Vapor−Liquid Equilibrium and Liquid−Liquid Equilibrium of Methyl Acetate + Methanol + 1-Ethyl-3-methylimidazolium Acetate

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Vapor−liquid equilibrium (VLE) and liquid−liquid equilibrium (LLE) were measured for the ternary system of methyl acetate + methanol + 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]). The experimental LLE data were correlated by the NRTL model and the binary interaction parameters obtained from LLE were used to predict the ternary VLE, and the results agreed well with the experimental data. The results showed that the ionic liquid ([EMIM][Ac]) produced a notable salting-out effect, which enhanced the relative volatility of methyl acetate and methanol.

Introduction

Ionic liquids (IL) are chemicals composed of organic cations and anions with very low melting points (mainly below 373 K). They have excellent properties: low vapor pressure, thermally stable up to 573 K, good solvents for inorganic, organic, and polymeric materials, and less caustic.[1−3] Because of these unique properties, ionic liquids can be used in separation processes such as extractive distillation and extraction.[4]

The use of ionic liquids as entrainers in extractive distillation for separation of azeotropic mixture was first reported by Arlt et al.[5,6] They reported the effects of various ionic liquids on different systems such as ethanol + water, propanone + methanol, water + acetic acid, oxolane + water, methanol + oxolane, and hex-1-ene + hexane.[7−12] Ionic liquids can also be used as solvents in extraction processes. Arce reported the liquid−liquid equilibrium of ternary systems 1-ethyl-3-methylimidazolium + ethanol + 2-ethoxy-2-methylpropane and ethanol + 2-ethoxy-2-methylpropane + 1-butyl-3-methylimidazolium trifluoromethanesulfonate.[13,14] Meindersma reported liquid−liquid equilibrium of ternary system an aromatic + an aliphatic hydrocarbon +1-butyl-4-methylpyridinium tetrafluoroborate.[15] Vapor−liquid equilibria (VLE) and liquid−liquid equilibria (LLE) are important data for the extractive distillation and extraction process. However, the VLE and LLE data for the mixtures containing ionic liquids are still rare.

The azeotropic mixture methyl acetate + methanol is involved in the industrial manufacturing process of poly(vinyl alcohol), which is made from poly(vinyl acetate) by alcoholysis with methanol. The resulting methyl acetate is hydrolyzed to obtain methanol, which is recycled to the alcoholysis stage, and acetic acid, which is returned to the vinyl acetate plant.[16,17] The equilibrium data are essential for the analysis and design of industrial separation process of methyl acetate-methanol. Orchillés has reported the isobaric vapor−liquid equilibrium of methyl acetate + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][triflate]).[18]

We calculated the infinite dilution activity coefficients of methyl acetate and methanol in [EMIM][triflate] and [EMIM][Ac], respectively, using the COSMO-SAC model[19,20] and found the solvent selectivity of [EMIM][Ac] was greater than that of [EMIM][triflate]. The prices of the two ILs are almost the same. [EMIM][Ac] is a promising solvent for the separation of azeotropic mixture methyl acetate + methanol. In this paper, we aim to measure the vapor−liquid equilibrium (VLE) and liquid−liquid equilibrium (LLE) for the ternary mixture methyl acetate (1) + methanol (2) + 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]) (3). The liquid−liquid equilibrium (LLE) data of the ternary mixture were correlated by NRTL model, and the interaction parameters obtained by LLE were utilized to predict the vapor−liquid equilibrium. The entrainers [EMIM][Ac] and [EMIM][triflate] for the separation of methyl acetate-methanol were compared according to the relative volatility of methyl acetate and methanol in ionic liquids.

Experimental Section

Materials. Methyl acetate and methanol were purchased from Jiangtian Chemical Reagents Co., Tianjin, China. Their purities checked by gas chromatography were greater than 0.997 in mass fraction. [EMIM][Ac] was purchased from Chengjie Chemical Reagents Co., Shanghai, China, with a minimum mass fraction 0.99 (observed by liquid chromatography). The water mass fraction in ionic liquid determined by Karl Fischer titration was less than 0.0001. All chemicals were used without further purification, but were carefully degassed.

Apparatus and Procedure. Each solution was prepared gravimetrically using an electronic balance (Acculab Alc 210.4) with a standard uncertainty of 0.0001 g.

The VLE for the ternary mixture methyl acetate (1) + methanol (2) + 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]) (3) was measured by a circulation vapor−liquid equilibrium still (a modified Othmer still),[21,22] as shown in Figure 1. In this apparatus, energy was applied to the still through a heating rod, and the equilibrium temperature was measured by a precision and calibrated thermometer with a standard uncertainty of 0.01 K. When a given liquid solution was put into the boiling chamber and heated, the vapor was condensed in the condenser and returned into the equilibrium chamber at the same time. Equilibrium was usually reached in about 1 h, which was indicated by the constant boiling

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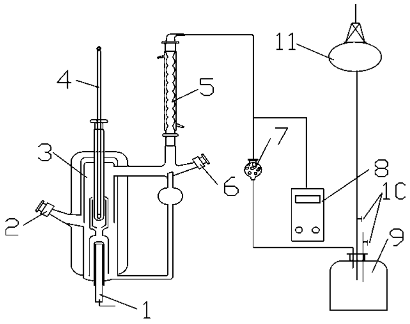

Figure 1. Schematic diagram of vapor−liquid equilibrium still: 1, heating rod; 2, liquid-phase sampling point; 3, equilibrium chamber; 4, thermometer; 5, condenser; 6, vapor-phase sampling point; 7, desiccator; 8, manometer; 9, gas buffer; 10, valve; 11, N_2 vessel.

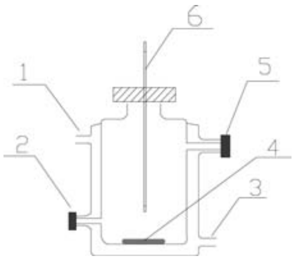

Figure 2. Schematic diagram of liquid−liquid equilibrium cell. 1, 3-outlet and inlet of thermostatic water; 2, 5-sampling point; 4-magnetic stirrer; 6-thermometer.

temperature. The system was maintained in the equilibrium state for about 30 min; then samples were taken every 20 min, from the vapor and liquid phase of the system. At least five samples of vapor phase and liquid phase were taken, respectively. If the standard deviations of the compositions of five samples of vapor phase and liquid phase were both less than 0.0015 (mole fraction), then the measurement process was stopped; otherwise, more samples should be taken until the standard deviations were less than 0.0015. The total sampling process lasted for about 2 h at equilibrium. The sampling process could ensure the vapor and liquid phases are in equilibrium state. The apparatus pressure was measured by manometer whose standard uncertainty was 0.05 kPa.

LLE was measured by a self-designed apparatus (Figure 2). The mixture was put into the equilibrium cell, and stirred by a magnetic stirrer, and the temperature in the equilibrium cell was kept constant by thermostatic water. The uncertainty of the temperature was 0.01 K. The sample mixture was stirred rigorously in the equilibrium cell for about 8 h and then allowed to settle for about 24 h at constant temperature; then eight samples of extract phase and raffinate phase were taken, respectively. The standard deviations of the compositions of extract phase and raffinate phase were both less than 0.0015 (mole fraction).

Sample Analysis. For the samples of VLE, compositions of the condensed vapor and the concentration of methanol and methyl acetate in liquid phase were analyzed by gas chromatography. The gas chromatograph (SP-1000) was equipped with a FID detector and the column was SE-30 (50 m × 0.32 mm). The operating conditions were as follows: both injector and detector temperatures were 473 K, and the oven temperature was 323 K. A calibration correction factor was obtained from gravimetrically prepared standard solutions. The reproducibility of the GC measurements was established by repetitive measurements of the same sample using the calibrated GC. The standard deviation was evaluated to be below 0.0005 (mole fraction). The quality of the calibration was evaluated by measuring samples of known compositions. Each sample was analyzed five times with calibrated GC. The deviations between the compositions of the gravimetrically composed samples and the GC measurements indicated a standard deviation of less than 0.0008 (mole fraction). The expanded uncertainty of the gas chromatographic composition analysis was below 0.004 (mole fraction, with 95% confidence).

Table 1. Vapor−Liquid Equilibrium Data for the Methyl Acetate (1) + Methanol (2) System at P = 101.3 kPa[a]

T/K	x_1	y_1	σy_1
337.57	0.000	0.000	0.000
332.82	0.102	0.260	0.002
330.08	0.203	0.379	0.001
328.51	0.299	0.468	0.001
327.65	0.406	0.535	0.002
326.96	0.511	0.573	0.002
326.79	0.603	0.628	0.002
326.60	0.706	0.687	0.001
326.96	0.806	0.748	0.000
327.89	0.902	0.845	0.001
329.97	1.000	1.000	0.000

[a] $\sigma y_1 = |y_1^{\text{exp}} - y_1^{\text{cal}}|$.

The liquid phase was analyzed by an external standard method of HPLC (waters 490E) with an ultraviolet detector. The UV detector wavelength was 240 nm and the mobile phase was methanol + water. The calibration curve was obtained from a series of gravimetrically prepared standard solutions, and the correlation coefficient of the calibration curve was R^2 = 0.999 86. The reproducibility of the HPLC measurements was established by repetitive measurements of the same sample using the calibrated HPLC. The standard deviation was evaluated to be below 0.0006 (mole fraction). To evaluate the quality of the calibration curve, we measured five samples of known composition. The results showed that the standard deviation between the known compositions and the HPLC measurements was below 0.0018 (mole fraction). The expanded uncertainty of the HPLC composition analysis was assumed to be below 0.004 (mole fraction, with 95% confidence). In this way, the ratio of the IL to methyl acetate was obtained by HPLC, and the ratio of methanol to methyl acetate was obtained by GC, so the mole fraction of the methanol, methyl acetate, and [EMIM][Ac] in the liquid phase could be calculated. The quality of this method was evaluated by measuring five samples of known composition. Each sample was analyzed by calibrated GC and HPLC five times. The deviations between the compositions of the gravimetrically composed samples and calculated results indicated a standard deviation of less than 0.002 (mole fraction). The expanded uncertainty of the liquid composition analysis was below 0.006 (mole fraction, with 95% confidence).

For the LLE, both extract phase and raffinate phase were analyzed by gas chromatography and HPLC. The apparatus and operating conditions were the same as VLE.

Results and Discussion

To test the performance of the VLE apparatus, the vapor−liquid equilibrium for the binary system of methyl acetate + methanol was measured at 101.3 kPa. The experimental results were compared to the calculated results obtained from software CHEMCAD. The experimental results as well as the absolute deviations between experimental and calculated data are shown in Table 1. Comparison between our results and those reported by Gmehling et al.[23] is given in Figure 3. In Figure 3, ■ represents our results, ○ represents the results reported by

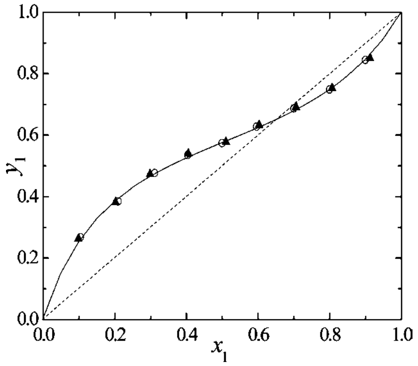

Figure 3. Isobaric VLE diagram for the binary system of methyl acetate (1) + methanol (2) at 101.3 kPa: ▲, this work; ○, Gmehling et al.;[23] solid line, calculated by the NRTL model; dash line, $y_1 = x_1$.

Table 2. Liquid−Liquid Equilibrium Data for the Ternary Mixture Methyl Acetate (1) + Methanol (2) + [EMIM][Ac] (3) at 299.15 K

	extract phase			raffinate phase		
T/K	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}
299.15	0.938	0.000	0.062	0.129	0.000	0.871
299.15	0.930	0.007	0.063	0.133	0.041	0.826
299.15	0.927	0.019	0.055	0.150	0.103	0.759
299.15	0.901	0.039	0.059	0.187	0.168	0.645
299.15	0.882	0.056	0.062	0.198	0.214	0.589
299.15	0.851	0.083	0.065	0.228	0.263	0.499
299.15	0.818	0.119	0.063	0.253	0.303	0.444
299.15	0.770	0.152	0.078	0.306	0.329	0.366
299.15	0.732	0.175	0.092	0.355	0.340	0.305
299.15	0.695	0.213	0.092	0.375	0.349	0.276
299.15	0.662	0.234	0.104	0.413	0.348	0.239

Gmehling, and the solid line is calculated by NRTL model using CHEMCAD. It can be seen that our experimental data agree well with those reported in literature and the maximum absolute deviations between the calculated and measured mole fractions of methyl acetate in the vapor phase was less than 0.003.

The liquid−liquid equilibrium of the ternary system methyl acetate (1) + methanol (2) + [EMIM][Ac] (3) was measured at 299.15 K, and the results are listed in Table 2. The LLE of the ternary mixture was correlated by NRTL activity coefficient model.

The NTRL model has been used to correlate the liquid−liquid equilibrium and vapor−liquid equilibrium of solvent + IL systems.[24] The NTRL model we used is as follows:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{G_{ij} x_j}{G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_l \tau_{lj} G_{lj} x_l}{\sum_k G_{kj} x_k} \right) \tag{1}$$

$$\tau_{ji} = B_{ji}/T \tag{2}$$

$$G_{ji} = \exp(-\alpha_{ji} \times \tau_{ji}) \tag{3}$$

where B_{ij} is binary interaction parameter, K; α_{ij} is nonrandomness parameter; and T is temperature, K.

In this work, the binary interaction parameters of the NRTL model (B_{12} and B_{21}) were obtained from the database in the commercial software CHEMCAD, and the other binary interaction parameters were correlated from ternary experimental liquid−liquid equilibrium data using the binary interaction parameter (BIP) regression function in CHEMCAD. The correlated results are given in Table 3.

Table 3. Values of Binary Interaction Parameters B_{ij} and B_{ji} in the NRTL Model

i component	j component	α_{ij}	B_{ij}/K	B_{ji}/K
methyl acetate	methanol	0.296	146.111	223.376
methyl acetate	[EMIM][Ac]	0.100	812.261	138.323
methanol	[EMIM][Ac]	0.390	−257.142	−78.436

The ternary LLE phase diagram is plotted in Figure 4, which shows the experimental and calculated LLE data agree well. The root-mean-square deviations between calculated and measured values for x_{11}, x_{21}, x_{12}, and x_{22} were 0.0028, 0.0019, 0.0042, and 0.0012, respectively. Figure 4 shows that the methyl acetate (1) and [EMIM][Ac] (3) are partially miscible at 299.15 K only when the methanol content is low (less than 0.348, mole fraction).

Liquid−liquid equilibrium is affected by temperature. The liquid−liquid equilibrium of methyl acetate (1) + methanol (2) + [EMIM][Ac] (3) at different temperatures were calculated by the NRTL equation, and the results are shown in Figure 5. It indicates that the area of the two-phase region decreases with increasing temperature.

The vapor−liquid equilibrium for the ternary system of methyl acetate (1) + methanol (2) + [EMIM][Ac] (3) was measured at 101.3 kPa, and the concentrations of ionic liquid added to the system were kept at x_3 = 0.1, 0.2, and 0.3, respectively. The results are shown in Table 4. In the table, x_3 represents the mole fraction of ionic liquid in the liquid phase and x_1' represents the mole fraction of methyl acetate in the

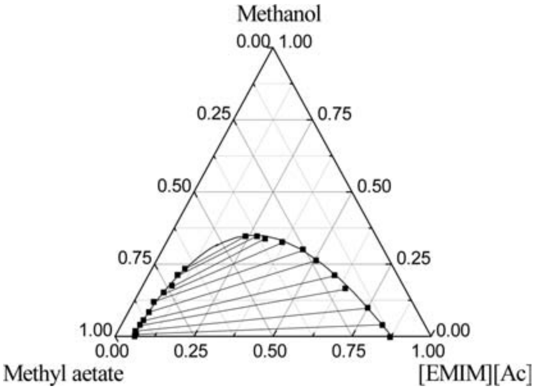

Figure 4. LLE of the ternary system of methyl acetate (1) + methanol (2) + [EMIM][Ac] (3) at 299.15 K: ■, experimental value; solid line, correlated using the NRTL model.

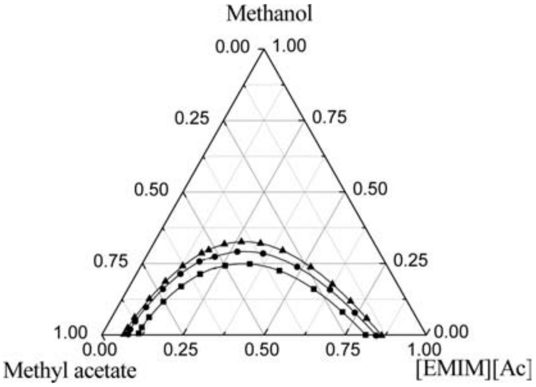

Figure 5. LLE of the ternary system of methyl acetate (1) + methanol (2) + [EMIM][Ac] (3) at various temperatures (calculated by NRTL model): ■, 343.15 K; ●, 323.15 K; ▲, 303.15 K.

Table 4. Vapor−Liquid Equilibrium Data for the Ternary System Methyl Acetate (1) + Methanol (2) + [EMIM][Ac] (3) at P = 101.3 kPa

x_3	T/K	x_1'	y_1	α_{12}
0.100	335.21	0.000	0.000	
0.099	334.82	0.101	0.278	3.475
0.101	332.43	0.201	0.437	3.114
0.101	330.21	0.304	0.524	2.575
0.098	329.22	0.396	0.598	2.239
0.100	328.62	0.499	0.668	2.015
0.099	328.82	0.596	0.718	1.700
0.100	329.18	0.698	0.781	1.531
0.097	329.93	0.799	0.842	1.333
0.099	330.49	0.893	0.908	1.104
0.100	331.43	1.000[a]	1.000	
0.200	338.31	0.000	0.000	
0.200	337.82	0.101	0.310	4.043
0.199	334.78	0.199	0.486	3.789
0.199	332.12	0.299	0.594	3.416
0.199	330.40	0.399	0.652	2.820
0.197	329.53	0.492	0.724	2.629
0.200	329.68	0.600	0.784	2.428
0.200	329.80	0.699	0.842	2.292
0.200	330.48	0.800	0.892	2.071
0.200	330.71	0.900[a]	0.941	1.778
0.200	331.60	1.000[a]	1.000	
0.300	342.82	0.000	0.000	
0.296	341.19	0.101	0.348	4.814
0.288	337.30	0.188	0.516	4.864
0.301	332.00	0.368	0.701	4.034
0.304	331.52	0.405	0.724	3.863
0.296	330.21	0.498	0.786	3.713
0.295	330.18	0.599	0.845	4.006
0.300	330.37	0.699[a]	0.885	3.733
0.296	330.59	0.788[a]	0.921	3.498
0.299	331.22	0.896[a]	0.954	2.446
0.300	332.18	1.000[a]	1.000	

[a] Vapor−liquid−liquid equilibrium.

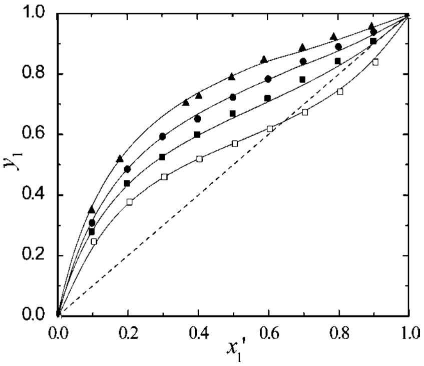

Figure 6. Isobaric VLE diagram for methyl acetate (1) + methanol (2) + [EMIM][Ac] (3) system at 101.3 kPa: □, x_3 = 0; ■, x_3 = 0.1; ●, x_3 = 0.2; ▲, x_3 = 0.3; solid lines, calculated by the NRTL model; dashed line, $y_1 = x_1'$.

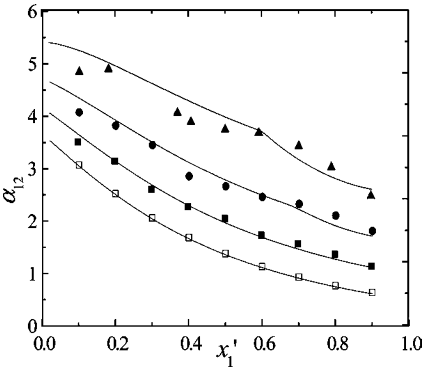

Figure 7. Relative volatility of methyl acetate (1) to methanol (2) at 101.3 kPa: □, x_3 = 0; ■, x_3 = 0.1; ●, x_3 = 0.2; ▲, x_3 = 0.3; solid lines, calculated by the NRTL model.

liquid phase excluding IL, y_1 is mole fraction of methyl acetate in the vapor phase, T is the equilibrium temperature, α_{12} is the relative volatility of methyl acetate and methanol. Since the vapor pressure of IL is very low, there are only methyl acetate and methanol in the vapor phase.

Since the liquid mixture of methyl acetate (1) + methanol (2) + [EMIM][Ac] (3) can form liquid−liquid equilibrium even at relative high temperature (such as 343.15 K, see Figure 5), a vapor−liquid−liquid equilibrium will form in some cases. The VLE data of the ternary system were measured at about (330 to 343) K (in such temperatures, the two liquids region in the ternary LLE diagram was small) and the concentrations of ionic liquid in liquid phase were low; most of the data points were in the vapor−liquid equilibrium, and only a few data points formed vapor−liquid−liquid equilibrium (VLLE). Actually only when the concentration of IL was high and the concentration of methanol was low could vapor−liquid−liquid equilibrium be formed. The VLLE data points in Table 4 are labeled, and in such cases, x_1' is the mole fraction of methyl acetate excluding IL considering the two liquids as a whole.

The VLE of the ternary system were predicted by a VLLE calculation program, because VLLE could be formed in the mixture of methyl acetate (1) + methanol (2) + [EMIM][Ac] (3) in some cases. The binary interaction parameters of the NRTL model obtained from LLE data were used to predict the vapor−liquid equilibrium of the ternary system, and the results are shown in Figures 6−8. In these figures the solid lines are calculated by the NRTL model, and the binary interaction parameters obtained from LLE data were used.

Figures 6−8 show that the calculated results agree well with the experimental results. The mean absolute deviations between the experimental and calculated values of vapor-phase mole fractions and the equilibrium temperature for ternary systems are given in Table 5.

Figure 6 shows the ability of IL ([EMIM][Ac]) to increase the relative volatility of methyl acetate to methanol, which indicates a salting-out effect for methyl acetate. Since the interaction between methyl acetate and [EMIM][Ac] is less than that between methanol and [EMIM][Ac], the relative volatility of methyl acetate to methanol can be increased by [EMIM][Ac]. The azeotropic point can be totally eliminated if enough IL ([EMIM][Ac]) is added. The relative volatility of methyl acetate to methanol increases with the concentration of [EMIM][Ac] in the liquid phase, as shown in Figure 7.

Orchillés et al. used [EMIM][triflate] as an entrainer for the separation of methyl acetate + methanol and measured the VLE of the system.[18] They found the minimum mole fraction of IL ([EMIM][triflate]) to eliminate the azeotropic point was 0.129 at 100 kPa. We used [EMIM][Ac] as the entrainer to separate methyl acetate + methanol. The minimum mole fraction of [EMIM][Ac] is estimated to be 0.087 at 100 kPa, which is lower than that of [EMIM][triflate]. The comparison of [EMIM][triflate] with [EMIIM][Ac] is made in Figure 9. In this figure, all solid lines are calculated by the NRTL model.

Figure 9 shows that [EMIM][Ac] exhibits a higher selectivity at x_3 = 0.30 than that of [EMIM][triflate]. The difference of the selectivity results from the different anions in IL. [EMIM][triflate] is totally miscible in methyl acetate and methanol, while [EMIM][Ac] is miscible in methanol but partially miscible in methyl acetate. This indicates that the interaction between [EMIM][Ac] and methyl acetate is weaker than that between [EMIM][triflate] and methyl acetate. The interactions of [EMIM][Ac] and [EMIM][triflate] to methanol are both strong. Therefore, the selectivity of [EMIM][Ac] is larger than that of [EMIM][triflate] for the separation of methyl acetate + methanol by extractive distillation.

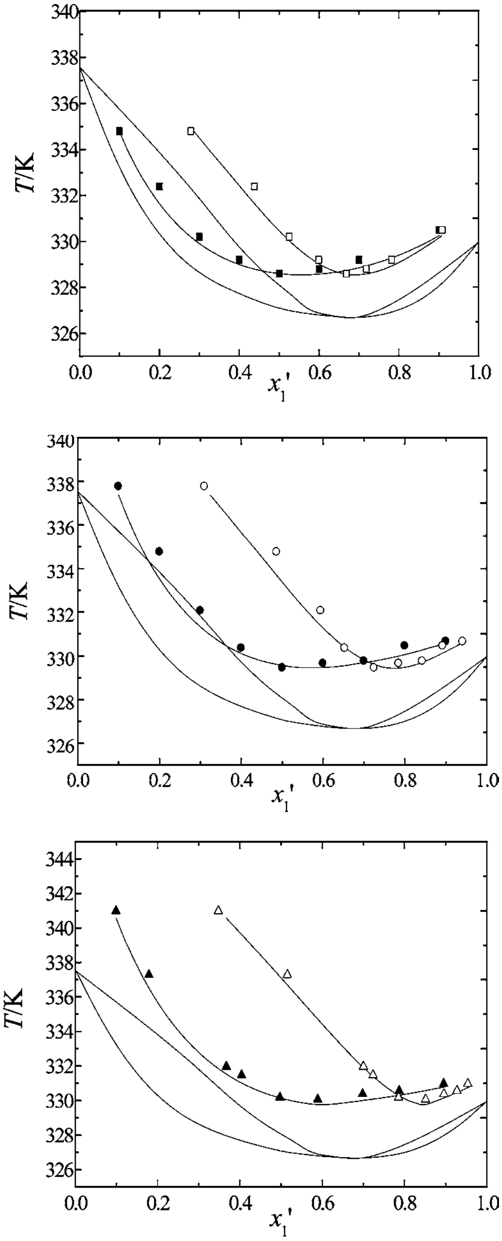

Figure 8. *T*, *x*, *y* diagram for the ternary system of methyl acetate (1) + methanol (2) containing [EMIM][Ac] (3) at different contents of IL: ■, x_1' ($x_3 = 0.1$); □, y_1 ($x_3 = 0.1$); ●, x_1' ($x_3 = 0.2$); ○, y_1 ($x_3 = 0.2$); ▲, x_1' ($x_3 = 0.3$); △, y_1 ($x_3 = 0.3$); solid lines, calculated by the NRTL model.

Table 5. Mean Absolute Deviations σy and σT and Standard Deviations $\delta y'$ and $\delta T'$ between Experimental and Calculated Values of the Vapor-Phase Mole Fractions and the Equilibrium Temperatures[a]

system	σy	$\delta y'$	σT/K	$\delta T'$/K
methyl acetate (1) + methanol (2)	0.003	0.001	0.143	0.062
methyl acetate (1) + methanol (2) + [EMIM][Ac] (3)	0.012	0.006	0.245	0.164

[a] $\sigma y = (1/N)\Sigma|y_{\text{exptl}} - y_{\text{calcd}}|$; $\delta y' = [1/(N-1)][\Sigma(y_{\text{exptl}} - y_{\text{calcd}})^2]^{1/2}$; $\sigma T/\text{K} = (1/N)\Sigma|T_{\text{exptl}} - T_{\text{calcd}}|$; $\delta T'/\text{K} = [1/(N-1)]\,[\Sigma(T_{\text{exptl}} - T_{\text{calcd}})^2]^{1/2}$.

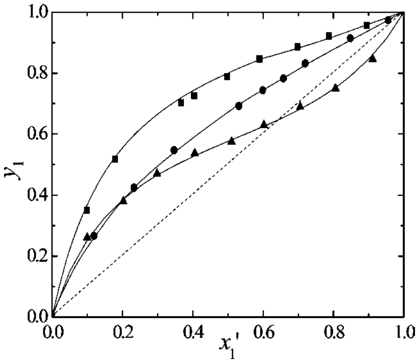

Figure 9. Salting-out effect of [EMIM][Ac] and [EMIM][triflate] on the vapor−liquid equilibrium of the methyl acetate (1) + methanol (2) system at 100 kPa for an IL mole fraction of $x_3 = 0.3$: ●, [EMIM][triflate] (ref 18); ■, [EMIM][Ac]; ▲, IL-free system; solid lines, calculated by NRTL model; dash line, $y_1 = x_1'$.

Conclusions

The isobaric VLE and LLE of the ternary mixture methyl acetate + methanol + [EMIM][Ac] were measured. The results show that the addition of the IL ([EMIM][Ac]) to the methyl acetate + methanol mixture produces a noticeable salting-out effect on methyl acetate. And the salting-out effect of [EMIM][Ac] increases with the concentration of [EMIM][Ac] in the liquid phase.

The NRTL model was used to correlate the LLE data for methyl acetate + methanol + [EMIM][Ac], and the binary interaction parameters obtained from LLE data were utilized to predict the vapor−liquid equilibrium of the ternary system. The calculated results for VLE of methyl acetate + methanol + [EMIM][Ac] agree well with the experimental results.

[EMIM][Ac] is a promising entrainer for the separation of methyl acetate + methanol mixture[25] by extractive distillation. The azeotropic point of methyl acetate + methanol can be eliminated if the mole fraction of [EMIM][Ac] in the liquid phase is larger than 0.087.

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