

## Isobaric vapor-liquid equilibrium for methanol+benzene+1-octyl-3-methylimidazolium tetrafluoroborate

Qunsheng Li\*, Wei Zhu\*, Yongquan Fu\*, Magtuf Zuhir\*, Lun Li\*, and Baohua Wang\*\*†

\*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology,  
Box 35, Beijing 100029, China

\*\*College of Chinese Pharmacology, Beijing University of Chinese Medicine and Pharmacology, Beijing 10029, China  
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**Abstract**—Isobaric vapor-liquid equilibrium (VLE) data for {methanol (1)+benzene (2)+1-octyl-3-methylimidazolium tetrafluoroborate (3)} where 3 is an ionic liquid ([OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>) at atmospheric pressure (101.32 kPa) were measured with a modified Othmer still. The results showed that the ionic liquid studied can transfer the azeotropic point and eliminate the azeotropic phenomena when its concentration is up to  $x_3=0.30$ . This means that [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> can be used as a promising entrainer in the application of extractive distillation. The measured ternary data were correlated using the NRTL model.

Key words: Vapor-liquid Equilibrium, Methanol, Benzene, 1-Octyl-3-methylimidazolium Tetrafluoroborate, Entrainer

### INTRODUCTION

Extractive distillation or salt distillation is widely used for azeotropic or close-boiling mixtures [1-3]. However, the entrainers used in extractive distillation such as solid salts and organic substances have many disadvantages, which have been handicaps for further application of extractive distillation. The solid salts may corrode the column and pipeline, and the organic solvents will not only give rise to volatile organic compound (VOC) emission but also demand high energy. On the other hand, ionic liquids (ILs) might be used as a suitable solvent salt and be superior to the commonly used entrainers due to their nonvolatility, less causticity, and good performance in improving the separation efficiency [4-6]. Furthermore, thermodynamic data for IL-containing systems are essential for a better understanding of the thermodynamic behavior of such systems, for separation design purposes, and for the development of the thermodynamic models.

Methanol-benzene mixture is widely encountered in the pharmaceutical industry. However, the existence of an azeotropic point of this binary mixture at atmospheric pressure makes it difficult to obtain high purity methanol from the mixtures by conventional distillation or rectification. Two special separation technologies are under development that could provide higher methanol from the mixture than the conventional separation method. Both them are added salt extractive distillation [7] and membrane separation [8]. But to the best of our knowledge, the method of extractive distillation with ionic liquid as entrainer has not been reported yet.

In this work, isobaric VLE data for methanol+benzene system containing [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> is presented at atmospheric pressure (101.325 kPa), and the effect of [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> on the VLE of methanol+benzene system is also discussed.

### EXPERIMENTAL SECTION

#### 1. Chemicals

The chemical reagents used were methanol, benzene and IL. AR grade methanol and benzene with a mass fraction purity of above 99.7% were purchased from Beijing Chemical Reagents Company, China. The purity of reagents was checked by gas chromatography (SP6890, China) and used without further purification. Karl Fischer analysis indicated water content of 230 ppm for methanol. The IL, [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>, was provided by Shanghai Cheng Jie Chemical Co. LTD (China), with a mass fraction purity >98% observed by liquid chromatography. Furthermore, before the experiments, the IL was dried for 48 h at 383 K under a vacuum by the rotary evaporation to separate the IL from volatile byproducts and water. After experiments, the IL was reused after the rotary evaporation to eliminate the volatile components.

#### 2. Apparatus and Procedure

Each solution was prepared gravimetrically using an electronic balance (Sartorius, the uncertainty was 0.1 mg).

The VLE data were measured by a circulation vapor-liquid equilibrium still (a modified Othmer still) [9,10] as shown in Fig. 1. The total volume of the still was about 60 cm<sup>3</sup>, of which about 50 cm<sup>3</sup> was occupied by the liquid solution. Energy was applied to the still through a heating rod controlled by an electric thermocouple. In the operation, a given liquid solution was put into the boiling chamber and heated. The vapor was condensed in the condenser and at the same time returned to the equilibrium chamber through the vapor-phase sampling port. Equilibrium was usually reached in about (0.5 to 1) h as indicated by the constant boiling temperature. The system was maintained in the equilibrium state for about 30 min, and samples of the vapor and liquid phase were taken from the sampling ports and then analyzed. The equilibrium temperature was measured by a precision and calibrated thermometer with an uncertainty of 0.1 K.

†To whom correspondence should be addressed.  
E-mail: zhuweiEpaper@hotmail.com

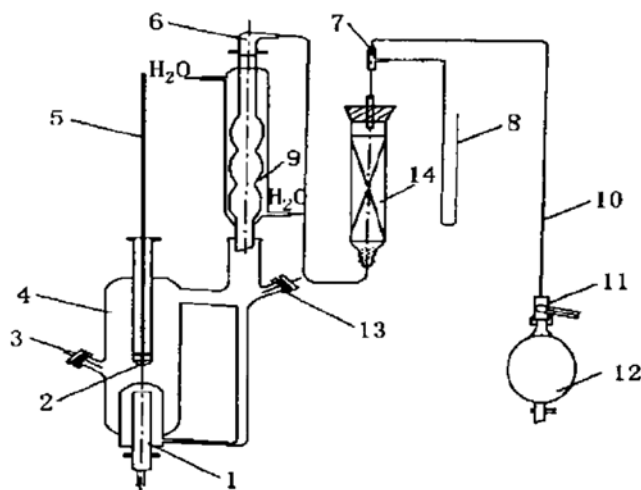


Fig. 1. Experimental setup for VLE measurement.

- |                               |                               |
|-------------------------------|-------------------------------|
| 1. Heating bar                | 8. U-style manometer          |
| 2. Glycerol                   | 9. Condenser                  |
| 3. Liquid-phase sampling port | 10. Latex rubber tube         |
| 4. Equilibrium chamber        | 11. Three-way valve           |
| 5. Thermometer                | 12. Gas pressure ball         |
| 6. Ground joint               | 13. Vapor-phase sampling port |
| 7. Three-way pipe             | 14. Desiccators.              |

The equilibrium composition of the volatile components in the vapor and liquid phase were analyzed by gas chromatography. The gas chromatograph (SP6900, China) was equipped with a TCD detector. The chromatographic column (3 m×0.3 mm) was packed with Porapak-Q. The carrier gas was hydrogen flowing at 45 cm<sup>3</sup>·min<sup>-1</sup>, and the operating conditions were as follows: the injector and oven temperatures at 433 K and the detector temperature at 453 K. A calibration correction factor was obtained from a set of gravimetrically prepared standard solutions. In this way, the maximum uncertainty of mole fraction of the components in the liquid and vapor phase was 0.003. The IL content in the liquid phase was determined using the gravimetric method by measuring the mass difference of liquid samples with and without IL. The equilibrium pressure was kept constant by an on-off pressure controller whose standard uncertainty was 0.10 kPa.

## RESULTS AND DISCUSSION

### 1. Apparatus Performance Test

To test the performance of the equilibrium apparatus, the binary vapor-liquid equilibria for the systems of methanol+benzene were measured at 101.32 kPa. Our experimental data were in good agreement with those reported by Hudson and Nagata [11], thus verifying that the experimental apparatus was reliable. The experimental results for the binary system of methanol (1)+benzene (2) are listed in Table 1 and compared to the literature in Fig. 2.

### 2. Ternary Mixture VLE Data

Measurements were made for the ternary system of methanol (1)+benzene (2)+[OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> (3) by keeping the IL mole fraction constant in each set of the experiments. Results of isobaric VLE data for the methanol+benzene system containing IL [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>

Table 1. Vapor-liquid equilibrium data for the methanol (1)+benzene (2) system at 101.32 kPa

T/K	x <sub>1</sub>	y <sub>1</sub>
337.1	0.000	0.000
335.2	0.107	0.470
334.6	0.198	0.535
333.4	0.258	0.544
332.5	0.312	0.548
331.9	0.353	0.557
331.8	0.412	0.561
331.6	0.461	0.580
331.3	0.511	0.588
331.2	0.598	0.618
331.2	0.662	0.626
331.3	0.707	0.643
331.6	0.743	0.659
332.0	0.812	0.676
332.5	0.843	0.719
333.6	0.899	0.770
353.2	1.000	1.000

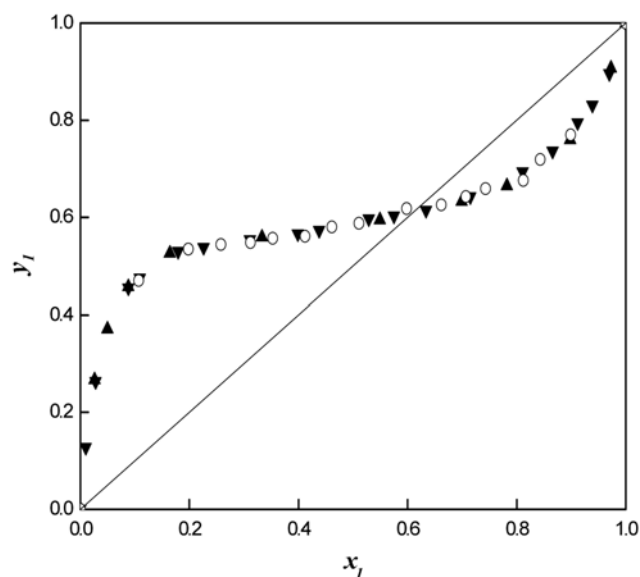


Fig. 2. Isobaric VLE diagram for the binary system of methanol (1)+benzene (2) at 101.32 kPa: ▲, ▼, ref 11; ○, this work.

at different IL mole fraction contents (from x<sub>3</sub>=0.10 to 0.30) are listed in Table 2. The x, y diagrams are also plotted in Fig. 3. It should be mentioned that the mole fractions for the liquid components given in the figures are on an IL-free basis.

### 3. Equilibrium Equation and Activity Coefficients

The effect of IL on the solution nonideality could be expressed by the activity coefficient of component i,  $\gamma_i$ , which could be calculated by the following equation:

$$\gamma_i = \frac{y_i \phi_i^L P}{x_i \phi_i^S P_i^S} \quad (1)$$

To simplify, the IL is treated as a nondissociating component,

**Table 2. Vapor-liquid equilibrium data for the ternary system methanol (1)+benzene (2)+[OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> (3) at 101.32 kPa**

100x <sub>3</sub>	T/K	x <sub>1</sub>	y <sub>1</sub>	γ <sub>1</sub>	γ <sub>2</sub>	α <sub>12</sub>
10.085	345.5	0.108	0.266	1.83	1.19	2.658
10.108	340.0	0.181	0.413	2.09	1.25	2.797
10.160	337.3	0.258	0.502	1.98	1.31	2.504
10.081	336.8	0.316	0.538	1.77	1.35	2.153
10.263	335.6	0.356	0.551	1.68	1.47	1.872
10.186	335.2	0.456	0.586	1.42	1.69	1.376
10.104	334.8	0.543	0.641	1.32	1.84	1.176
10.110	334.6	0.626	0.713	1.29	1.94	1.085
10.104	334.5	0.716	0.764	1.22	2.37	0.835
10.205	336.4	0.806	0.854	1.12	2.68	0.686
18.446	349.3	0.126	0.243	1.24	1.27	1.711
19.292	345.3	0.174	0.345	1.48	1.35	1.889
19.444	343.5	0.235	0.462	1.57	1.30	2.062
19.435	342.6	0.279	0.496	1.47	1.36	1.836
19.156	341.8	0.322	0.541	1.43	1.38	1.753
19.363	341.6	0.398	0.573	1.24	1.55	1.353
19.273	340.8	0.474	0.642	1.20	1.64	1.231
19.119	340.2	0.548	0.719	1.19	1.70	1.177
19.231	339.6	0.622	0.803	1.20	1.72	1.163
19.321	339.1	0.714	0.890	1.18	2.01	0.980
30.740	356.3	0.102	0.190	0.94	1.24	1.383
30.540	353.3	0.159	0.292	1.03	1.31	1.404
30.507	352.0	0.202	0.385	1.11	1.29	1.540
30.455	351.7	0.280	0.491	1.04	1.27	1.447
30.276	351.2	0.334	0.553	0.99	1.30	1.356
30.219	350.9	0.410	0.641	0.95	1.33	1.267
30.244	350.5	0.472	0.733	0.96	1.27	1.328
30.435	350.2	0.526	0.798	0.95	1.28	1.303
30.587	349.8	0.578	0.849	0.93	1.38	1.184
30.409	349.1	0.608	0.893	0.95	1.32	1.269

and the assumption of an ideal behavior is adopted for the vapor. The fugacity coefficients  $\phi_i$  and  $\phi_i^s$  are equal to unity at a low pressure [12]. Therefore, Eq. (1) could be rewritten as

$$\gamma_i = \frac{y_i P}{x_i P_i^s} \quad (2)$$

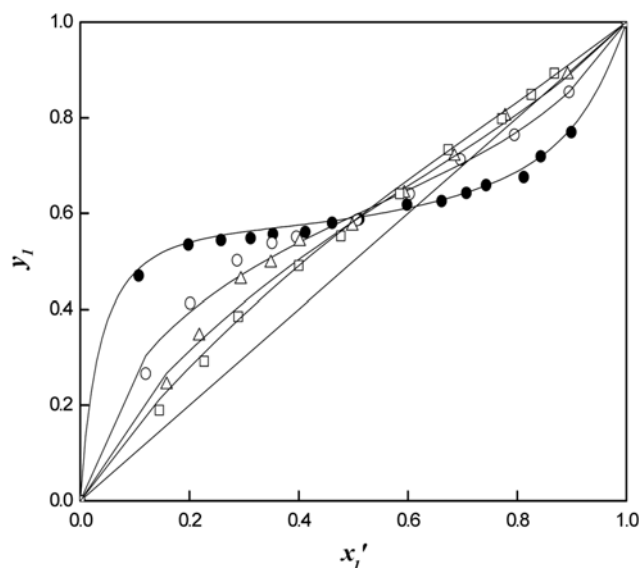
Note that IL does not appear in the vapor phase due to its nonvolatility. However, its mole fraction in liquid phase is considered when calculating activity coefficients of methanol or benzene. In addition to the activity coefficient, the relative volatility of methanol to benzene is also calculated as follows:

$$\alpha_{12} = \frac{y_1/x_1'}{y_2/x_2'} \quad (3)$$

where  $x_1'$  and  $x_2'$  are mole fraction of methanol and benzene, respectively, on an IL-free basis. The calculated activity coefficients and relative volatilities are also given in Table 2.

#### 4. Activity Coefficients Correlation

As suggested in previous works [13,14], the binary interaction

**Fig. 3. Isobaric VLE diagram for methanol (1)+benzene (2)+[OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> (3) system at 101.32 kPa: ●, x<sub>3</sub>=0 (IL-free); ○, x<sub>3</sub>=0.10; △, x<sub>3</sub>=0.20; □, x<sub>3</sub>=0.30; solid lines, correlated using the NRTL model.****Table 3. Estimated values of binary interaction parameters  $\Delta g_{ij}$  and  $\Delta g_{ji}$  in the NRTL Model**

i Component	j Component	$\alpha_{ij}$	$\Delta g_{ij}$ J·mol <sup>-1</sup>	$\Delta g_{ji}$ J·mol <sup>-1</sup>
Methanol (1)	Benzene (2)	0.4837	2972.1	4754.1
Methanol (1)	[OMIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>-</sup> (3)	0.2835	20006.3	-8372.2
Benzene (2)	[OMIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>-</sup> (3)	0.3289	31781.3	-16974.4

**Table 4. The average relative deviation, ARDy and ARDT, for calculation of binary and ternary VLE**

System	ARDy	ARDT
Methanol (1)+benzene (2)	0.014	0.006
Methanol (1)+benzene (2)+[OMIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>-</sup> (3)	0.036	0.031

parameters of NRTL model were first obtained from the VLE data of {methanol (1)+benzene (2)}, and then other binary interaction parameters were obtained from ternary VLE data. The Marquardt method was used for data correlation, and the correlated results are given in Table 3, where the average relative deviation (ARD) is defined as

$$\text{ARD}(\%) = \frac{1}{n} \sum \left| \frac{\gamma_i^{\text{exptl}} - \gamma_i^{\text{calcd}}}{\gamma_i^{\text{exptl}}} \right| \cdot 100 \quad (4)$$

In the NRTL model, only the nonrandomness parameter  $\alpha$  is set to be the same as those in ref [11]. In this case, the average absolute deviation of the vapor phase composition (ARDy) and the temperature (ARDT) for the methanol (1)+benzene (2) system and methanol (1)+benzene (2)+[OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> system are presented in Table 4.

#### 5. The Salt Effect of IL

The IL investigated increased the relative volatility of methanol to benzene, and thus showed a salting-out effect for methanol, as

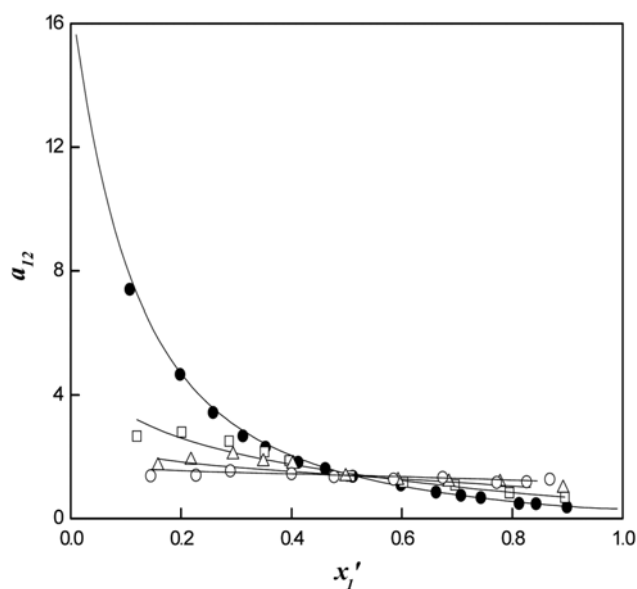


Fig. 4. Relative volatility of methanol (1) to benzene (2) at 101.32 kPa: ●,  $x_3=0$  (IL-free); □,  $x_3=0.10$ ; △,  $x_3=0.20$ ; ○,  $x_3=0.30$ ; solid lines, correlated using the NRTL model.

shown in Figs. 3 to 5. Moreover, the azeotropic point at  $x_1 \approx 0.610$  for the methanol+benzene binary mixture is shifted upward with the addition of IL, and even the azeotropic phenomena could be totally eliminated at a specific IL content ( $x_3=0.30$ ).

Figs. 3 to 5 also indicate the complex effect of IL on the VLE of methanol+benzene system. In the methanol-rich region, an increase of the IL content leads to a higher methanol content in the vapor phase and, therefore, to a large relative volatility of methanol to benzene. This may be due to the strong selective interaction between the IL and benzene molecule. The effect of IL on the VLE of methanol+benzene system may be ascribed to the affinity difference between ionic liquid and solute moles. More specifically, the ions resulting from the dissociation of IL have a stronger attraction to benzene than to methanol due to the polar difference of ionic solvation energy, which lead to a preferential solvation of ions and enhancement of relative volatility of methanol. In the benzene-rich region, benzene molecules are preferentially “bonded” by ions. However, with an increase of IL content, for example, from  $x_3=0.10$  to 0.30, more and more methanol molecules are also bounded and thus the relative volatility of methanol to benzene decreases (at  $x'_l$  below 0.5).

To further investigate the salt effect of IL on methanol+benzene, relative volatilities of methanol to benzene were plotted in Fig. 4 where the system contains 0.10 to 0.30 mole fraction of IL. With an increase in the IL component, the relative volatility of methanol to benzene increases (except for  $x'_l$  below 0.5). So the salting-out effect follows the order:  $0.30 > 0.20 > 0.10$ .

The measured VLE containing the azeotropic system methanol+benzene and the IL [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> are presented in a pseudo-binary way in Fig. 3, where the liquid-phase composition of the low-boiling component is the amount of this substance in the volatile part of the liquid phase. The IL component is demonstrated for each curve separately. The  $x, y$  diagram is shown in Fig. 3, and the  $T, x, y$  diagram is shown in Fig. 5. Fig. 5 demonstrates that the equilibrium temperatures increase when high mole fractions of the ILs are added

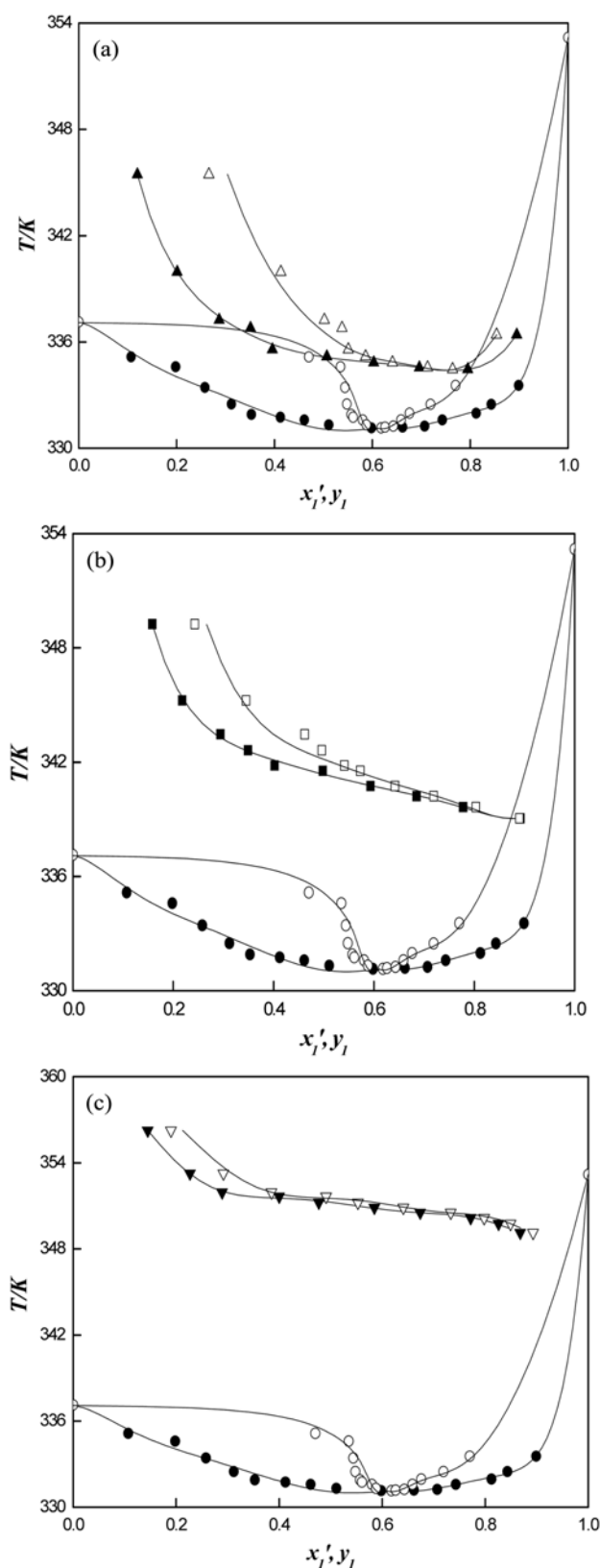


Fig. 5.  $T, x, y$  diagram for the ternary system of methanol (1)+benzene (2) containing [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> (3) at different contents of IL: ●,  $x_1=x_1$  ( $x_3=0$ ); ○,  $y_1$  ( $x_3=0$ ); a) ▲,  $x_1$  ( $x_3=0.10$ ); △,  $y_1$  ( $x_3=0.10$ ); b) ■,  $x_1$  ( $x_3=0.20$ ); □,  $y_1$  ( $x_3=0.20$ ); c) ▼,  $x_1$  ( $x_3=0.30$ ); ▽,  $y_1$  ( $x_3=0.30$ ); solid lines, correlated using the NRTL model.

into the system, which means that the heat quality of the extractive distillation column will increase. Moreover, the reboiler of the solvent recovery column that is used to recover the entrainer will need extra heat. In addition, for a given purity of the distillate, the reflux ratio of the extractive distillation column can be reduced when the relative volatility of methanol to benzene becomes higher. This indicates that the energy demand for the extractive distillation process can be saved.

## CONCLUSIONS

ILs are becoming new alternative entrainers in special distillation processes. The isobaric VLE data for methanol+benzene containing [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> were measured at atmospheric pressure (101.32 kPa) and correlated using the NRTL model. The mole fraction of methanol in the vapor phase increases with the increase of concentration of [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> in the liquid phase. The results indicated that the IL studied showed a salting-out effect, which led to an elimination of the azeotropic phenomenon at a specific IL content. Therefore, the results implied that [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> is promising additive for special distillation processes due to its notable salt effect and desirable properties, such as nonvolatility, nonflammability, and chemical stability. Moreover, because of its nonvolatility, the IL can be regenerated by different methods such as stripping, evaporating, or drying.

## ACKNOWLEDGEMENT

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## NOMENCLATURE

ARD : the average relative deviation

P : total pressure [MPa]

P<sub>i</sub><sup>s</sup> : vapor pressure of pure component [MPa]

T : temperature [K]

x<sub>i</sub> : mole fraction in the liquid phase (including IL)

x<sub>i</sub><sup>'</sup> : mole fraction in the liquid phase (IL-free)

y<sub>i</sub> : mole fraction in the vapor phase

Δg<sub>ij</sub> : binary interaction parameters in the NRTL model [J·mol<sup>-1</sup>]

α<sub>12</sub> : the relative volatility of mixture

α<sub>ij</sub> : the nonrandomness parameter in the NRTL model

φ<sub>i</sub> : fugacity coefficient in the vapor mixture

φ<sub>i</sub><sup>s</sup> : fugacity coefficient of pure component in its saturated state

γ<sub>i</sub> : activity coefficient

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