



# Measurement and correlation of the vapor–liquid equilibrium for methanol + acetonitrile + imidazolium-based ionic liquids at 101.3 kPa



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## ABSTRACT

Two imidazolium-based ionic liquids: 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]) and 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM][BF<sub>4</sub>]) were studied as entrainer candidates for the separation of methanol + acetonitrile system. Isobaric vapor–liquid equilibrium (VLE) for the binary methanol + acetonitrile and the ternary mixtures containing imidazolium-based ionic liquids were determined at atmospheric pressure (101.3 kPa). The experimental VLE results indicated ionic liquids (ILs) studied both showed a crossover salting effect for methanol. More importantly, when the amount of IL added increases, the azeotropic point of methanol + acetonitrile will disappear at one specific content. Meanwhile, the separation capacity of imidazolium-based ionic liquids follows the order: [OMIM][BF<sub>4</sub>] > [EMIM][BF<sub>4</sub>]. Finally, two different excess Gibbs free energy models were used to correlate the VLE data: the non-random two-liquid (NRTL), and the universal quasi-chemical (UNIQUAC).

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## 1. Introduction

Methanol and acetonitrile both are extremely important solvents in chemical processes. Also, the mixture of them, known as cosolvent [1,2], can be extensively applied in the pharmaceutical industry [3,4] as well as in chromatography techniques [5]. Inevitably, it will generate a large amount of wasted methanol + acetonitrile mixture during the above processes. In order to recover methanol or/and acetonitrile from the wasted liquid, an appropriate and efficient method should be chosen. Unfortunately, the conventional distillation process cannot efficiently separate methanol and acetonitrile as the binary system forms a minimum azeotrope at atmospheric pressure.

As one enhanced distillation-based separation technique, extractive distillation is widely accepted for azeotropic separation at an industrial scale. The core of extractive distillation is the selection of entrainer, which ensures an effective and economical operation of separation process. During the past few years, ionic liquids have been proposed as “green” entrainers for extractive distillation [6–9]. This is mainly due to its unique properties, i.e., nearly unperceivable volatility, wide liquid range and high dissolvability. Besides, ionic liquids are recognized as “designer solvents” since

the properties of ILs for specific task can be tuned by judicious combining cations with anions.

To the best of our knowledge, there is rarely report on the separation of methanol and acetonitrile, not to mention using extractive distillation method. The purpose of this paper is to investigate whether the ILs could be used as suitable entrainers for the extractive distillation of methanol + acetonitrile system. For this purpose, isobaric VLE data of two ternary systems {methanol + acetonitrile + [EMIM][BF<sub>4</sub>]} and {methanol + acetonitrile + [OMIM][BF<sub>4</sub>]} were measured at 101.3 kPa. Furthermore, the effects of ILs on the methanol + acetonitrile binary system were discussed and compared. Finally, the experimental VLE data were correlated by NRTL and UNIQUAC models.

## 2. Experimental

### 2.1. Chemicals

The chemical reagents used in this work were methanol, acetonitrile and ILs. The analytical grade of methanol and acetonitrile were purchased from Beijing Chemical Reagents Company, China. The purities of methanol and acetonitrile were checked by gas chromatography (SP6890, China). ILs, [EMIM][BF<sub>4</sub>] and [OMIM][BF<sub>4</sub>], were provided by Shanghai Cheng Jie Chemical Co. LTD, China. The mass fraction purities of ILs were observed by HPLC

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(Agilent 1200, USA) and the water mass fractions in ILs were obtained by Karl Fisher titration. ILs were dried and recovered by a rotary evaporator for 48 h at 393 K under a vacuum (2 kPa), which could remove all volatile byproducts and water. The specifications of chemicals used were listed in Table 1 and the measured properties of methanol and acetonitrile were in good agreement with the literature [10] as shown in Table 2. Refractive indices were measured by WZS-I Abbe refractometer (Shanghai Optical Instruments Factory, China, an uncertainty of  $\pm 0.0001$ ). Densities were measured by DMA-4100 densimeter (AntoPaar GmbH, Germany, an uncertainty of  $\pm 0.0001 \text{ g} \cdot \text{cm}^{-3}$ ).

## 2.2. Apparatus and procedures

All VLE data were measured in an all-glass circulation vapor-liquid equilibrium still at 101.3 kPa. A detailed description of still can be found in our previous publications [11,12].

The equilibrium compositions of methanol and acetonitrile in the condensed vapor and liquid phase were analyzed by gas chromatography (SP6900, China) which was equipped with a TCD detector and a PEG-20000 packed column (3 m  $\times$  3 mm). The carrier gas was hydrogen flowing at 45 mL  $\cdot$  min<sup>-1</sup>. The gas chromatography operating conditions were as follows: the injector temperature at 423.15 K, the oven temperature at 393.15 K and the detector temperature at 443.15 K. The amounts of methanol and acetonitrile in the samples were calculated by a calibration curve, which was determined from a set of known composition solutions prepared using an electronic balance (Satorius CP124S,

**Table 1**  
Specification of chemical samples.

Chemical name	Source	Mass fraction purity	Purification method	Final water mass fraction	Analysis method
Methanol	Beijing Chemical Reagents Company	0.995		Not detected	GC <sup>c</sup>
Acetonitrile	Beijing Chemical Reagents Company	0.998		Not detected	GC
[EMIM][BF <sub>4</sub> ] <sup>a</sup>	Shanghai Cheng Jie Chemical Co. LTD	0.980	Vacuum desiccation	0.0005	KF <sup>d</sup> and HPLC <sup>e</sup>
[OMIM][BF <sub>4</sub> ] <sup>b</sup>	Shanghai Cheng Jie Chemical Co. LTD	0.970	Vacuum desiccation	0.0005	KF and HPLC

<sup>a</sup> [EMIM][BF<sub>4</sub>] = 1-ethyl-3-methylimidazolium tetrafluoroborate.

<sup>b</sup> [OMIM][BF<sub>4</sub>] = 1-octyl-3-methylimidazolium tetrafluoroborate.

<sup>c</sup> GC = gas chromatography.

<sup>d</sup> KF = Karl Fischer titration.

<sup>e</sup> HPLC = High Performance Liquid Chromatography.

**Table 2**  
Density  $d$ , refractive index  $n_D$ , and normal boiling point  $T_b$  of pure components at 101.3 kPa.

Component	$d$ ( $\text{g} \cdot \text{cm}^{-3}$ ) (293.15 K)		$n_D$ (293.15 K)		$T_b$ (K)	
	Exp.	Lit. [10]	Exp.	Lit. [10]	Exp.	Lit. [10]
Methanol	0.7911	0.7913	1.3283	1.3286	337.56	337.66
Acetonitrile	0.7821	0.7822	1.3439	1.3441	354.59	354.75

Standard uncertainties  $u$  are  $u(d) = 0.0001 \text{ g} \cdot \text{cm}^{-3}$ ,  $u(n_D) = 0.0001$ ,  $u(T) = 0.15 \text{ K}$ .

the uncertainty was about  $\pm 0.1 \text{ mg}$ ). According to the above way, the standard uncertainties of mole fractions of methanol and acetonitrile in the liquid and vapor phase was  $\pm 0.002$ . The mole fractions of IL in the liquid phase were gravimetrically determined by measuring the mass difference of prepared samples with and without IL. The VLE pressure was kept at 101.3 kPa by an on-off pressure controller with a standard uncertainty of 0.1 kPa. The VLE temperature was measured by a precisely calibrated thermometer with a standard uncertainty of 0.15 K.

## 3. Results and discussion

### 3.1. Experimental data

The isobaric VLE data for the methanol and acetonitrile binary system at atmospheric pressure (101.3 kPa) were determined in order to test the performance of our VLE apparatus and the procedure used. The binary VLE data for methanol (1) + acetonitrile (2) are listed in Table 3 and compared with those reported by Tamir [13] and Li [14] as shown in Fig. 1. It can be seen from Fig. 1 that our experimental data agree well with literature data that means our apparatus and procedure were reliable. Moreover, the system of methanol and acetonitrile forms a azeotrope at  $x_1 \approx 0.809$  at 101.3 kPa as seen in Fig. 1.

The isobaric VLE data for methanol (1) + acetonitrile (2) systems containing ILs [EMIM][BF<sub>4</sub>] (3) and [OMIM][BF<sub>4</sub>] (3) at various IL mole fractions (from about 0.01 or 0.05 to 0.20) were measured at 101.3 kPa. The results were listed in Tables 4 and 5, in which  $x'_1$  is the mole fraction of methanol in the liquid phase on an IL-free basis.

### 3.2. Correlation of VLE data

The activity coefficient of component  $i$ ,  $\gamma_i$ , in the ternary system was used for the sake of describing the effect of different ILs on the azeotrope. Because the experimental pressure is atmospheric pressure plus the vapor pressure of ILs can be neglected, the activity coefficient of component  $i$ ,  $\gamma_i$ , could be calculated by the following equation:

$$\gamma_i = (y_i P) / (x_i P_i^S), \quad (1)$$

In which  $y_i$  and  $x_i$  are the mole fraction of component  $i$  in the vapor and liquid phase, respectively;  $P$  and  $P_i^S$  denote the vapor pressure of system (atmospheric pressure) and pure component  $i$  (saturated vapor pressure) at the VLE temperature, respectively;

**Table 3**  
Isobaric VLE for the system methanol (1) + acetonitrile (2) at 101.3 kPa.

$T/\text{K}$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
354.59	0.000	0.000		
351.02	0.042	0.129	1.967	1.022
348.19	0.089	0.266	2.083	0.987
344.04	0.184	0.405	1.774	1.017
341.32	0.284	0.509	1.587	1.045
339.57	0.394	0.580	1.386	1.123
338.40	0.498	0.631	1.245	1.240
337.59	0.595	0.688	1.168	1.342
337.09	0.697	0.739	1.091	1.529
336.59	0.752	0.772	1.075	1.669
336.57	0.800	0.802	1.050	1.798
336.64	0.849	0.838	1.030	1.951
337.11	0.901	0.882	1.002	2.151
337.42	0.949	0.932	0.993	2.400
337.56	1.000	1.000		

Standard uncertainties  $u$  are  $u(x) = u(y) = 0.002$ ,  $u(T) = 0.15 \text{ K}$ ,  $u(P) = 0.1 \text{ kPa}$ .

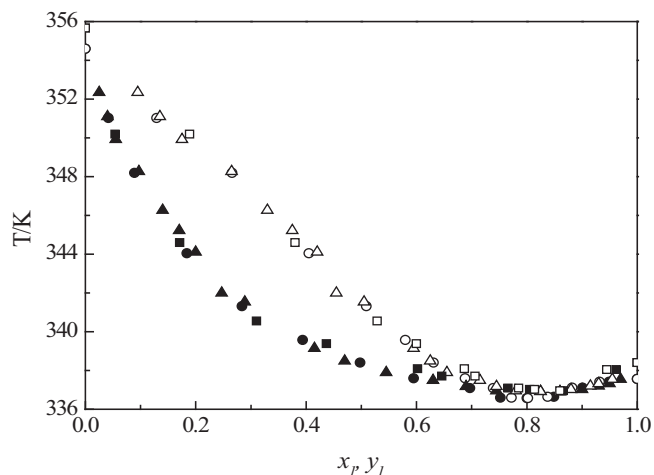


Fig. 1.  $T$ - $x$ - $y$  diagram for methanol (1) + acetonitrile (2) binary system at 101.3 kPa: ( $\blacktriangle$ ,  $\triangle$ ) Ref. [13]; ( $\blacksquare$ ,  $\square$ ) Ref. [14]; ( $\bullet$ ,  $\circ$ ) this work.

Table 4

Vapor–liquid equilibrium data for temperature  $T$ , liquid phase mole fraction  $x$ , liquid-phase mole fraction  $x'$  (IL-free basis), vapor-phase mole fraction  $y$ , calculated activity coefficient  $\gamma$  and relative volatility  $\alpha$  for the ternary system methanol (1) + acetonitrile (2) + [EMIM][BF<sub>4</sub>] (3) at 101.3 kPa.

$T/K$	$x_1$	$x_3$	$x'_1$	$y_1$	$\gamma_1$	$\gamma_2$	$\alpha_{12}$
348.61	0.093	0.014	0.094	0.260	1.846	1.011	3.387
344.65	0.184	0.014	0.187	0.412	1.703	1.018	3.045
341.76	0.284	0.012	0.288	0.503	1.507	1.081	2.505
339.85	0.384	0.012	0.389	0.570	1.363	1.161	2.088
338.58	0.484	0.014	0.491	0.640	1.272	1.221	1.842
338.10	0.536	0.015	0.544	0.669	1.223	1.273	1.694
337.66	0.590	0.012	0.597	0.690	1.170	1.367	1.507
337.09	0.690	0.013	0.699	0.753	1.114	1.492	1.310
336.70	0.791	0.013	0.801	0.813	1.066	1.731	1.079
337.62	0.891	0.013	0.902	0.890	0.999	2.015	0.873
353.04	0.073	0.100	0.081	0.233	1.793	0.987	3.436
348.86	0.159	0.100	0.177	0.395	1.619	0.993	3.027
345.52	0.257	0.100	0.286	0.504	1.449	1.045	2.535
342.83	0.347	0.100	0.385	0.602	1.424	1.065	2.414
341.44	0.441	0.100	0.490	0.664	1.301	1.136	2.053
341.05	0.490	0.101	0.545	0.696	1.245	1.167	1.908
340.04	0.533	0.101	0.593	0.727	1.243	1.210	1.830
339.74	0.629	0.100	0.699	0.789	1.158	1.278	1.612
339.35	0.720	0.100	0.800	0.851	1.107	1.382	1.421
339.31	0.811	0.100	0.901	0.920	1.065	1.504	1.256
358.09	0.070	0.197	0.087	0.226	1.526	0.966	3.054
354.28	0.131	0.198	0.163	0.365	1.513	0.970	2.965
350.47	0.207	0.197	0.258	0.490	1.468	0.991	2.770
347.73	0.299	0.197	0.373	0.585	1.338	1.043	2.369
346.06	0.384	0.200	0.480	0.672	1.271	1.048	2.223
344.82	0.435	0.200	0.543	0.719	1.257	1.067	2.146
344.15	0.469	0.200	0.586	0.743	1.236	1.099	2.043
343.25	0.554	0.200	0.692	0.808	1.177	1.141	1.865
342.27	0.647	0.200	0.808	0.871	1.129	1.262	1.611
342.18	0.721	0.198	0.898	0.928	1.085	1.343	1.454

Standard uncertainties  $u$  are  $u(x) = u(x') = u(y) = 0.002$ ,  $u(T) = 0.15$  K,  $u(P) = 0.1$  kPa.

In addition, Antoine equation was used to calculate  $P_i^S$  and the Antoine constants of component  $i$ , which were taken from the literature [14] and are given in Table 6.

The relative volatility of methanol (1) to acetonitrile (2),  $\alpha_{12}$ , was also calculated to illustrate the salt effect of IL on the azeotrope as expressed by

$$\alpha_{12} = (y_1/x_1)/(y_2/x_2), \quad (2)$$

The calculated activity coefficients  $\gamma_i$  and relative volatilities  $\alpha_{12}$  are given in Tables 4 and 5.

Table 5

Vapor–liquid equilibrium data for temperature  $T$ , liquid phase mole fraction  $x$ , liquid-phase mole fraction  $x'$  (IL-free basis), vapor-phase mole fraction  $y$ , calculated activity coefficient  $\gamma$  and relative volatility  $\alpha$  for the ternary system methanol (1) + acetonitrile (2) + [OMIM][BF<sub>4</sub>] (3) at 101.3 kPa.

$T/K$	$x_1$	$x_3$	$x'_1$	$y_1$	$\gamma_1$	$\gamma_2$	$\alpha_{12}$
350.49	0.093	0.052	0.098	0.251	1.674	1.007	3.107
346.34	0.188	0.052	0.198	0.393	1.504	1.049	2.630
342.84	0.287	0.052	0.303	0.522	1.486	1.068	2.511
340.20	0.373	0.052	0.393	0.589	1.433	1.150	2.220
339.89	0.467	0.052	0.493	0.66	1.293	1.154	1.995
339.35	0.514	0.053	0.542	0.684	1.245	1.208	1.830
339.17	0.568	0.052	0.599	0.718	1.192	1.238	1.708
338.65	0.665	0.053	0.702	0.774	1.119	1.358	1.457
338.26	0.762	0.052	0.804	0.835	1.069	1.532	1.232
338.30	0.856	0.053	0.904	0.906	1.030	1.785	1.019
353.87	0.081	0.100	0.090	0.236	1.588	0.968	3.115
349.66	0.175	0.100	0.194	0.401	1.458	0.978	2.777
346.55	0.264	0.100	0.293	0.512	1.382	1.005	2.526
344.23	0.353	0.100	0.392	0.601	1.324	1.030	2.336
342.56	0.444	0.100	0.493	0.668	1.248	1.086	2.070
342.04	0.490	0.100	0.545	0.702	1.210	1.106	1.967
341.27	0.537	0.100	0.597	0.729	1.181	1.165	1.815
340.45	0.630	0.100	0.700	0.790	1.127	1.245	1.616
340.21	0.722	0.100	0.802	0.855	1.074	1.313	1.458
340.19	0.811	0.100	0.901	0.921	1.030	1.436	1.279
360.73	0.082	0.197	0.102	0.237	1.252	0.894	2.737
357.56	0.148	0.198	0.185	0.363	1.174	0.906	2.501
354.90	0.219	0.197	0.273	0.491	1.186	0.879	2.574
350.45	0.335	0.197	0.417	0.624	1.153	0.933	2.311
349.34	0.374	0.200	0.467	0.657	1.131	0.962	2.188
348.05	0.425	0.200	0.531	0.710	1.126	0.966	2.155
347.18	0.464	0.200	0.580	0.740	1.110	0.993	2.060
346.16	0.555	0.200	0.693	0.805	1.050	1.052	1.830
345.15	0.634	0.200	0.792	0.865	1.025	1.111	1.684
344.60	0.728	0.198	0.907	0.937	0.991	1.174	1.536

Standard uncertainties  $u$  are  $u(x) = u(x') = u(y) = 0.002$ ,  $u(T) = 0.15$  K,  $u(P) = 0.1$  kPa.

Table 6

Antoine equation<sup>a</sup> and UNIQUAC parameters.

Components	$T/K$ range	Antoine constants [15]			UNIQUAC parameters [16–18]	
		A	B	C	$r_i$	$q_i$
Methanol	288 to 357	8.08097	1582.27	239.726	1.4311	1.4320
Acetonitrile	246 to 355	7.33986	1482.29	250.523	1.8701	1.7240
[EMIM][BF <sub>4</sub> ]	–	–	–	–	8.1424	5.3930
[OMIM][BF <sub>4</sub> ]	–	–	–	–	12.1888	8.6330

<sup>a</sup> Antoine equation:  $\log_{10}(P_i^S/\text{mmHg}) = A - B/(T/^\circ\text{C} + C)$ .

In this work, the NRTL [19] and UNIQUAC [20] models were used to correlate the binary and ternary VLE data, although these two local-composition models were originally developed for systems not involving electrolytes or ILs. This is mainly because they have been proven to adequately model the phase equilibrium for IL-containing systems [21–26]. On the other hand, we also tried to use the predictive COSMO-RS model (ADF version), which is developed by Zhigang Lei's group, to predict the VLE for the systems investigated in this work, and found that the COSMO-RS model for ILs can give a qualitatively correct prediction (see Figs. S1–S4 in Supporting Data). For more details on the COSMO-RS model for ILs, please see the website at [https://www.scm.com/documentation/Tutorials/COSMO-RS/Ionic\\_Liquids/](https://www.scm.com/documentation/Tutorials/COSMO-RS/Ionic_Liquids/).

For ternary system, the NRTL model is expressed by the following form:

$$\ln \gamma_i = \frac{\sum_{j=1}^3 \tau_{ij} G_{ji} x_j}{\sum_{k=1}^3 G_{ki} x_k} + \sum_{j=1}^3 \frac{x_j G_{ij}}{\sum_{k=1}^3 G_{ki} x_k} \left( \tau_{ij} - \frac{\sum_{j=1}^3 x_i \tau_{ij} G_{ij}}{\sum_{k=1}^3 x_k G_{kj}} \right) \quad (i = 1, 2, 3) \quad (3)$$

with

$$\tau_{ij} = \frac{g_{ij} - g_{ii}}{RT} = \frac{\Delta g_{ij}}{RT}, \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (j = 1, 2, 3) \quad (4)$$

and

$$\tau_{ii} = 0, \quad G_{ii} = 1, \quad \alpha_{ij} = \alpha_{ji}, \quad (5)$$

where  $\Delta g_{ij}$  is the cross interaction energy parameter between component  $i$  and component  $j$ ;  $\alpha_{ij}$  is the non-randomness parameter of the ternary solution;  $R$  is the ideal gas constant and  $T$  is the VLE temperature.

For ternary system, the UNIQUAC model is given by two contributions, which can be expressed as

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \quad (i = 1, 2, 3). \quad (6)$$

In Eq. (6), the  $\gamma_i^c$  term is called the combinatorial contribution, which is related to the size and shape of molecules. The  $\gamma_i^r$  term is named the residual contribution, related to the energy interactions.

$$\ln \gamma_i^c = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^3 x_j l_j, \quad (7)$$

$$\ln \gamma_i^r = q_i \left( 1 - \ln \sum_{j=1}^3 \theta_j \tau_{ji} - \sum_{j=1}^3 \frac{\theta_j \tau_{ij}}{\sum_{k=1}^3 \theta_k \tau_{kj}} \right), \quad (8)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1), \quad (9)$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^3 q_j x_j}, \quad \Phi_i = \frac{r_i x_i}{\sum_{j=1}^3 r_j x_j}, \quad (10)$$

$$\tau_{ij} = \exp\left(-\frac{u_{ij} - u_{ii}}{RT}\right) = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) \quad \text{and} \quad \tau_{ii} = 1 \quad (j = 1, 2, 3), \quad (11)$$

where  $r_i$  and  $q_i$  are the van der Waals volume and surface area of pure component  $i$ , respectively;  $z$  is the coordination number, which is frequently set to 10;  $u_{ij}$  is the interaction energy between molecules  $i$  and  $j$  and  $\Delta u_{ij}$  is the binary interaction energy parameter;  $R$  and  $T$  are the same as in NRTL model. The structural parameters ( $r_i$  and  $q_i$ ) used in this work are listed in Table 6.

According to the suggested models, there are nine adjustable parameters in NRTL model ( $\alpha_{12}$ ,  $\alpha_{13}$ ,  $\alpha_{23}$ ,  $\Delta g_{12}$ ,  $\Delta g_{21}$ ,  $\Delta g_{23}$ ,  $\Delta g_{32}$ ,  $\Delta g_{13}$ ,  $\Delta g_{31}$ ) and six adjustable parameters in UNIQUAC model ( $\Delta u_{12}$ ,  $\Delta u_{21}$ ,  $\Delta u_{13}$ ,  $\Delta u_{31}$ ,  $\Delta u_{23}$ ,  $\Delta u_{32}$ ) for ternary system. Moreover, all of the adjustable parameters are obtained from the VLE data correlation by minimization of the objective function ARD (see Eq. (12)) using Levenberg–Marquardt method. More specifically, the 1–2 pair parameters were obtained from binary VLE data and 1–3 and 2–3 pair parameters were regressed from ternary data.

$$\text{ARD} (\%) = \frac{1}{n} \sum_n \left| \frac{\gamma_i^{\text{exptl}} - \gamma_i^{\text{calcd}}}{\gamma_i^{\text{exptl}}} \right| \cdot 100, \quad (12)$$

In Eq. (12),  $n$  represents the total number of VLE data points,  $\gamma_i^{\text{calcd}}$  and  $\gamma_i^{\text{exptl}}$  are the calculated and experimental activity coefficient of component  $i$  in ternary system, respectively. In above way, the regressed NRTL and UNIQUAC results for all VLE data are listed in Tables 7 and 8, respectively.

**Table 7**

Estimated values of binary interaction parameters  $\Delta g_{ij}$  and  $\Delta g_{ji}$  in the NRTL model.

$i$ component	$j$ component	$\alpha_{ij}$	$\Delta g_{ij}/J \cdot \text{mol}^{-1}$	$\Delta g_{ji}/J \cdot \text{mol}^{-1}$
Methanol (1)	Acetonitrile (2)	0.1594	3419.4	−642.1
Methanol (1)	[EMIM][BF <sub>4</sub> ] (3)	0.3000	10955.0	−5423.0
Acetonitrile (2)	[EMIM][BF <sub>4</sub> ] (3)	0.3400	3653.0	−4260.0
Methanol (1)	[OMIM][BF <sub>4</sub> ] (3)	0.0399	1377.6	−5142.4
Acetonitrile (2)	[OMIM][BF <sub>4</sub> ] (3)	0.4599	3653.0	−5278.5
Methanol (1) + acetonitrile (2) + [EMIM][BF <sub>4</sub> ] (3): ARD = 1.4128				
Methanol (1) + acetonitrile (2) + [OMIM][BF <sub>4</sub> ] (3): ARD = 1.3523				

**Table 8**

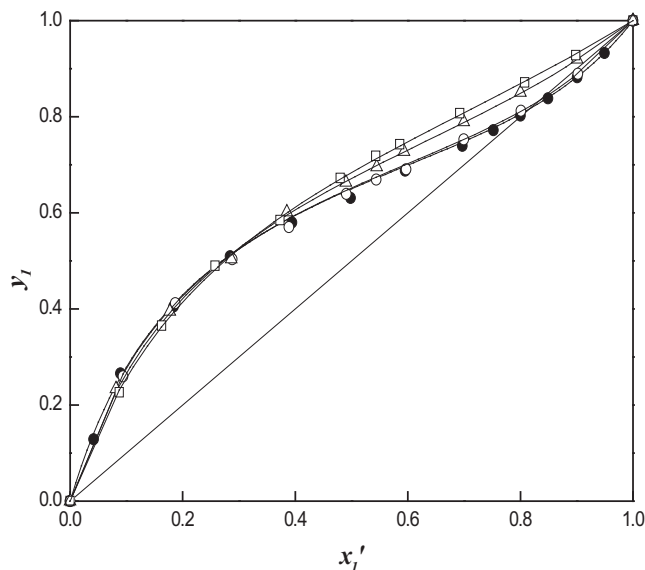
Estimated values of binary interaction parameters  $\Delta u_{ij}$  and  $\Delta u_{ji}$  in the UNIQUAC model.

$i$ component	$j$ component	$\Delta u_{ij}/J \cdot \text{mol}^{-1}$	$\Delta u_{ji}/J \cdot \text{mol}^{-1}$
Methanol (1)	Acetonitrile (2)	984.4	724.9
Methanol (1)	[EMIM][BF <sub>4</sub> ] (3)	−325.5	1279.8
Acetonitrile (2)	[EMIM][BF <sub>4</sub> ] (3)	−2988.9	9531.3
Methanol (1)	[OMIM][BF <sub>4</sub> ] (3)	55.6	539.1
Acetonitrile (2)	[OMIM][BF <sub>4</sub> ] (3)	−347.6	304.4
Methanol (1) + acetonitrile (2) + [EMIM][BF <sub>4</sub> ] (3): ARD = 1.3866			
Methanol (1) + acetonitrile (2) + [OMIM][BF <sub>4</sub> ] (3): ARD = 1.6402			

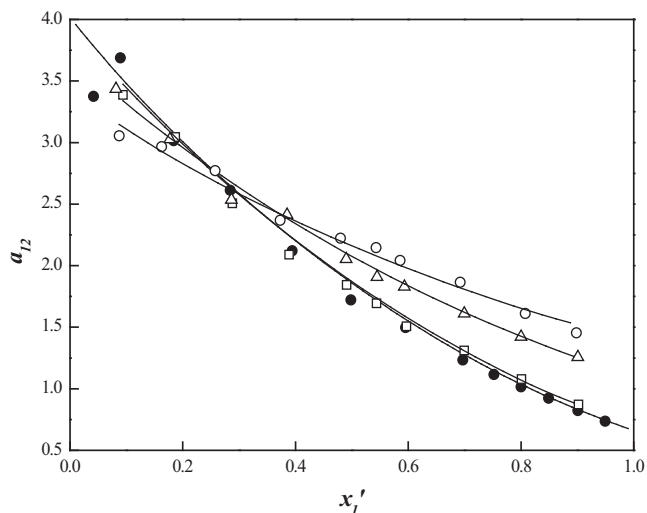
### 3.3. Discussion

To make it easier to observe and illustrate the effects of ILs on methanol (1) and acetonitrile (2) binary system, the pseudobinary  $x'_1$ – $y$  and  $x'_1$ – $\alpha_{12}$  diagrams for methanol (1) + acetonitrile (2) + IL (3) ternary system were shown in Figs. 2–5, in where  $x'_1$  is the mole fraction of methanol that on the IL-free basis.

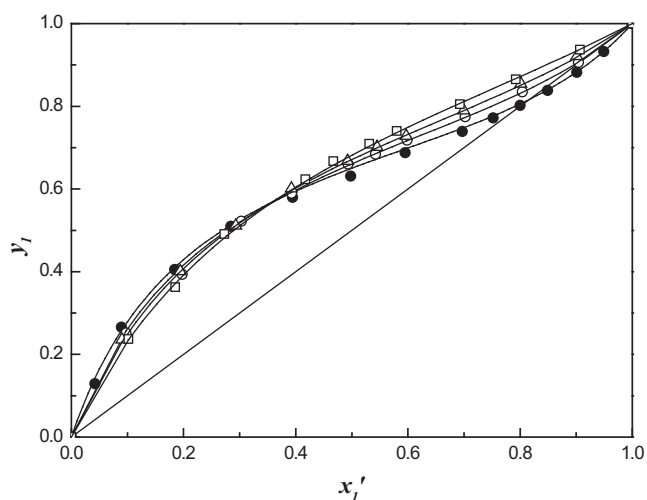
It can be seen from Figs. 2–5 that the addition of each of ILs makes a strong crossover effect between salting-in and salting-out on the VLE of methanol and acetonitrile binary system, which means the mole fraction of methanol in the vapor phase decreases in acetonitrile-rich region and it increases in methanol-rich region. More importantly, with an increase in the IL concentration this effect is more obvious. Meanwhile, the addition of IL also moves up the azeotropic point for methanol and acetonitrile. Finally, the azeotropic phenomena could be totally ruptured at specific IL mole



**Fig. 2.** Isobaric VLE diagram for methanol (1) + acetonitrile (2) + [EMIM][BF<sub>4</sub>] (3) system at 101.3 kPa: ●,  $x_3 = 0$ ; ○,  $x_3 = 0.01$ ; △,  $x_3 = 0.10$ ; □,  $x_3 = 0.20$ ; solid lines, correlated using the NRTL model.



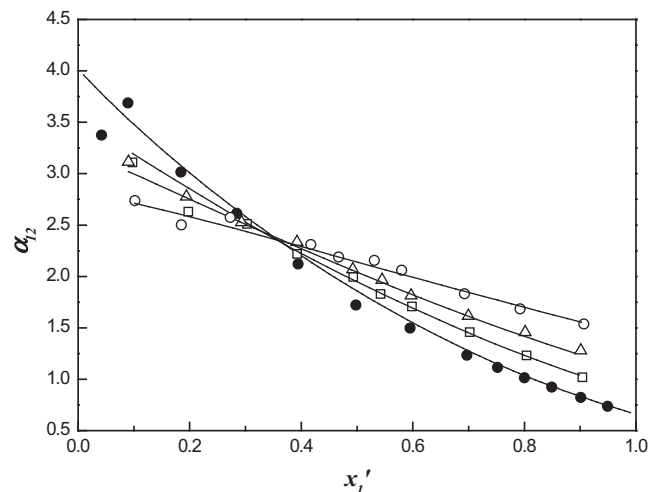
**Fig. 3.** Methanol/acetonitrile relative volatility of methanol (1) + acetonitrile (2) + IL (3) system at 101.3 kPa: ●,  $x_3 = 0$  (IL-free); □,  $x_3 = 0.01$  ([EMIM][BF<sub>4</sub>]); △,  $x_3 = 0.10$  ([EMIM][BF<sub>4</sub>]); ○,  $x_3 = 0.20$  ([EMIM][BF<sub>4</sub>]); solid lines, correlated using the NRTL model.



**Fig. 4.** Isobaric VLE diagram for methanol (1) + acetonitrile (2) + [OMIM][BF<sub>4</sub>] (3) system at 101.3 kPa: ●,  $x_3 = 0$ ; ○,  $x_3 = 0.05$ ; △,  $x_3 = 0.10$ ; □,  $x_3 = 0.20$ ; solid lines, correlated using the NRTL model.

fraction. From the results of VLE experiments, the azeotropic point of methanol and acetonitrile is broken when the minimum mole fraction of [EMIM][BF<sub>4</sub>] and [OMIM][BF<sub>4</sub>] both are  $x_3 = 0.10$ . Consequently, it concluded that [EMIM][BF<sub>4</sub>] and [OMIM][BF<sub>4</sub>] both can be selected as potential entrainers to separate methanol and acetonitrile. Nevertheless, [OMIM][BF<sub>4</sub>] makes a more stronger salting-out effect than [EMIM][BF<sub>4</sub>] in methanol-rich region.

The relative volatility of methanol to acetonitrile,  $\alpha_{12}$ , measured at different IL mole fractions are plotted in Figs. 3 and 5. It is observed that the addition of IL changes the relative volatility for the methanol and acetonitrile system: an increase of the IL content leads to a larger relative volatility in methanol-rich region and a smaller one in acetonitrile-rich region. Moreover, the salting-out effects of [EMIM][BF<sub>4</sub>] and [OMIM][BF<sub>4</sub>] follow the order:  $0.20 > 0.10 > 0.01$  and  $0.20 > 0.10 > 0.05$ , respectively. It is also seen that the values of relative volatility became greater than unity with the addition of IL, which demonstrates that the extractive distillation method could be used for the separation of methanol and



**Fig. 5.** Methanol/acetonitrile relative volatility of methanol (1) + acetonitrile (2) + IL (3) system at 101.3 kPa: ●,  $x_3 = 0$  (IL-free); □,  $x_3 = 0.05$  ([OMIM][BF<sub>4</sub>]); △,  $x_3 = 0.10$  ([OMIM][BF<sub>4</sub>]); ○,  $x_3 = 0.20$  ([OMIM][BF<sub>4</sub>]); solid lines, correlated using the NRTL model.

acetonitrile. But the relative volatility increased by the [OMIM][BF<sub>4</sub>] is larger than [EMIM][BF<sub>4</sub>] in methanol-rich region.

Tables 4 and 5 indicated that the VLE temperature increases with the increase of the amount of IL and that the VLE temperatures for two ternary systems are almost equal when the added IL content are identical. From the viewpoint of distillation, greater relative volatility leads to a lower invest cost, to adding the greater amount of IL. However, the increase of the amount of IL means higher VLE temperature, which causes a higher operating cost. Thus, in order to minimize total cost of distillation, the optimal content of IL must be selected.

It was mentioned that both ILs make a strong crossover effect on the VLE of methanol and acetonitrile system. Some possible reasons are given for this tendency of salting-out and salting-in effect as below. IL actually is organic molten salt, it exists some extent of dissociation in solution. Especially, in the extremely dilute solution, ionic liquid tends to fully dissociate, which means IL exists in ionic state. As the mole fraction of IL increases, the extent of dissociation decreases, which leads to the increase of “molecular” state IL [27–29]. In methanol-rich region, due to the strong interaction between acetonitrile molecule and “molecular” state IL, the activity of acetonitrile was decreased and thus leads to a greater relative volatility of methanol. However, in acetonitrile-rich region, the methanol molecule much prefer ionic state IL to acetonitrile molecule, which results in a smaller relative volatility of methanol. Anyway, the selective interactions between different existing states of IL and solvent molecules become stronger with the mole fraction of IL increases. According to the above analysis, [OMIM][BF<sub>4</sub>] should make a more stronger salting-out effect on methanol than [EMIM][BF<sub>4</sub>], because the dissociation capability of [OMIM][BF<sub>4</sub>] is weaker than [EMIM][BF<sub>4</sub>], that is to say [OMIM][BF<sub>4</sub>] contains more “molecular” states of IL than [EMIM][BF<sub>4</sub>] at the same adding mole fraction.

#### 4. Conclusions

The VLE data for one binary system of methanol + acetonitrile and two ternary systems of methanol + acetonitrile containing [EMIM][BF<sub>4</sub>] or [OMIM][BF<sub>4</sub>] were measured at 101.3 kPa. The VLE results showed that the addition of [EMIM][BF<sub>4</sub>] or [OMIM][BF<sub>4</sub>] produces a stronger crossover salting effect on methanol and acetonitrile binary system, which could change the relative



volatility of methanol to acetonitrile, even leads to eliminate the azeotropic point ultimately. The salting-out effect of ILs on methanol is in the following order: [OMIM][BF<sub>4</sub>] > [EMIM][BF<sub>4</sub>]. This tendency of salt effect can be ascribed to the selective interactions between different existing states of IL and solvent molecules. This work also indicated that ILs can be used as potential entrainers for the separation of methanol + acetonitrile using extractive distillation. Besides, all of VLE data were correlated by NRTL and UNIQUAC models, and the regression results are quietly agreement with VLE data.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2016.05.011>.

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