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

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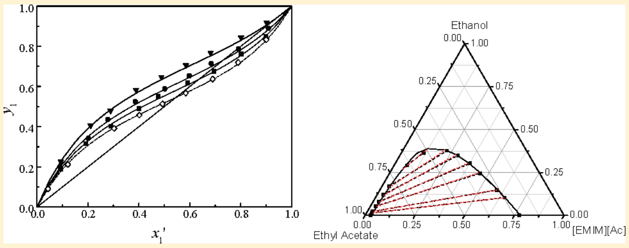
ABSTRACT: The vapor−liquid equilibrium (VLE) and liquid−liquid equilibrium (LLE) of the ternary system of ethyl acetate + ethanol + 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]), together with the vapor−liquid−liquid equilibrium (VLLE) for the binary system of ethyl acetate + [EMIM][Ac], were measured. The experimental VLE, LLE, and VLLE data were correlated by the nonrandom two-liquid (NRTL) equation, and the calculated results agreed well with the experimental results. The VLE and VLLE results show that [EMIM][Ac] can enhance the relative volatility of ethyl acetate to ethanol, and the azeotrope of ethyl acetate + ethanol can be eliminated. The LLE data indicate that [EMIM][Ac] is a potential solvent for the separation of ethyl acetate + ethanol via liquid−liquid extraction.



INTRODUCTION

Ionic liquids (ILs) are organic salts composed of organic cations and organic or inorganic anions with special properties, such as negligible vapor pressure at room temperature and atmospheric pressure, high thermal and chemical stability, low flammability, solubility in polar and nonpolar compounds, and high conductivity and large electrochemical windows.[1,2] Due to their special properties, ILs are promising solvents for separation processes such as extractive distillation and liquid−liquid extraction.[3−25] Vapor−liquid equilibrium (VLE) and liquid−liquid equilibrium (LLE) data are essential for the development of the new separation process and predictive thermodynamic model; however, VLE and LLE data for systems including ILs are not enough up to now.

In many chemical processes, alkanol + ester systems must be separated to obtain pure alcohol and pure ester. For example, in the esterification process, such as the esterification of methanol, ethanol, 1-propanol, and 1-butanol with acetic acid to obtain methyl acetate, ethyl acetate, 1-propyl acetate, and 1-butyl acetate, the reactant alkanol must be separated from the product ester. Ethyl acetate and ethanol form a minimum-boiling azeotrope at atmospheric pressure, and the conventional methods to separate the azeotrope are azeotropic distillation,[26] extractive distillation,[27] extractive dehydration,[28] and membrane separation.[29] Recently, some scholars focused on the separation of ethyl acetate and ethanol using ILs as entrainers and solvents. Orchillés et al. and Li et al.[30−32] separated the azeotrope via extractive distillation with ILs as entrainers; they measured the isobaric VLE of ethyl acetate + ethanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][triflate]) and ethyl acetate + ethanol + 1-alkyl-3-methylimidazolium tetrafluoroborate at 101.3 kPa (alkyl = ethyl, butyl, octyl). Zhang et al.[33] and Hu et al.[34] separated the azeotropic mixture via extraction with ILs as solvents.

In our previous paper, we found that 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]) was an effective entrainer or solvent for the separation of azeotropic mixture of methyl acetate + methanol.[16] Since the systems of methyl acetate+ methanol and ethyl acetate + ethanol are similar, [EMIM][Ac] may be an potential entrainer or solvent for the separation of ethyl acetate + ethanol. The infinite dilution activity coefficients of ethyl acetate and ethanol in [EMIM][Ac] were calculated by COSMO-SAC,[35,36] and it was found that [EMIM][Ac] was also a potential effective entrainer or solvent for the separation of ethyl acetate + ethanol.

In this paper, the VLE and LLE of ethyl acetate + ethanol + [EMIM][Ac], together with the vapor−liquid−liquid equilibrium (VLLE) of ethyl acetate + [EMIM][Ac], were measured. The VLE, VLLE, and LLE data were correlated by the nonrandom two-liquid (NRTL) equation. Furthermore, the effects of entrainers [EMIM][Ac] 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][triflate])[30] and 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM][BF_4])[37] to the system of ethyl acetate + ethanol were also compared.

EXPERIMENTAL SECTION

Materials. Ethanol and ethyl acetate were purchased from Jiangtian Chemical Reagents Co., Tianjin (China), with a purity of above 0.997. Their purities were checked by gas chromatography (SP-1000, China). The IL [EMIM][Ac] was provided by Chengjie Chemical Reagents Co., Shanghai (China), with a minimum mass fraction of 0.99, observed by liquid chromatography (Waters 490E). The water mass fraction in ILs determined by Karl Fischer titration was less than 0.0001.

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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 0.1 mg.

The VLE data were measured by a circulation VLE still (a modified Othmer still). The details about this apparatus were described in our previous publications.[16] The equilibrium temperature was measured by a precision and calibrated thermometer with a standard uncertainty of 0.06 K. The pressure was measured by manometer with a standard uncertainty of 0.05 kPa.

The VLLE data were first measured by the same apparatus as for VLE measurements, but the equilibrium temperature oscillated sometimes. Gomis et al. found that circulation equilibrium stills were not useful for systems of limited miscibility in the liquid phase, because of the mass transfer problems in two liquid phases.[17] To obtain more reliable equilibrium temperatures for VLLE, another equilibrium still (Figure 1) with a stirrer was used, and the stirrer could enhance the mass transfer between the two liquid phases.[38]

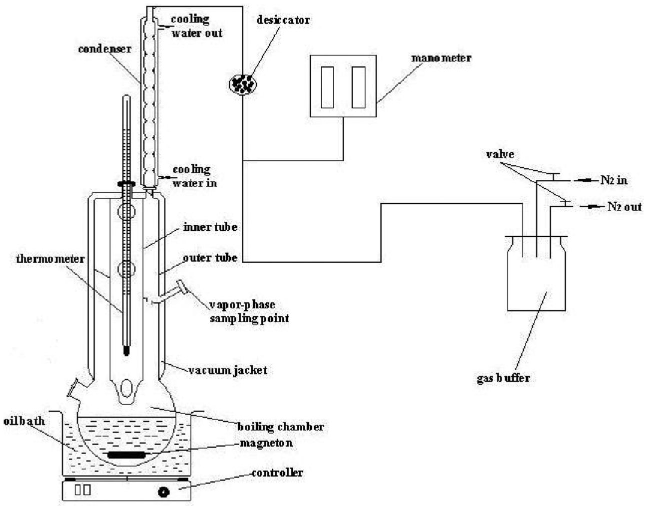

Figure 1. Apparatus for VLLE experiments.

In this apparatus, the oil bath was used to heat the system, and the equilibrium temperature was measured by a precision and calibrated thermometer. A given liquid solution was prepared gravimetrically and put into the boiling chamber. The liquid was stirred by a magnetic stirrer and heated by the oil bath. The vapor passed through the elliptical holes near the bottom of the inner tube and went out from the circle holes at the top of inner tube, then condensed by the condenser and returned to the boiling chamber. Equilibrium was reached indicating by constant temperature, and the system continuously maintained in the equilibrium state for 30 min.

The limited miscible system of cyclohexane + water was used to check the accuracy of this instrument. A series of solutions with the mass fractions of cyclohexane 0.300, 0.401, and 0.508, respectively, were prepared gravimetrically and put into the boiling chamber. The experimental temperatures of VLLE for the system were 342.61 K, 342.64 K, and 342.60 K respectively, and the standard uncertainty is 0.07 K. Verhoeye[39] reported that the azeotropic point for cyclohexane + water was 342.55 K. It indicated that this instrument could be used to measure equilibrium temperatures for VLLE. The VLLE of binary limited miscible mixture of ethyl acetate + [EMIM][Ac] was measured by the equilibrium still (Figure 1), and the standard uncertainty of temperature was below 0.07 K. The samples of vapor phase were taken from the vapor-phase sampling point and analyzed by high-performance liquid chromatography (HPLC). Because the composition in the liquid phase (considering the two liquid phases as a whole) is important, but the two liquid phases are difficult to be taken accurately from the still, the initial composition of the solution added to the still (feed composition) can be considered as the liquid composition. Since the volume of condensed vapor in vapor phase sampling point is only 0.5 % of the total solution added to the still (feed), the feed composition stands for the liquid composition in the still.

The LLE data were measured by a self-designed apparatus, and the details of the apparatus were also described in our previous publication.[16]

Sample Analysis. For the samples in VLE and VLLE, the mole fractions of ethyl acetate, ethanol, and the IL ([EMIM][Ac]) were analyzed by a HPLC (waters 490E) equipped with a differential refractive index detector and a C_{18} column. The mobile phase of HPLC is methanol + water (v/v = 1:1). If the mole fraction of IL ([EMIM][Ac]) in the ternary mixture is less than 0.12, ethyl acetate, ethanol, and IL were completely separated in a C_{18} column. In VLE and VLLE measurements, the mole fraction of [EMIM][Ac] in liquid phase is less than or equal to 0.10, and its composition in vapor phase can be neglected, so the analytical method described above can be used. The area normalization method was used with response factors to calculate the compositions of ethyl acetate, ethanol, and IL in the sample. The method was evaluated by a set of gravimetrically prepared solutions. The expanded uncertainty of the HPLC composition analysis was below 0.005 (mole fraction, with 95 % confidence).

For the samples in LLE, gas chromatography (GC) and HPLC were both used. The compositions of ethyl acetate and ethanol were analyzed by GC, while the composition of ethyl acetate and IL were analyzed by HPLC. The gas chromatography (SP-1000, China) was equipped with a flame ionization (FID) detector and a SE-30 column. The area normalization method was used with response factors to calculate the compositions of ethyl acetate and ethanol in the samples (excluding IL). The GC method was evaluated by a set of gravimetrically prepared solutions. The expanded uncertainty of the GC analysis was below 0.004 (mole fraction, with 95 % confidence). The compositions of ethyl acetate and IL were analyzed by HPLC with an ultraviolet detector. The ultraviolet detector wavelength was 240 nm, and the mobile phase was the same as that mentioned above. A calibration curve was obtained by a set of standard solutions prepared gravimetrically. The expanded uncertainty of the HPLC composition analysis was below 0.006 (mole fraction, with 95 % confidence). In this way, the mole ratio of the IL to ethyl acetate was calculated by the HPLC, while the mole ratio of ethyl acetate to ethanol was obtained by GC, so that the mole fractions of ethyl acetate, ethanol, and IL in the LLE samples were calculated, respectively.

RESULTS AND DISCUSSION

Experimental Data. The LLE of the ternary system ethyl acetate (1) + ethanol (2) + [EMIM][Ac] (3) was measured at 288.15 K, 299.15 K, and 308.15 K, respectively. The LLE data

Table 1. Liquid−Liquid Equilibrium Data for Ethyl Acetate (1) + Ethanol (2) + [EMIM][Ac] (3) at T = 288.15 K, 299.15 K, and 308.15 K[a]

	raffinate phase			extract phase				
T/K	x_1^R	x_2^R	x_3^R	x_1^E	x_2^E	x_3^E	β	S
288.15	0.970	0.000	0.030	0.206	0.000	0.794		
288.15	0.960	0.010	0.031	0.232	0.098	0.670	9.800	40.552
288.15	0.944	0.027	0.029	0.261	0.202	0.537	7.481	27.059
288.15	0.912	0.059	0.029	0.298	0.301	0.401	5.102	15.613
288.15	0.821	0.149	0.030	0.374	0.401	0.225	2.691	5.908
288.15	0.770	0.196	0.034	0.411	0.412	0.176	2.102	3.938
288.15	0.670	0.281	0.049	0.491	0.398	0.111	1.416	1.933
288.15	0.620	0.320	0.060	0.535	0.376	0.089	1.175	1.362
299.15	0.974	0.000	0.027	0.224	0.000	0.776		
299.15	0.960	0.014	0.026	0.247	0.104	0.649	7.429	28.872
299.15	0.950	0.023	0.027	0.263	0.148	0.589	6.435	23.244
299.15	0.919	0.054	0.027	0.298	0.246	0.456	4.556	14.049
299.15	0.893	0.079	0.028	0.320	0.304	0.376	3.848	10.739
299.15	0.848	0.121	0.031	0.358	0.350	0.292	2.893	6.852
299.15	0.795	0.169	0.036	0.399	0.377	0.223	2.231	4.445
299.15	0.645	0.291	0.064	0.523	0.365	0.112	1.254	1.547
308.15	0.960	0.000	0.040	0.226	0.000	0.774		
308.15	0.953	0.006	0.042	0.240	0.050	0.710	8.333	33.090
308.15	0.937	0.022	0.041	0.271	0.151	0.578	6.864	23.731
308.15	0.908	0.053	0.039	0.311	0.252	0.437	4.755	13.882
308.15	0.881	0.080	0.039	0.339	0.302	0.359	3.775	9.811
308.15	0.825	0.133	0.042	0.387	0.353	0.260	2.654	5.658
308.15	0.725	0.220	0.055	0.469	0.367	0.164	1.668	2.579
308.15	0.625	0.295	0.080	0.558	0.336	0.106	1.139	1.276

[a] Standard uncertainties u_C is $u_C(T)$ = 0.07 K, and the combined expanded uncertainty U are $U(x^R) = U(x^E) = 0.007$ (95 % level of confidence).

for ethyl acetate (1) + ethanol (2) + [EMIM][Ac] (3) were listed in Table 1. In Table 1, x_1^E, x_2^E, and x_3^E represent the mole fractions of ethyl acetate, ethanol, and IL in extract phase; x_1^R, x_2^R, and x_3^R represent the mole fractions of ethyl acetate, ethanol, and IL in the raffinate phase, respectively.

The VLE of the ternary system ethyl acetate (1) + ethanol (2) + [EMIM][Ac] (3) was measured at 101.30 kPa. The concentration of IL in the liquid phase in the ternary system was kept approximately at x_3 = 0.025, 0.05, and 0.1 (mole fraction), respectively.

Experimental isobaric VLE data of the ternary system of ethyl acetate (1) + ethanol (2) + [EMIM][Ac] (3) are shown in Table 2. In Table 2, x_3 represents the mole fraction of IL in the liquid phase, and T represents the equilibrium temperature in the ternary system; x_1' is the mole fraction of ethyl acetate in the liquid phase excluding IL. y_1 is the mole fraction of ethyl acetate in vapor phase, and α_{12} is the relative volatility of ethyl acetate to ethanol. Because of the negligible vapor pressure of IL, the IL does not exist in the vapor phase. In Table 2, most of data points are in VLE, and only a few data points are in VLLE. The VLLE data points in Table 2 are labeled, and x_1' is the mole fraction of ethyl acetate excluding ILs considering the two liquid phases as a whole.

Correlation of Phase Equilibrium. The NRTL equation was often used in correlation of VLE and LLE with ILs. Li and co-workers,[37] Shiflett and Yokozeki,[40] and Cai et al.[16,18] used the NRTL equation to correlate the VLE and LLE systems containing ILs, and the correlation results agreed well with the experimental results. Here, we also use the NRTL equation to correlate the experimental data. The NRTL equation is as follows:

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

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

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

where B_{ji} is the binary interaction parameter, K; a_{ji} is the nonrandomness parameter; T is the temperature, K.

In this work, the binary interaction parameters (B_{12}, B_{21}) of the NRTL equation and the nonrandomness (α_{12}) were obtained from the database in software CHEMCAD and the other binary interaction parameters (B_{13}, B_{31}, B_{23}, B_{32}) and the nonrandomness parameters (a_{13}, a_{23}) were correlated from VLE, VLLE, and LLE data by the minimization of the objective function F:

$$F = \sum_{j=1}^{N}\left\{\sum_{i=1}^{C}(x_{j,i}^{\mathrm{cal,E}} - x_{j,i}^{\mathrm{ex,E}})^2 + \sum_{i=1}^{C}(x_{j,i}^{\mathrm{cal,R}} - x_{j,i}^{\mathrm{ex,R}})^2 + \left(\frac{T_j^{\mathrm{cal}} - T_j^{\mathrm{ex}}}{1000}\right)^2 + \sum_{i=1}^{C}(y_{j,i}^{\mathrm{cal}} - y_{j,i}^{\mathrm{ex}})^2\right\}$$

Table 2. Vapor−Liquid Equilibrium Data for the Ternary System Ethyl Acetate (1) + Ethanol (2) + [EMIM][Ac] (3) System at 101.30 kPa[a]

x_3	T/K	x_1'	y_1	α_{12}
0.025	352.25	0.000	0.000	
0.025	349.07	0.093	0.190	2.288
0.025	347.35	0.192	0.316	1.944
0.025	346.36	0.290	0.402	1.646
0.025	345.86	0.400	0.490	1.441
0.026	345.75	0.476	0.550	1.345
0.026	345.76	0.591	0.619	1.124
0.025	346.18	0.695	0.675	0.911
0.025	347.14	0.802	0.762	0.790
0.025	348.13	0.898	0.850	0.644
0.026	350.13	1.000[b]	1.000	
0.050	353.36	0.000	0.000	
0.051	350.15	0.091	0.198	2.466
0.049	348.07	0.202	0.342	2.053
0.051	346.98	0.278	0.436	2.008
0.051	346.36	0.386	0.525	1.758
0.051	346.31	0.502	0.588	1.416
0.051	346.33	0.598	0.653	1.265
0.050	346.88	0.684	0.714	1.153
0.050	347.65	0.791	0.786	0.970
0.050	348.81	0.909	0.890	0.810
0.051	350.12	1.000[b]	1.000	
0.100	354.89	0.000	0.000	
0.100	351.61	0.094	0.227	2.830
0.110	349.25	0.211	0.406	2.556
0.105	348.24	0.289	0.480	2.271
0.110	347.36	0.389	0.583	2.196
0.101	347.18	0.489	0.648	1.924
0.109	347.44	0.585	0.706	1.704
0.105	347.77	0.682	0.768	1.544
0.108	348.92	0.801	0.844	1.344
0.102	349.95	0.902	0.919	1.233
0.099	350.12	1.000[b]	1.000	

[a] Standard uncertainties u_C are $u_C(P)$ = 0.05 kPa, $u_C(T)$ = 0.07 K, and the combined expanded uncertainty U_c are $U_c(x_3) = U_c(x_1') = U_c(y_1)$ = 0.005 (95 % level of confidence). [b] Vapor−liquid−liquid equilibrium.

where N is the number of data points; C is the number of components; the superscripts E and R represent the extract phase and raffinate phase, respectively; T represents the temperature of VLE or VLLE; y represents the vapor composition of VLE or VLLE; Superscripts cal and ex represent the calculated and experimental values, respectively. Since the values of temperatures are large, they are divided by 1000 to get the same order as those of liquid or vapor compositions. The correlated results are listed in Table 3.

Table 3. Binary Interaction Parameters B_{ij} and B_{ji} and Nonrandomness Parameters a_{ij} in the NRTL Equation

i component	j component	a_{ij}	B_{ij}/K	B_{ji}/K
ethyl acetate (1)	ethanol (2)	0.299	154.208	162.349
ethyl acetate (1)	[EMIM][Ac] (3)	0.086	1460.048	−371.4852
ethanol (2)	[EMIM][Ac] (3)	0.351	54.16021	−555.4942

The feasibility of using ILs as a solvent to separate the azeotrope via liquid−liquid extraction was evaluated by the distribution coefficient (β) and selectivity (S). These parameters were defined as:

$$\beta = \frac{x_2^{\mathrm{E}}}{x_2^{\mathrm{R}}} \tag{4}$$

$$S = \frac{x_2^{\mathrm{E}}\,x_1^{\mathrm{R}}}{x_2^{\mathrm{R}}\,x_1^{\mathrm{E}}} \tag{5}$$

where x is the mole fraction, superscripts E and R refer to the extract phase and raffinate phase, respectively, and subscripts 1 and 2 refer to ethyl acetate and ethanol, respectively. The values of β and S are shown in Table 1, together with the experimental equilibrium data.

As shown in Table 1, the selectivity of [EMIM][Ac] is larger than 10, if the mole fraction of ethanol in raffinate phase is less than 0.1. It indicates that [EMIM][Ac] is a promising solvent. Hu et al.[34] found that [C_2OHmim][BF_4] (1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate) was a potentially candidate to separate ethyl acetate and ethanol by liquid−liquid extraction. We compared the selectivity of [EMIM][Ac] with [C_2OHmim][BF_4], and the result is shown in Figure 2. In Figure 2, x_2 refers to the mole fraction of ethanol in the raffinate phase. As shown in Figure 2, the selectivity of [EMIM][Ac] is much larger than that of [C_2OHmim][BF_4], if the mole fraction of ethanol in raffinate phase is less than 0.2.

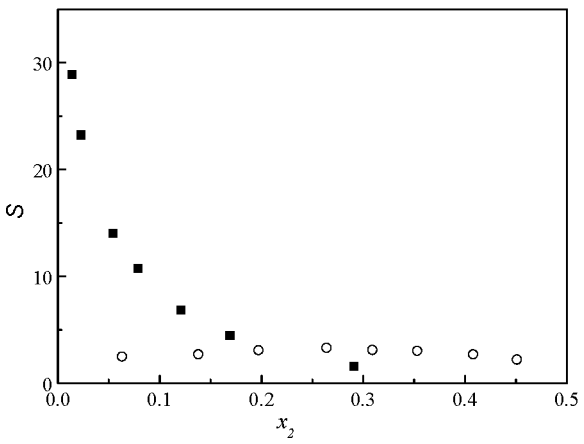

Figure 2. Comparison of selectivity of [C_2OHmim][BF_4] and [EMIM][Ac]: ○, [C_2OHmim][BF_4]; ■, [EMIM][Ac].

The ternary LLE diagrams at different temperatures are plotted in Figure 3, and the experimental and correlated results of VLE and VLLE are shown in Figures 4 to 6. The correlated values agree well with the experimental values. The mean absolute deviation and standard deviation of the extract phase and the raffinate phase σx^{E}, δx^{E}, σx^{R}, and δx^{R} ($\sigma x^{\mathrm{E}} = (1/NC)\sum_{j=1}^{N}\sum_{i=1}^{C}|x_{j,i}^{\mathrm{E,cal}} - x_{j,i}^{\mathrm{E,ex}}|$; $\delta x^{\mathrm{E}} = [(1/NC)\sum_{j=1}^{N}\sum_{i=1}^{C}(x_{j,i}^{\mathrm{E,cal}} - x_{j,i}^{\mathrm{E,ex}})^2]^{1/2}$; $\sigma x^{\mathrm{R}} = (1/NC)\sum_{j=1}^{N}\sum_{i=1}^{C}|x_{j,i}^{\mathrm{R,cal}} - x_{j,i}^{\mathrm{R,ex}}|$; $\delta x^{\mathrm{R}} = [(1/NC)\sum_{j=1}^{N}\sum_{i=1}^{C}(x_{j,i}^{\mathrm{R,cal}} - x_{j,i}^{\mathrm{R,ex}})^2]^{1/2}$) are 0.011, 0.017, 0.011, and 0.016, respectively. The mean absolute deviation and standard deviation of vapor phase mole fraction σy_1 and δy_1 ($\sigma y_1 = (1/N)\sum|y_1^{\mathrm{ex}} - y_1^{\mathrm{cal}}|$; $\delta y_1 = \{\sum(y_1^{\mathrm{ex}} - y_1^{\mathrm{cal}})^2/(N-1)\}^{1/2}$) are 0.005 and 0.007, respectively. The mean absolute deviation and standard deviation of equilibrium temperature σT and δT ($\sigma T = (1/N)\sum|T^{\mathrm{ex}} - T^{\mathrm{cal}}|$; $\delta T = \{\sum(T^{\mathrm{ex}} - T^{\mathrm{cal}})^2/(N-1)\}^{1/2}$) are 0.26 and 0.46 K, respectively.

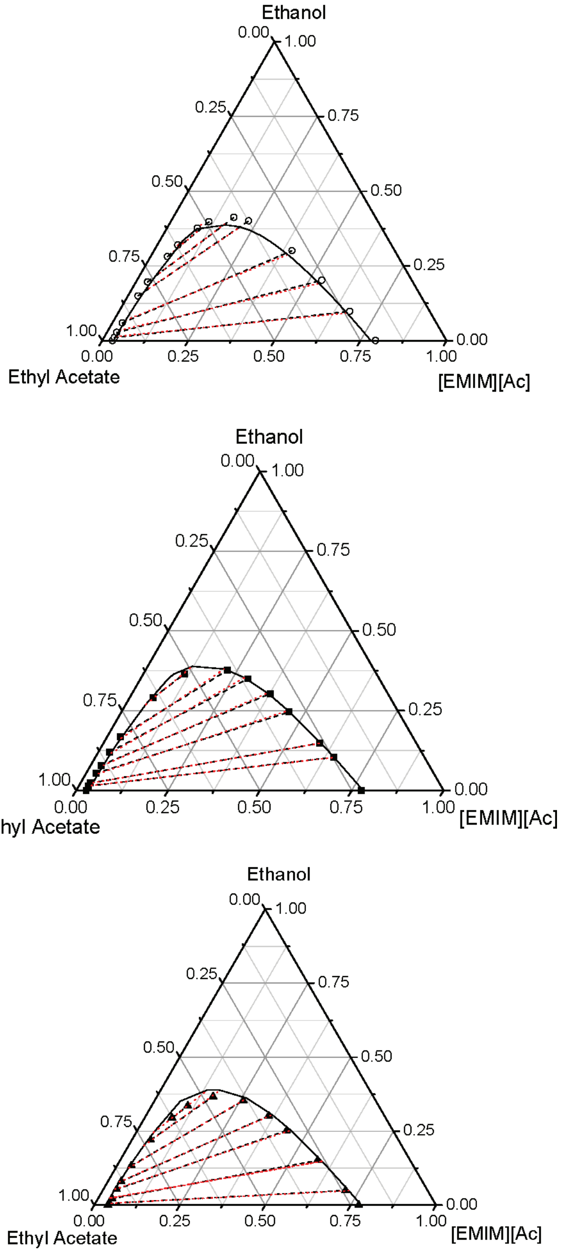

Figure 3. LLE of ethyl acetate (1) + ethanol (2) + [EMIM][Ac] (3) at different temperatures: ○ 288.15 K; ■, 299.15 K; ▲, 308.15 K;. Solid line, solubility line correlated by the NRTL equation; dashed line, experimental tie lines; dotted line, calculated tie lines.

In Figure 4, the mole fraction of ethyl acetate in the vapor phase increases with the concentration of IL in the liquid phase. The azeotrope of ethyl acetate−ethanol will disappear if enough IL [EMIM][Ac] is added. It indicates that the IL ([EMIM][Ac]) produces a salting-out effect for ethyl acetate, so that the relative volatility of ethyl acetate to ethanol can be enhanced by [EMIM][Ac] (see Figure 6). This phenomena are attributed to the interaction between ethyl acetate and [EMIM][Ac] which is less than that between ethanol and [EMIM][Ac].

Li and co-workers[31] investigated the effects of ILs [EMIM]-[BF$_4$], [BMIM][BF$_4$], and [OMIM][BF$_4$] to the system of ethyl acetate + ethanol, and they found that the separation ability of ILs is in the order of [EMIM]$^+$[BF$_4$]$^-$ > [BMIM]$^+$[BF$_4$]$^-$ > [OMIM]$^+$[BF$_4$]$^-$ at low IL concentrations, while at high IL

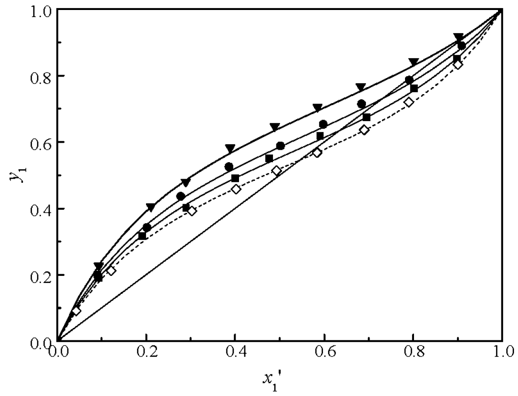

Figure 4. Isobaric VLE diagram for the ternary system of ethyl acetate (1) + ethanol (2) + [EMIM][Ac] at 101.30 kPa: ■, experimental for $x_3 \approx 0.025$; ●, experimental for $x_3 \approx 0.05$; ▼, experimental for $x_3 \approx 0.1$; ◇, experimental for $x_3 = 0$;[30] solid and dashed line, calculated by the NRTL equation.

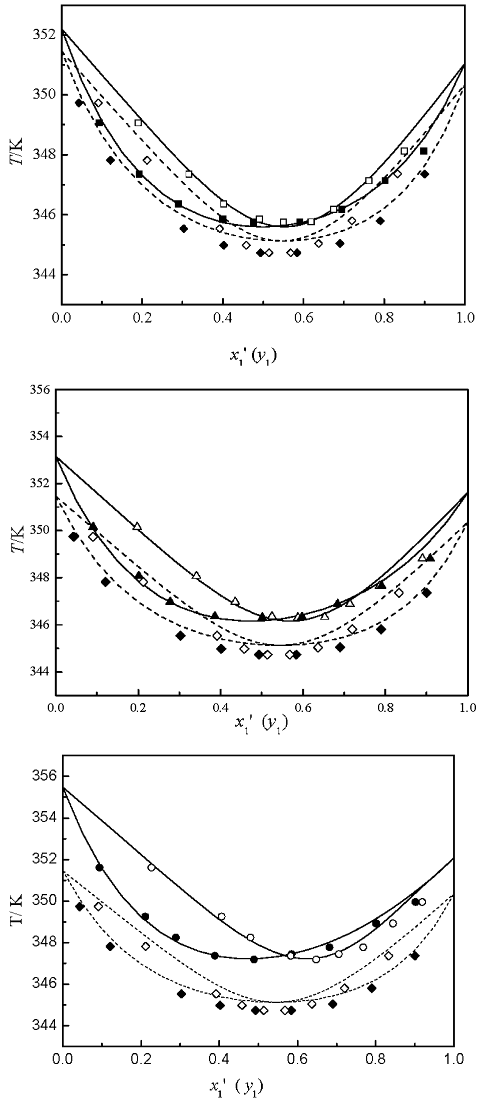

Figure 5. T, x, y diagram for the ternary system of ethyl acetate (1) + ethanol (2) + [EMIM][Ac] (3) at different concentrations of IL: ■, x_1' (experimental for $x_3 \approx 0.025$); □, y_1 (experimental for $x_3 \approx 0.025$); ▲, x_1' (experimental for $x_3 \approx 0.05$); △, y_1 (experimental for $x_3 \approx 0.05$); ●, x_1' (experimental for $x_3 \approx 0.1$); ○, y_1 (experimental for $x_3 \approx 0.1$); ◆, x_1 (experimental for $x_3 = 0$[30]), ◇, y_1 (experimental for $x_3 = 0$[30]); solid and dashed lines, calculated by the NRTL equation.

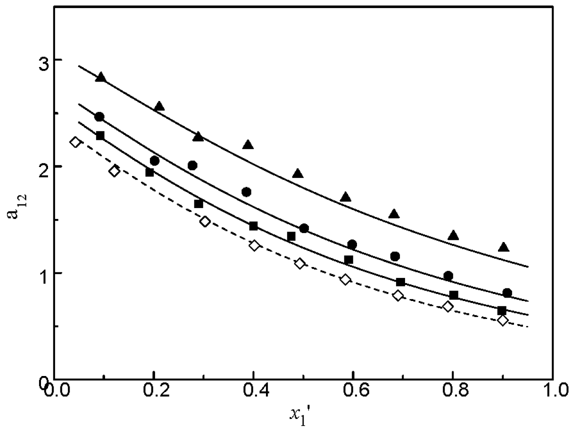

Figure 6. Relative volatility of ethyl acetate (1) to ethanol (2) at 101.30 kPa: ■, experimental for $x_3 \approx 0.025$; ●, experimental for $x_3 \approx 0.05$; ▲, experimental for $x_3 \approx 0.1$; ◇, experimental for $x_3 = 0$;[30] solid and dashed lines, calculated by the NRTL equation.

concentrations (x_3 = 0.10−0.30), the separation ability of ILs is in the order of $[OMIM]^+[BF_4]^-$ > $[EMIM]^+[BF_4]^-$ > $[BMIM]^+[BF_4]^-$. Orchillés et al.[30] also reported the effects of IL [EMIM][triflate] to the system of ethyl acetate + ethanol. They reported that the minimum mole fractions of [OMIM]-$[BF_4]$[31] and [EMIM][triflate][30] to eliminate the azeotropic point were 0.1 and 0.2 at about 101.30 kPa, respectively. We used the [EMIM][Ac] as the entrainer for the same system, and the effects of [OMIM]$[BF_4]$, [EMIM][triflate], and [EMIM][Ac] are compared in Figure 7. The minimum mole fraction of IL ([EMIM][Ac]) in the liquid phase to eliminate the azeotrope was 0.1 at 101.30 kPa (calculated by NRTL equation), which was equal to that of [OMIM]$[BF_4]$ and less than that of [EMIM][triflate].

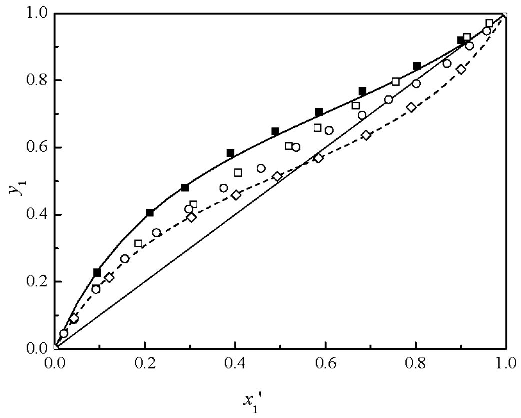

Figure 7. Salting-out effect of [EMIM][Ac], [EMIM][triflate], and [OMIM] $[BF_4]$ on ethyl acetate (1) + ethanol (2) system at 101.30 kPa (mole fraction of IL 0.1): □, experimental for [OMIM]$[BF_4]$;[35] ○, experimental for [EMIM][triflate];[29] ■, experimental for [EMIM]-[Ac]; ◇, experimental for $x_3 = 0$;[30] solid line, [EMIM][Ac], calculated by NRTL equation; dashed line, calculated by NRTL equation without ILs.

■ CONCLUSIONS

The LLE and VLE of ethyl acetate (1) + ethanol (2) + [EMIM][Ac] (3), together with the VLLE of ethyl acetate (1) + [EMIM][Ac](3), were measured. The results show that the IL [EMIM][Ac] produces a notable salting-out effect on ethyl acetate. The azeotrope of ethyl acetate + ethanol can be eliminated when the mole fraction of [EMIM][Ac] is larger than 0.1.

The NRTL equation was used to correlate the LLE data, the VLE data, and the VLLE data simultaneously, and the calculated data agreed well with those of the experiment.

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Notes

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■ REFERENCES

(1) Wang, J. F.; Li, Z. B.; Li, C. X.; Wang, Z. H. Density Prediction of Ionic Liquids at Different Temperatures and Pressures Using a Group Contribution Equation of State Based on Electrolyte Perturbation Theory. *Ind. Eng. Chem. Res.* **2010**, *49*, 4420−4425.

(2) Rogers, R. D.; Voth, G. A. Ionic Liquids. *Acc. Chem. Res.* **2007**, *40*, 1077−1078.

(3) Jork, C.; Seiler, M.; Beste, Y.; Arlt, W. Influence of Ionic Liquids on the Phase Behavior of Aqueous Azeotropic Systems. *J. Chem. Eng. Data* **2004**, *49*, 852−857.

(4) Arlt, W.; Seiler, M.; Jork, C.; Schneider, T. Ionic Liquids as Selective Additives for the Separation of Close-Boiling or Azeotropic Mixtures. *PCT Int. Appl.* WO 02/074718 A2, 2002.

(5) Seiler, M.; Jork, C.; Kavarnou, A.; Arlt, W.; Hirsch, R. Separation of Azeotropic Mixtures Using Hyperbranched Polymers or Ionic Liquids. *AIChE J.* **2004**, *50*, 2439−2454.

(6) Seiler, M.; Jork, C.; Schneider, W.; Arlt, W. Ionic Liquids and Hyperbranched Polymers-Promising New Classes of Selective Entrainers for Extractive Distillation. In *Proceedings of the International Conference on Distillation & Absorption*; GVC-VDI: Dusseldorf, 2002.

(7) Lei, Z.; Arlt, W.; Wasserscheid, P. Separation of 1-Hexene and N-Hexane with Ionic Liquids. *Fluid Phase Equilib.* **2006**, *241*, 290−299.

(8) Li, Q.; Xing, F.; Lei, Z.; Wang, B.; Chang, Q. Isobaric Vapor-Liquid Equilibrium for Isopropanol + Water + 1-Ethyl-3-Methyl-imidazolium Terafluoroborate. *J. Chem. Eng. Data* **2008**, *53*, 275−279.

(9) Verevkin, S. P.; Safarov, J.; Bich, E.; Hassel, E.; Heintz, A. Thermodynamic Properties of Mixtures Containing Ionic Liquids: Vapor Pressures and Activity Coefficients of N-alcohols and Benzene in Binary Mixtures with 1-Methyl-3-Butyl-imidazolium Bis-(trifluoromethyl-sulfonyl) imide. *Fluid Phase Equilib.* **2005**, *236*, 222−228.

(10) Verevkin, S. P.; Vasiltsova, T. V.; Bich, E.; Hassel, E.; Heintz, A. Thermodynamic Properties of Mixtures Containing Ionic Liquids: Activity Coefficients of Aldehydes and Ketones in 1-Methyl-3-Ethyl-imidazolium Bis(trifluoromethyl-sulfonyl) imide using the Transpiration Method. *Fluid Phase Equilib.* **2004**, *218*, 165−175.

(11) Heintz, A.; Lehmann, J. K.; Wertz, C. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 3. Liquid−Liquid Equilibria of Binary Mixtures of 1-Ethyl-3-methylimidazolium Bis-(trifluoromethylsulfonyl)imide with Propan-1-ol, Butan-1-ol, and Pentan-1-ol. *J. Chem. Eng. Data* **2003**, *48*, 472−474.

(12) Kato, R.; Krummen, M.; Gmehling, J. Measurement and Correlation of Vapor−Liquid Equilibria and Excess Enthalpies of Binary Systems Containing Ionic Liquids and Hydrocarbons. *Fluid Phase Equilib.* **2004**, *224*, 47−54.

(13) Kato, R.; Gmehling, J. Measurement and Correlation of Vapor−Liquid Equilibria of Binary Systems Containing the Ionic Liquids $[EMIM][(CF_3SO_2)_2N]$, $[BMIM][(CF_3SO_2)_2N]$, [MMIM]-$[(CH_3)_2PO_4]$ and Oxygenated Organic Compounds Respectively Water. *Fluid Phase Equilib.* **2005**, *231*, 38−43.

(14) Döker, M.; Gmehling, J. Measurement and Prediction of Vapor−Liquid Equilibria of Ternary Systems Containing Ionic Liquids. *Fluid Phase Equilib.* **2005**, *227*, 255−266.

(15) Nebig, S.; Bölts, R.; Gmehling, J. Measurement of Vapor−Liquid Equilibria (VLE) and Excess Enthalpies (H^{e}) of Binary Systems with 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide and Prediction of These Properties and γ^{∞} Using Modified UNIFAC (Dortmund). *Fluid Phase Equilib.* **2007**, *258*, 168−178.

(16) Cai, J. L.; Cui, X. B.; Zhang, Y.; Li, R.; Feng, T. Y. Vapor−Liquid Equilibrium and Liquid−Liquid Equilibrium of Methyl Acetate + Methanol + 1-Ethyl-3-methylimidazolium Acetate. *J. Chem. Eng. Data* **2011**, *56*, 282−287.

(17) Gomis, V.; Ruiz, F.; Asensi, J. A. The Application of Ultrasound in the Determination of Isobaric Vapor-Liquid-Liquid Equilibrium Data. *Fluid Phase Equilib.* **2000**, *172*, 254−259.

(18) Cai, J. L.; Cui, X. B.; Zhang, Y.; Li, R.; Feng, T. Y. Isobaric Vapor−Liquid Equilibrium for Methanol + Methyl Acetate + 1-Octyl-3-methylimidazolium Hexafluorophosphate at 101.3 kPa. *J. Chem. Eng. Data* **2011**, *56*, 2884−2888.

(19) Simoni, L. D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M. A. Modeling Liquid−Liquid Equilibrium of Ionic Liquid Systems with NRTL, Electrolyte-NRTL, and UNIQUAC. *Ind. Eng. Chem. Res.* **2008**, *47*, 256−272.

(20) Banerjee, T.; Verma, K. K.; Khanna, A. Liquid−liquid Equilibrium for Ionic Liquid Systems Using COSMO-RS: Effect of Cation and Anion Dissociation. *AIChE J.* **2008**, *54*, 1874−1885.

(21) Banerjee, T.; Sahoo, R. K.; Rath, S. S.; Kumar, R.; Khanna, A. Multicomponent Liquid−Liquid Equilibria Prediction for Aromatic Extraction Systems Using COSMO-RS. *Ind. Eng. Chem. Res.* **2007**, *46*, 1292−1304.

(22) Naydenov, D.; Bart, H. J. Ternary Liquid-Liquid Equilibria for Six Systems Containing Ethyl acetate + Ethanol or Acetic Acid + an Imidazolium-Based Ionic Liquid with a Hydrogen Sulfate Anion at 313.2 K. *J. Chem. Eng. Data* **2007**, *52*, 2375−2381.

(23) Pereiro, A. B.; Rodríguez, A. A Study on the Liquid−Liquid Equilibria of 1-Alkyl-3-Methylimidazolium Hexafluorophosphate with Ethanol and Alkanes. *Fluid Phase Equilib.* **2008**, *270*, 23−29.

(24) Domańska, U.; Żołek-Tryznowska, Z.; Pobudkowska, A. Separation of Hexane/Ethanol Mixtures. LLE of Ternary Systems (Ionic Liquid or Hyperbranched Polymer + Ethanol + Hexane) at T = 298.15 K. *J. Chem. Eng. Data* **2009**, *54*, 972−976.

(25) Pereiro, A. B.; Araújo, J. M. M.; Esperança, J. M. S. S.; Marrucho, I. M.; Rebelo, L. P. N. Ionic liquids in separations of azeotropic systems—A review. *J. Chem. Thermodyn.* **2012**, *46*, 2−28.

(26) Berg, L. Separation of Ethyl Acetate from Ethanol by Azeotropic Distillation. U.S. Patent 5993610, 1999.

(27) Izak, N.; Van, D. B. Separation of Ethanol and Ethyl Acetate from Mixtures Thereof by Extractive Distillation. WO Patent 0044696, 2000.

(28) Lei, H. L.; Wang, H. Y. Extractive Dehydrate Ethyl acetate by Saturated Salt Water. CN Patent 1020896, 2003.

(29) Horan, K. A. Process Improvement for Continuous Ethyl Acetate Production. WO Patent 01/46117, 2001.

(30) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric Vapor-Liquid Equilibria for Ethyl Acetate + Ethanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 2325−2330.

(31) Li, Q.; Zhang, J.; Lei, Z.; Zhu, J.; Huang, X. Selection of Ionic Liquids as Entrainers for the Separation of Ethyl Acetate and Ethanol. *Ind. Eng. Chem. Res.* **2009**, *48*, 9006−9012.

(32) Li, Q.; Zhang, J.; Lei, Z.; Zhu, J.; Xing, F. Isobaric Vapor-liquid Equilibrium for Ethyl Acetate + Ethanol + 1-ethyl-3-methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2009**, *54*, 193−197.

(33) Zhang, D. L.; Deng, Y. F.; Li, C. B.; Chen, J. Separation of Ethyl Acetate-Ethanol Azeotropic Mixture Using Hydrophilic Ionic Liquids. *Ind. Eng. Chem. Res.* **2008**, *47*, 1995−2001.

(34) Hu, X.; Li, Y.; Cui, D.; Chen, B. Separation of Ethyl Acetate and Ethanol by Room Temperature Ionic Liquids with the Tetrafluoroborate Anion. *J. Chem. Eng. Data* **2008**, *53*, 427−433.

(35) Lin, S. T.; Sandler, S. I. A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model. *Ind. Eng. Chem. Res.* **2002**, *41*, 899−913.

(36) Mullins, E.; Oldland, R.; Liu, Y. A.; Wang, S.; Sandler, S. I.; Chen, C. C.; Zwolak, M.; Seavey, K. C. Sigma-Profile Database for Using COSMO-Based Thermodynamic Methods. *Ind. Eng. Chem. Res.* **2006**, *45*, 4389−4415.

(37) Li, Q.; Huang, X.; Zhang, J.; Wang, B.; Ni, J. Isobaric Vapor-Liquid Equilibrium for Ethyl Acetate + Ethanol + 1-Octyl-3-methylimidazolium Tetrafluoroborate. *Petrochem. Technol.* **2009**, *11*, 1211−1214.

(38) Lee, L.; Shen, H. Azeotropic Behavior of a Water + *n*-Propanol + Cyclohexane Mixture Using Cyclohexane as an Entrainer for Separating the Water + *n*-Proponal Mixture at 760 mmHg. *Ind. Eng. Chem. Res.* **2003**, *42*, 5905−5914.

(39) Verhoeye, L. A. J. The System Cyclohexane-2-Propanol-Water. *J. Chem. Eng. Data* **1968**, *13*, 462−467.

(40) Shiflett, M. B.; Yokozeki, A. Binary Vapor-Liquid and Vapor-Liquid-Liquid Equilibria of Hydrofluorocarbons (HFC-125 and HFC-143a) and Hydrofluoroethers (HFE-125 and HFE-143a) with Ionic Liquid [emim][$\mathrm{Tf_2N}$]. *J. Chem. Eng. Data* **2008**, *53*, 492−497.