml/min. To remove the irregular pressure effect of the reciprocating pump, a small chamber was inserted in the fluid line.

To remove any entrapped air present inside the fluid line and the mixing cell, decahydronaphthalene was used for purging for 24 hours. Once the decahydronaphthalene was purged fully, ethanol and aqueous ionic liquids were input into the system. All flow rates of the pumps were calibrated for determining the exact flow rates in this study by using a balance with an accuracy of 1 mg. The mole fraction of the ionic liquid was calculated on the basis of a known amount.

When two fluids were input, they were mixed by the mixing cell. When the mixing occurred, the heat peak from exothermic or endothermic mixing was observed, directly. The heat peak represents the mean value during 1 min. When the peak was stabilized for a few minutes, we regarded this heat peak as the heat of mixing at fixed mole fraction and temperature. The fluctuation of the peak by flow conditions lay in approximately  $1 \mu\text{W}$ . The size of fluctuation was so small that the effect of the fluctuation on the results was not observed.

After one set of experiments was finished at a fixed mole fraction, more ethanol was put into the mixing cell, and the mole fraction of the new set of the experimental system was recalculated.

### THEORY

In rigorous models, NRTL, e-NRTL, UNIQUAC models are used to depict the system containing electrolyte. The e-NRTL model has the PDH term for considering interaction that depends on the range. In case of a system containing ILs that are either molecular or completely dissociated, it is partial ionization that occurs in the mixing. Simoni et al. [15] introduced the asymmetric e-NRTL model related to partial dissociation. In this study, a comparison between NRTL, e-NRTL, and UNIQUAC models was used in correlating with the vapor liquid equilibrium (VLE) data.

#### 1. NRTL and UNIQUAC [11]

When all pure liquids are at constant temperature  $T$  and pressure  $P$ , the total Gibbs energy is given by the molar Gibbs energy of mixing  $g^M$ , which, in this case, is

$$\frac{g^M}{RT} = \sum_{i=1}^n x_i \ln(x_i) + \frac{g^E}{RT} \quad (1)$$

The NRTL model introduced by Renon and Prausnitz was originally intended for non-electrolyte systems. But it has been widely used in a variety of electrolyte systems for modeling equilibria. For the NRTL model,

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{k=1}^n G_{ki} x_k} \quad (2)$$

$$\text{where, } G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \text{ and } \tau_{ij} = \frac{g_{ji} - g_{ij}}{RT} = \frac{\Delta g_{ji}}{RT}.$$

An energy parameter,  $g_{ij}$  characterizes the interaction of species  $i$  and  $j$ , and the parameter  $\alpha_{ij}=\alpha_{ji}$  is related to the non-randomness factor in the mixture ( $\alpha=0$  corresponds to complete randomness, or an ideal solution). To compare only binary interaction parameters of each model,  $\alpha_{ij}$  was fixed at 0.3 in this study.

For the UNIQUAC model,

$$\frac{g}{RT} = \frac{g_{comb}}{RT} + \frac{g_{res}}{RT} \quad (3)$$

$$\frac{g_{comb}}{RT} = \sum_{i=1}^n x_i \ln \left( \frac{\Phi_i}{x_i} \right) + 5 \sum_{i=1}^n q_i x_i \ln \left( \frac{\Theta_i}{\Phi_i} \right) \quad (4)$$

$$\frac{g_{res}}{RT} = - \sum_{i=1}^n q_i x_i \ln \left( \sum_{j=1}^n \Theta_j \tau_{ji} \right) \quad (5)$$

$$\text{where, } \Phi_i = \frac{r_i x_i}{\sum_{j=1}^n r_j x_j}, \Theta_i = \frac{q_i x_i}{\sum_{j=1}^n q_j x_j} \text{ and } \tau_{ij} = \exp \left( \frac{-\Delta u_{ij}}{RT} \right).$$

Here,  $r_i$  and  $q_i$  represent the relative volume and the surface area, respectively, for component  $i$ . It follows that  $\Phi_i$  and  $\Theta_i$  are volume and surface area fractions for component  $i$ . The binary interaction parameters  $\Delta u_{ij}$  are estimated from experimental data. The UNIQUAC parameters of pure IL have been developed depending on the systems that are chosen. However, the data for the determination of the parameters is not sufficient enough for us to want to use it. To estimate the UNIQUAC parameter, relative van der Waals volumes and surface areas were calculated according to the Zhao et al. [19] method using Bondi radius.

## 2. Electrolyte NRTL with Partial Dissociation

Tokuda et al. [20] discussed the fractional dissociations for several pure ILs with the observations that they occurred by an ion type, as well as the length of the cation substituent alkyl chain. Simoni et al. [16] suggested a model that accounts for the partial dissociation in the e-NRTL model. In the e-NRTL partial dissociation model,

$$\begin{aligned} \frac{g_{LC}}{RT} = & 2y_{\pm} \left( \frac{y_2 G_{21} \tau_{21} + y_3 G_{31} \tau_{31}}{y_{\pm} + y_1 + y_2 G_{21} + y_3 G_{31}} \right) + y_1 \left( \frac{y_2 G_{21} \tau_{21} + y_3 G_{31} \tau_{31}}{2y_{\pm} + y_1 + y_2 G_{21} + y_3 G_{31}} \right) \\ & + y_2 \left( \frac{2y_{\pm} G_{12} \tau_{12} + y_1 G_{12} \tau_{12} + y_3 G_{32} \tau_{32}}{2y_{\pm} G_{12} + y_1 G_{12} + y_2 + y_3 G_{32}} \right) \\ & + y_3 \left( \frac{2y_{\pm} G_{13} \tau_{13} + y_1 G_{13} \tau_{13} + y_2 G_{23} \tau_{23}}{2y_{\pm} G_{13} + y_1 G_{13} + y_2 G_{23} + y_3} \right) \end{aligned} \quad (6)$$

$$\frac{g_{PDH}}{RT} = 2 \sqrt{\frac{1000}{M}} A_{\phi} y_{\pm,1} \left[ \frac{\sqrt{\frac{\xi_1}{1+\xi_1}} - 2 \left( \frac{\xi_1}{1+\xi_1} \right)^{3/2}}{1 + \rho \sqrt{\frac{\xi_1}{1+\xi_1}}} - \frac{2}{\rho} \ln \left( \frac{1 + \rho \sqrt{\frac{\xi_1}{1+\xi_1}}}{1 + \rho \sqrt{\frac{\xi_1}{1+\xi_1}}} \right) \right] \quad (7)$$

where,  $\xi_i$  is a parameter related to partial dissociation of ions for salt  $i$  component. The actual mole fractions  $y_i$  and  $y_{\pm,i}$  indicate the actual mole fraction that are related to the mean-ionic and observable mole fractions, where,  $A_{\phi}$  is the Pitzer Debye Hukel parameter and  $\rho$  is the distance of the closest ionic approach parameter and  $\xi$  is the degree of dissociation. The closest approach parameter was a fixed constant of 25.

## 3. Parameter Determinations

The following is the objective function used for model parame-

ter estimation:

$$\begin{aligned} \min \text{obj} = & \frac{1}{n_{VLE,i}} \sum \left( \frac{VLE_i^* - VLE_i}{VLE_i^*} \right)^2 + \frac{1}{n_{h^E,i}} \sum \left( \frac{h_i^{E*} - h_i^E}{h_i^{E*}} \right)^2 \\ & + \frac{1}{n_{r_2^{\infty},i}} \sum \left( \frac{r_{2,i}^{\infty*} - r_{2,i}^{\infty}}{r_{2,i}^{\infty*}} \right)^2 \end{aligned} \quad (8)$$

In above equation, an experimental property is represented by an asterisk, and  $n_i$  denotes the number of experimental data points of property  $i$ .  $\gamma_2^E$ ,  $h^E$ , and  $r_2^{\infty}$  for these models, NRTL, UNIQUAC, and e-NRTL can be obtained by the following thermodynamic fundamental relations:

$$\ln r_2 = \left( \frac{\partial \left( N \frac{g}{RT} \right)}{\partial (N_2)} \right)_{T, P, N_1} \quad (9)$$

$$h^E = -RT^2 \left( \frac{\partial \left( \frac{g}{RT} \right)}{\partial T} \right)_{P, x} \quad (10)$$

$$\ln r_2^{\infty} = \left( \frac{\partial \left( N \frac{g}{RT} \right)}{\partial N_2} \right)_{P, T, n_1, x_2 \rightarrow 0} \quad (11)$$

Here,  $N$  is the total actual moles present in solution and  $N_i$  is the number of observable moles of species  $i$ ,  $R$  is the gas constant, and  $T$  is the absolute temperature. We can obtain the expression of excess enthalpy by substituting excess Gibbs energy Eqs. (6) and (7) into Eq. (10).

### 3-1. NRTL Equation

$$H_m^E = RT x_1 x_2 \left[ \frac{x_1 G_{12} - x_2 (\alpha_{12} \tau_{12} - 1)}{(x_2 + x_1 G_{12})^2} G_{12} \tau_{12} + \frac{x_2 G_{21} - x_1 (\alpha_{12} \tau_{21} - 1)}{(x_1 + x_2 G_{21})^2} G_{21} \tau_{21} \right] \quad (12)$$

### 3-2. UNIQUAC Equation

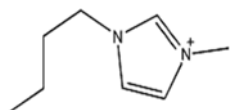
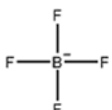
$$H_m^E = q_1 x_1 \frac{\tau_{21} \theta_2 \Delta u_{21}}{\tau_{21} \theta_2 + \theta_1} + q_2 x_2 \frac{\tau_{12} \theta_1 \Delta u_{12}}{\tau_{12} \theta_1 + \theta_2} \quad (13)$$

The degree of dissociation can be calculated by following a simple equation suggested by Simoni et al. [16]:

$$\xi = \frac{6 \pi \eta_{IL} \lambda_{IL} M_{IL}}{2 N_A e^2 d_{IL} \left( \frac{1}{s_+} + \frac{1}{s_-} \right)} \quad (14)$$

$\eta_{IL}$ ,  $\lambda_{IL}$ ,  $d_{IL}$  and  $M_{IL}$  are the viscosity, conductivity, density and molecular weight of the pure IL at 298.15 K, respectively. In fact, the degree of dissociation should be considered a function of the composition in the mixture, but we considered the degree of dissociation is not an adjustable parameter and assumed that it is constant in the entire composition range. Thus, we also used the above equation for determining the degree of dissociation in this study.

**Table 1. Chemical structure and CAS registry number of [BMIM] [BF<sub>4</sub>]**

Cation	Anion	Cas No	Abbreviation	Name
		79917-90-1	[BMIM][BF <sub>4</sub> ]	1-Butyl-3-methylimidazolium tetrafluoroborate

## RESULTS AND DISCUSSION

By changing the anion of an ionic liquid, the properties of the mixture are changed. Tables 3 and 4 show the physical and electric properties of the pure component used in this study. UNIQUAC segment numbers and surface area parameters depend on the size and bondings of the molecules. Although several parameters have been suggested, there is a large range of different values in the literature. Bondi radius was used in this study to estimate the relative volume and surface area of the molecules as shown in Table 5-6.

Heat of mixing (excess enthalpy) data for ternary systems was measured using an isothermal microcalorimeter. The experimental results for the systems, water+ethanol with 1-butyl 3-methylimidazole tetrafluoroborate [BMIM] [BF<sub>4</sub>] at 298.15 K, are provided in

**Table 2. Data types and sources for binary and ternary system used to obtain binary interaction parameters of several models**

System	Component (1)/(2)/(3)	Data	Ref.
Binary system	[BMIM] [BF <sub>4</sub> ]/ethanol	VLE, $H^E$ , $r^\infty$	[19]
	[BMIM] [BF <sub>4</sub> ]/water	VLE, $H^E$ , $r^\infty$	[20]
	Ethanol/water	VLE, $H^E$ , $r^\infty$	[21]
Ternary system	[BMIM] [BF <sub>4</sub> ]/ethanol/water	VLE, $H^E$	[This work]

**Table 3. Physical properties of BMIM BF<sub>4</sub> at 298.15 K and 1 atm [22]**

Ionic liquid	Viscosity (mPa s)	Density (g/cm <sup>3</sup> )	Conductivity (S/m)
BMIM BF <sub>4</sub>	94.26	1.2015	0.352

**Table 4. Physical properties of solvents at 298.15 K and 1 atm [23]**

Solvent	Vapor pressure (kPa)	Density (g/cm <sup>3</sup> )	Dielectric constant
Ethanol	7.831	0.783924	24.3
Water	3.157	0.998946	78.57

**Table 5. Bondi radii of several atoms [17]**

Component	Bondi radius/Å	Component	Bondi radius/Å
H	1.20	P	1.80
C	1.70	S	1.80
N	1.55	F	1.47
O	1.52	B	2.13
F	1.47	Br	1.85
Cl	1.75	I	1.98

Table 7.

Binary interaction parameters of the NRTL, e-NRTL with partial dissociation and UNIQUAC models were determined from vapor liquid equilibrium (VLE) data, excess enthalpy ( $H^E$ ) data, and the infinite dilute activity coefficient. Binary data used for determining the parameters are listed in Table 2. Tables 8 and 9 show the parameters for each model. The estimated results of the VLE data from the  $H^E$  data are shown in Fig. 3 and Fig. 4. Considering both  $H^E$ , VLE, and the infinite dilution activity coefficients data, the UNIQUAC model has the most accurate data with a high relative deviation in the infinite dilute activity coefficient. In the case of only VLE and  $H^E$  data correlation, the UNIQUAC model was

**Table 6. UNIQUAC segment numbers and surface area parameters,  $R_k$  and  $Q_k$  for several functional groups [23]**

Main group	Subgroup	$R_k$	$Q_k$
Methylimidazolium	Methylimidazolium	2.9700	2.107
	Imidazolium	2.2486	1.626
CH <sub>3</sub>	CH <sub>3</sub>	0.9011	0.848
	CH <sub>2</sub>	0.6744	0.540
	CH	0.4469	0.228
	C	0.2195	0.000
Cl		0.9364	0.740
BF <sub>4</sub>		2.2066	1.967

**Table 7. Excess enthalpies for [BMIM] [BF<sub>4</sub>](1)/ethanol(2)/water(3) ternary system**

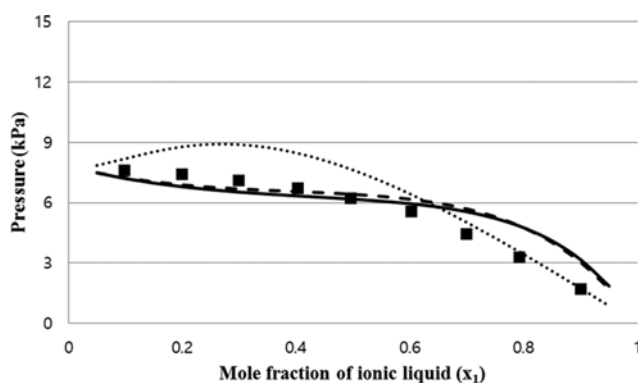
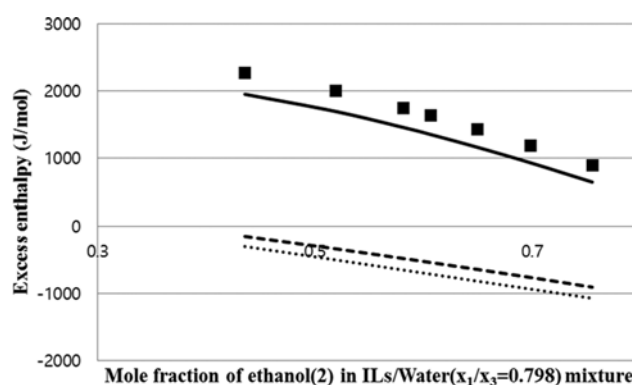
Mole fraction (x <sub>1</sub> )	Mole fraction (x <sub>2</sub> )	Mole fraction (x <sub>3</sub> )	$H^E$ (J/mol)
$x_1/x_3 = 3.989$ , $H^E = 755.1$ J/mol			
0.510	0.362	0.128	1110.2
0.374	0.532	0.094	1279.7
0.296	0.630	0.074	1168.8
0.208	0.740	0.052	868.5
0.144	0.820	0.036	524.7
0.120	0.850	0.030	362.7
0.102	0.872	0.026	237.0
$x_1/x_3 = 0.798$ , $H^E = 2128.5$ J/mol			
0.251	0.435	0.314	2273.7
0.213	0.519	0.268	2004.5
0.186	0.581	0.233	1750.1
0.175	0.607	0.219	1635.9
0.156	0.649	0.195	1434.2
0.134	0.698	0.168	1189.6
0.109	0.755	0.136	892.1

**Table 8. Binary interaction parameters of NRTL, UNIQUAC, and e-NRTL model for [BMIM] [BF<sub>4</sub>](1)/ethanol(2) system at 298.15 K**

	$\alpha$	$\rho$	$\xi$	Binary interaction parameter		RMS (%) for VLE	Data
NRTL	0.3	-	-	$\Delta g_{12}$	$\Delta g_{21}$		
				2223.6	2949.7	25.7	VLE, $H^E$
				487.4	2427.2	11.6	VLE, $H^E$ , $r^\infty$
UNIQUAC	-	-	-	$\Delta u_{12}$	$\Delta u_{21}$		
				1557.6	700.7	15.4	VLE, $H^E$
				1288.4	851.4	11.5	VLE, $H^E$ , $r^\infty$
e-NRTL with partial dissociation	0.3	25	0.37	$\Delta g_{12}$	$\Delta g_{21}$		
				2011.1	4431.6	24.4	VLE, $H^E$
				2025.0	2419.4	24.5	VLE, $H^E$ , $r^\infty$

**Table 9. Binary interaction parameters of NRTL, UNIQUAC, and e-NRTL model for [BMIM] [BF<sub>4</sub>](1)/water(3) system at 298.15 K**

	$\alpha$	$\rho$	$\xi$	Binary interaction parameter		RMS (%) for VLE	Data
NRTL	0.3	-	-	$\Delta g_{13}$	$\Delta g_{23}$		
				2157.9	2276.7	32.4	VLE, $H^E$
				466.1	1490.9	16.7	VLE, $H^E$ , $r^\infty$
UNIQUAC	-	-	-	$\Delta u_{13}$	$\Delta u_{23}$		
				2180.6	500.7	9.3	VLE, $H^E$
				1723.0	599.4	9.9	VLE, $H^E$ , $r^\infty$
e-NRTL with partial dissociation	0.3	25	0.37	$\Delta g_{13}$	$\Delta g_{23}$		
				1950.3	1982.3	31.4	VLE, $H^E$
				1953.5	1982.2	31.4	VLE, $H^E$ , $r^\infty$

**Fig. 3. P-x correlation results using several models with binary parameters obtained from the  $H^E$  data for ILs+ethanol binary system at 0.1013 MPa and 298.15 K (■: experiment results, solid line: NRTL, dashed line: e-NRTL, dotted line: UNIQUAC).****Fig. 4. Excess enthalpies of ternary system for ILs+ethanol+water ternary system at 0.1013 MPa and 298.15 K (■: experiment results, solid line: UNIQUAC, dashed line: e-NRTL, dotted line: NRTL0).**

in good agreement with the experimental data.

With changes in the number of variables (VLE,  $H^E$ ,  $r^\infty$ ), the value of NRTL parameters varied dramatically, whereas the parameters of e-NRTL with partial dissociation were less affected, relatively. In spite of the relatively small deviation in correlation VLE with excess enthalpy, the results from UNIQUAC model considering infinite dilute activity coefficient had a significant number of inconsistencies.

## CONCLUSIONS

An isothermal microcalorimeter (IMC) was used to measure

excess enthalpies of ternary system for 1-butyl 3-methylimidazolium tetrafluoroborate+water+ethanol at 298.15 K. The experimental results were correlated with vapor liquid equilibrium data by NRTL, e-NRTL with partial dissociation, and UNIQUAC models. The binary parameters of the models were determined by VLE,  $H^E$ , and  $r^\infty$  data. The degree of dissociation for describing the partial dissociation of the ionic liquid was determined from the electro-physical properties of the pure ionic liquid.

The relative van der Waals volume and surface area of UNIQUAC model for ionic liquid were determined using Bondi radius. The parameters of UNIQUAC model consisted of cation and anion

molecular groups. The proposed methods can be useful for predicting the undefined parameters of ionic liquids involving UNIQUAC with the advantages of being quick and facile.

A comparison between the experimental data and the correlated values showed that the UNIQUAC model is better fitted in the correlation of the VLE and HE data for ILs+ethanol binary system at 0.1013 MPa and 298.15 K compared to other models. The e-NRTL with partial dissociation was affected less than the original NRTL model when the number of data type was limited. Although e-NRTL had a little improvement in correlation with VLE and  $H^E$ , a large deviation still remained in the calculation of excess enthalpies rather than vapor liquid equilibrium.

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