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Vapor Pressure Measurement and Prediction for Ethanol + Methanol and Ethanol + Water Systems Containing Ionic Liquids

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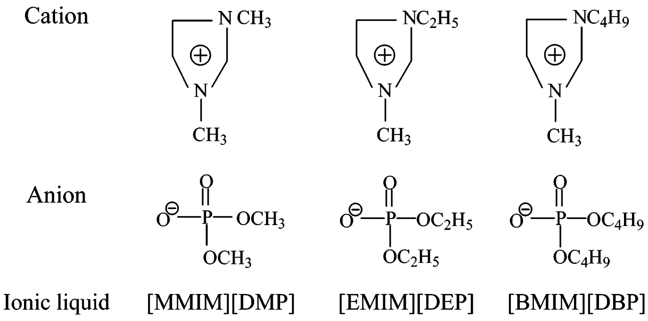
Vapor pressure data for ternary systems ethanol + methanol + [MMIM][DMP] (1-methyl-3-methylimidazolium dimethyl phosphate), ethanol + methanol + [EMIM][DEP] (1-ethyl-3-methylimidazolium diethyl phosphate), ethanol + methanol + [BMIM][DBP] (1-butyl-3-methyl imidazolium dibutyl phosphate), and ethanol + water + [MMIM][DMP] were measured at ionic liquid (IL) mass fraction of 50 % by a quasi-static method. The vapor pressure data were correlated with the NRTL model for nonelectrolyte solution, and the average absolute relative deviations of vapor pressure for the above systems were 0.55 %, 0.42 %, 0.67 %, and 1.68 %, respectively. On the basis of the predicted isothermal vapor−liquid equilibrium data for the ethanol + methanol and ethanol + water systems at 320 K and ionic liquid mass fraction of 50 %, it is found that all ILs show salting-out effect for ethanol. The salting-out effect follows the order [EMIM][DEP] > [MMIM][DMP] > [BMIM][DBP] for the ethanol + methanol system. Moreover, the azeotropic phenomenon in the ethanol + water system can be completely removed. Furthermore, the ethanol component in the ethanol + methanol system is converted from a heavy component to a light one due to the stronger affinity between methanol and IL involved, which is helpful for the separation of methanol and water from ethanol.

Introduction

Separation of water and methanol from ethanol is of vital importance in the food industry, as methanol is an inevitable companion of ethanol produced via fermentation processes.[1] For the edible ethanol used in the alcoholic beverage sector, the methanol residue is being restricted to an increasingly low limit of 2 to 150 $\mathrm{mg \cdot L^{-1}}$ by national standards (GB10343-2002). Distillation is a widely used industrial process for the separation of such mixtures; however, the separation efficiency is greatly restricted by the low relative volatility between methanol and ethanol and the appearance of azeotropic phenomenon for the ethanol + water mixture. To facilitate the separation for close-boiling or azeotropic mixtures, special distillation (e.g., extractive or salt distillation) is often used in which an entrainer (a salt or a solvent) is employed to increase the relative volatility and make the separation more efficient. However, salt distillation has some problems, such as the limited solubility of salts in some solvents and the corrosiveness of the salt solution for the facilities and pipelines. For solving these problems, new substitutes need to be explored. An ionic liquid (IL) used as an organic molten salt with dual functions of both solvent and salt might be one of such substitutes because of its nonvolatility, low corrosiveness, good thermal and chemical stability, and tunable solubility for both polar and nonpolar substances.[2−4] In addition, due to the nonvolatility of the IL, the overhead product in the distillation tower can be free of the contamination of IL. An industrial application of ILs for the separation of aliphatic from aromatic hydrocarbons by extractive distillation and extraction has been patented.[5] Despite the potential application of ILs in a special distillation process, only limited vapor−liquid equilibrium (VLE) data for the IL-containing systems have been reported.[6−9]

The objective of this work is to investigate the effect of ILs 1-methyl-3-methylimidazolium dimethyl phosphate ([MMIM]-[DMP]), 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM]-[DEP]), and 1-butyl-3-methyl imidazolium dibutyl phosphate ([BMIM][DBP]) on the VLE of ethanol + methanol and ethanol + water systems. For this reason, vapor pressure data for the ternary systems ethanol + methanol + [MMIM][DMP], ethanol + methanol + [EMIM][DEP], ethanol + methanol + [BMIM]-[DBP], and ethanol + water + [MMIM][DMP] at different compositions were measured by using a quasi-static method. The results were correlated with the nonelectrolyte NRTL model. With the fitted NRTL parameters, the isothermal VLE data for the ethanol + methanol + IL and ethanol + water + IL systems were predicted whereby the influence of IL on the VLE of the ethanol + methanol and ethanol + water systems was evaluated. The structures of the phosphoric ILs investigated are shown below:



Experimental Section

Materials. The chemical reagents used in this study were ethanol, methanol, deionized water, [MMIM][DMP], [EMIM]-[DEP], and [BMIM][DBP]. AR grade methanol and ethanol with purity of 99.7 % were purchased from Beijing Red Star Reagents

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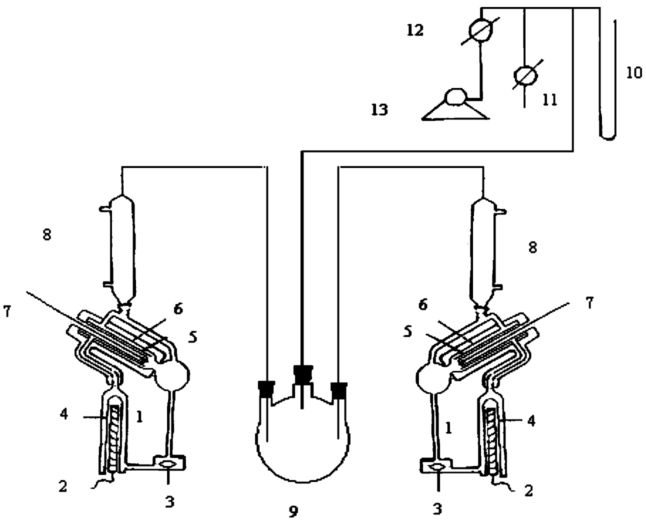

Figure 1. Experimental apparatus for vapor pressure measurement: 1, ebulliometer; 2, heating coil; 3, magnetic stirrer; 4, heating mantle; 5, inner casing; 6, vacuum jacket; 7, thermometer; 8, condenser; 9, buffer; 10, mercury manometer; 11, air inlet; 12, valve; 13, vacuum pump.

Table 1. Densities, ρ, Refractive Indices, n_D, at 298.15 K and the Normal Boiling Point, T, for Methanol and Ethanol Used in This Study

	$\rho/(\mathrm{kg \cdot m^{-3}})$		n_D		T/K	
compound	this work	lit[10]	this work	lit[10]	this work	lit[10]
methanol	786.59	786.37	1.3266	1.3265	337.75	337.70
ethanol	785.04	784.93	1.3596	1.3594	351.47	351.44

Company, China. The purity of reagents was checked by gas chromatography (GC2010, Japan). In addition, the densities, refractive indices, and boiling points of ethanol and methanol were measured and are listed in Table 1 along with the literature[10] values for comparison. The ILs used were prepared and purified in the laboratory according to the literature,[11] and the purity was more than 98 % in terms of NMR analysis. The water content of ILs measured by Karl Fischer method (CBS-1A) was less than 0.052 %. Furthermore, all ILs were purified by vacuum evaporation at 363 K and 1.325 kPa for 24 h to remove all volatile impurities before use.

Apparatus and Procedures. The experimental apparatus as shown in Figure 1 was composed of a working ebulliometer and a reference ebulliometer, two condensers, two temperature measurement and control systems, two magnetic stirrers, and a pressure control system. The two ebulliometers[12,13] were connected to a buffer to reduce the pressure fluctuation, and the equilibrium pressure of the system was determined by the boiling temperature of pure water in the reference ebulliometer using the temperature−pressure relationship represented by the Antoine equation. The equilibrium temperature of the ebulliometers were measured by two four-wire 25-Ω calibrated platinum resistance thermometers (type CST6601) with an uncertainty of ± 0.02 K, connected to a two-channel standard digital thermometer (CST6502). The uncertainty of the vapor pressure arising from the uncertainty of temperature measurement is estimated within ± 0.04 kPa, and the vapor pressure reproducibility for a replicate sample is within ± 0.07 kPa. The cooling temperature of the condensers was lowered to 274 K to minimize the composition variation of volatile components in the liquid phase.

The liquid sample with known composition was prepared by mixing definite weight of the corresponding components weighted by an electronic balance with a precision of 0.001 g (AR2130, USA). With the known weights of the components and the precision of the balance, the uncertainty of the mole fraction of the components in the mixtures is estimated to be within 0.0001. The sample solution of approximate 85 cm^3 was added to the working ebulliometer, and the same volume of deionized water was added to the reference one. The system was evacuated to a proper degree of vacuum, and then the solution was heated and stirred with magnetic stirrer to prevent superheating and inhomogeneity. When VLE was reached, the temperature of two ebulliometers was recorded. Next measurement was performed by adjusting the pressure of the system by air inlet. A series of equilibrium temperatures and vapor pressures were obtained for a specified mixture composition.

Table 2. Experimental and Calculated Vapor Pressure p by Antoine Equation[14] for Ethanol

T/K	p^{exp}/kPa	p^{cal}/kPa	$100\Delta^a$	T/K	p^{exp}/kPa	p^{cal}/kPa	$100\Delta^a$
292.33	5.59	5.56	−0. 54	330.56	41.76	41.73	−0.09
303.83	10.86	10.86	0.02	333.94	48.61	48.58	−0.05
311.14	16.15	16.12	−0.15	337.18	56.06	56.05	−0.02
317.90	22.84	22.80	−0.20	339.97	63.20	63.20	0.00
323.09	29.41	29.41	−0.01	342.30	69.73	69.78	0.08
326.80	35.11	35.07	−0.11				

[a] $\Delta = (p^{\mathrm{cal}} - p^{\mathrm{exp}})/p^{\mathrm{exp}}$.

To assess the reliability of the experimental apparatus, vapor pressure data of pure ethanol at different temperatures were measured and compared with that calculated using the Antoine equation.[14] The measured saturated vapor pressure data of ethanol at different temperatures and the results calculated by the Antoine equation are listed in Table 2. The experimental data were in excellent agreement with the calculated ones, suggesting the reliability of the experimental apparatus and procedure.

Results and Discussion

Vapor pressure data for the ternary systems ethanol + methanol + [MMIM][DMP], ethanol + methanol + [EMIM][DEP], ethanol + methanol + [BMIM][DBP], and ethanol + water + [MMIM][DMP] at IL mass fraction of 50 % were measured and are listed in Tables 3 to 6, respectively. The mole ratios of ethanol to methanol chosen for the systems containing ethanol, methanol, and ILs were 0.1481:0.8519, 0.3720:0.6280, 0.5528:0.4472, 0.7601:0.2399, and 0.9435:0.0565, respectively. The mole ratios of ethanol to water chosen for the ethanol + water + [MMIM][DMP] system were 0.1098:0.8902, 0.2066:0.7934, 0.4313:0.5687, 0.6098:0.3902, 0.8180:0.1820, and 0.9504:0.0496, respectively. The *T, p, x* diagrams for ternary systems ethanol (1) + methanol (2) + [MMIM][DMP] (3) and ethanol (1) + water (2) + [MMIM][DMP] (3) are shown in Figures 2 and 3, respectively, while the *T, p, x* diagrams for other systems were not shown as they were very similar to Figure 2.

It was seen from Figure 2 that the vapor pressure increased with temperature at fixed liquid composition and increased with mole fraction of methanol at specified temperature. Furthermore, the curves never overlap in the whole temperature and liquid composition range studied. This may be attributed to the close similarity between methanol and ethanol with respect to their structure, molecular size, and intermolecular interaction forces between IL and methanol and between IL and ethanol. However, this is not true for the ethanol + water + [MMIM][DMP] system, for which the vapor pressure does not monotonically increase with mole fraction of the light component, ethanol, at fixed temperature. This may be ascribed to the large difference in affinity between [MMIM][DMP] + water and [MMIM][DMP] + ethanol as well as the much stronger nonideality of

Table 3. Equilibria Temperature *T*, Vapor Pressure *p*, and Vapor-Phase Mole Fraction of Ethanol y_1 Calculated for the Ternary System Ethanol (1) + Methanol (2) + [MMIM][DMP] (3)

T/K	p/kPa	y_1	T/K	p/kPa	y_1
$x_1 = 0.1284$, $x_2 = 0.7384$					
305.19	14.70	0.2704	327.47	42.58	0.2663
312.11	20.94	0.2692	331.63	50.62	0.2655
317.69	27.49	0.2682	335.72	59.83	0.2647
322.89	34.73	0.2672	339.17	68.87	0.2640
$x_1 = 0.3186$, $x_2 = 0.5378$					
297.92	8.32	0.5172	327.40	36.84	0.5210
308.71	14.80	0.5192	332.00	45.30	0.5211
315.93	21.47	0.5201	336.59	55.05	0.5212
322.10	28.84	0.5207	340.45	65.18	0.5212
$x_1 = 0.4688$, $x_2 = 0.3792$					
301.76	8.97	0.6809	329.48	35.94	0.6853
311.38	15.18	0.6829	333.97	43.76	0.6856
318.52	21.53	0.6840	338.36	53.09	0.6859
324.54	28.63	0.6848	342.74	63.67	0.6862
$x_1 = 0.6375$, $x_2 = 0.2012$					
304.83	9.17	0.8446	333.48	37.24	0.8468
314.30	15.08	0.8457	338.17	45.80	0.8471
321.69	21.72	0.8463	342.48	54.79	0.8471
327.97	29.09	0.8466	346.55	65.06	0.8473
$x_1 = 0.7837$, $x_2 = 0.0470$					
304.94	7.90	0.9668	334.72	35.68	0.9672
315.32	14.05	0.9671	339.42	43.77	0.9672
322.78	20.54	0.9672	343.5	52.29	0.9672
329.24	28.01	0.9672	348.02	63.16	0.9672

Table 4. Equilibria Temperature *T*, Vapor Pressure *p*, and Vapor-Phase Mole Fraction of Ethanol y_1 Calculated for the Ternary System Ethanol (1) + Methanol (2) + [EMIM][DEP] (3)

T/K	p/kPa	y_1	T/K	p/kPa	y_1
$x_1 = 0.1312$, $x_2 = 0.7544$					
294.55	8.70	0.2894	322.19	35.03	0.2833
303.70	14.29	0.2875	327.00	43.20	0.2822
311.08	20.73	0.2859	331.29	51.96	0.2811
316.55	27.08	0.2846	335.87	63.20	0.2800
$x_1 = 0.3260$, $x_2 = 0.5503$					
297.77	8.68	0.5366	326.05	36.43	0.5392
307.50	14.85	0.5381	330.80	45.00	0.5393
314.76	21.38	0.5388	334.88	53.64	0.5392
321.25	29.14	0.5391	339.01	64.04	0.5392
$x_1 = 0.4805$, $x_2 = 0.3886$					
302.37	9.68	0.6993	329.41	37.26	0.7022
310.98	15.29	0.7006	333.66	45.06	0.7023
317.92	21.63	0.7014	337.71	53.78	0.7024
323.89	28.91	0.7018	342.16	64.46	0.7025
$x_1 = 0.6543$, $x_2 = 0.2065$					
303.19	8.66	0.8579	331.59	36.22	0.8587
313.08	14.84	0.8583	336.42	45.01	0.8586
320.36	21.32	0.8586	340.52	53.89	0.8587
326.25	28.29	0.8586	344.60	64.15	0.8585
$x_1 = 0.8054$, $x_2 = 0.0483$					
307.24	9.39	0.9707	334.42	36.41	0.9705
316.46	15.39	0.9707	339.04	44.92	0.9704
323.61	21.99	0.9707	343.55	54.83	0.9704
329.34	28.82	0.9705	347.61	64.91	0.9703

the ethanol + water mixture, a potential azeotropic mixture at appropriate conditions, compared to the methanol + ethanol mixture, merely a close-boiling mixture with low nonideality.

Under low pressures, the vapor phase is approximately ideal; hence, the vapor pressure for a ternary system solvent (1) + solvent (2) + IL (3) can be calculated using eq 1 considering the nonvolatility of IL, that is, $p_3^s = 0$:

$$p = \sum_{i=1}^{2} x_i \gamma_i p_i^s \tag{1}$$

Table 5. Equilibria Temperature *T*, Vapor Pressure *p*, and Vapor-Phase Mole Fraction of Ethanol y_1 Calculated for the Ternary System Ethanol (1) + Methanol (2) + [BMIM][DBP] (3)

T/K	p/kPa	y_1	T/K	p/kPa	y_1
$x_1 = 0.1349$, $x_2 = 0.7759$					
302.98	14.95	0.1445	326.03	44.61	0.1557
310.24	21.52	0.1483	330.36	53.74	0.1576
316.32	28.82	0.1513	334.08	62.99	0.1591
321.55	36.67	0.1538			
$x_1 = 0.3361$, $x_2 = 0.5673$					
298.90	10.25	0.4075	325.51	37.54	0.4279
307.25	15.72	0.4148	330.20	46.25	0.4307
314.17	22.12	0.4202	334.46	55.62	0.4331
320.33	29.60	0.4245	338.24	65.18	0.4350
$x_1 = 0.4962$, $x_2 = 0.4013$					
300.69	9.73	0.6203	327.30	36.51	0.6361
309.65	15.68	0.6265	331.43	43.85	0.6379
316.21	21.73	0.6304	335.63	52.86	0.6397
322.29	28.99	0.6337	339.47	62.14	0.6411
$x_1 = 0.6771$, $x_2 = 0.2137$					
302.47	9.00	0.8285	328.77	33.81	0.8353
311.79	14.82	0.8314	333.76	42.19	0.8362
318.49	20.72	0.8331	338.02	50.95	0.8369
324.11	27.22	0.8344	341.82	60.16	0.8374
$x_1 = 0.8349$, $x_2 = 0.05$					
305.84	9.24	0.9667	333.10	36.02	0.9677
315.23	15.31	0.9671	337.44	43.91	0.9677
322.12	21.62	0.9674	341.73	53.32	0.9678
327.78	28.27	0.9676	345.42	62.59	0.9679

Table 6. Equilibria Temperature *T*, Vapor Pressure *p*, and Vapor-Phase Mole Fraction of Ethanol y_1 Calculated for the Ternary System Ethanol (1) + Water (2) + [MMIM][DMP] (3)

T/K	p/kPa	y_1	T/K	p/kPa	y_1
$x_1 = 0.1003$, $x_2 = 0.8130$					
307.20	8.06	0.4924	339.19	37.90	0.4655
318.63	14.51	0.4828	343.94	46.65	0.4616
326.57	21.36	0.4761	348.51	56.40	0.4579
333.16	28.94	0.4706	352.80	66.70	0.4544
$x_1 = 0.1866$, $x_2 = 0.7166$					
309.85	10.99	0.5842	338.50	43.13	0.5676
319.82	18.16	0.5785	343.31	52.62	0.5648
327.22	25.82	0.5742	347.34	62.17	0.5624
333.51	34.51	0.5705	350.62	71.03	0.5605
$x_1 = 0.3798$, $x_2 = 0.5008$					
305.83	9.05	0.7027	337.18	42.23	0.6926
317.41	16.67	0.6991	341.56	51.02	0.6912
325.31	24.46	0.6965	345.51	60.03	0.6899
331.75	33.14	0.6944	349.04	69.23	0.6887
$x_1 = 0.5266$, $x_2 = 0.3369$					
308.14	9.99	0.7888	337.51	41.82	0.7812
318.95	17.53	0.7860	342.04	50.99	0.7800
326.85	25.70	0.7839	345.72	59.36	0.7790
332.42	33.29	0.7825	349.87	69.72	0.7780
$x_1 = 0.6906$, $x_2 = 0.1537$					
309.25	10.06	0.8984	338.41	41.60	0.8933
319.67	17.29	0.8965	342.92	50.55	0.8926
327.38	24.99	0.8952	346.99	59.97	0.8919
333.37	33.16	0.8942	350.44	69.00	0.8914
$x_1 = 0.7912$, $x_2 = 0.0413$					
309.79	10.01	0.9720	338.99	41.33	0.9702
320.17	17.14	0.9713	343.08	49.33	0.9701
328.40	25.42	0.9709	346.64	57.68	0.9699
334.45	33.57	0.9705	350.12	66.57	0.9697

Here p and p_i^s are vapor pressure of liquid mixture and pure component i at system temperature, respectively, and the latter can be calculated by the Antoine equation with Antoine constants taken from literature.[14] x_i is the liquid-phase mole fraction of component i, and γ_i is the activity coefficient of component i. As an original thermodynamic model for the IL-containing systems is not available by now, the NRTL model

Table 7. NRTL Binary Parameters α_{ij} and $(g_{ij} - g_{jj})$ Fitted and the Corresponding ARD and RMSDs of Vapor Pressure[a]

system	$(g_{13} - g_{33})$/J·mol^{-1}	$(g_{31} - g_{11})$/J·mol^{-1}	α_{13}	$(g_{23} - g_{33})$/J·mol^{-1}	$(g_{32} - g_{22})$/J·mol^{-1}	α_{23}	100 ARD	100 RMSDs
S1(1)−S2(2)−IL1(3)	−20181.1	−5935.3	0.2508	−30793.4	−13867.5	0.0998	0.55	0.69
S1(1)−S2 (2)−IL2(3)	−14427.2	−6386.5	0.2996	−26180.0	−17911.6	0.0796	0.42	0.51
S1(1)−S2 (2)−IL3(3)	−12377.7	−5960.6	0.4857	−11778.3	−34222.6	0.0146	0.67	0.87
S1(1)−S3(2)−IL1(3)	−20181.1	−5935.3	0.2508	−26242.2	−7233.2	0.1038	1.68	1.77

system[14]	$(g_{12} - g_{22})$/J·mol^{-1}	$(g_{21} - g_{11})$/J·mol^{-1}	α_{12}
S1(1)−S3(2)	−510.8	5612.1	0.3008
S1(1)−S2(2)	1580.2	−1292.9	0.3053

[a] S1, ethanol; S2, methanol; S3, water; IL1, [MMIM][DMP]; IL2, [EMIM][DEP]; IL3, [BMIM][DBP].

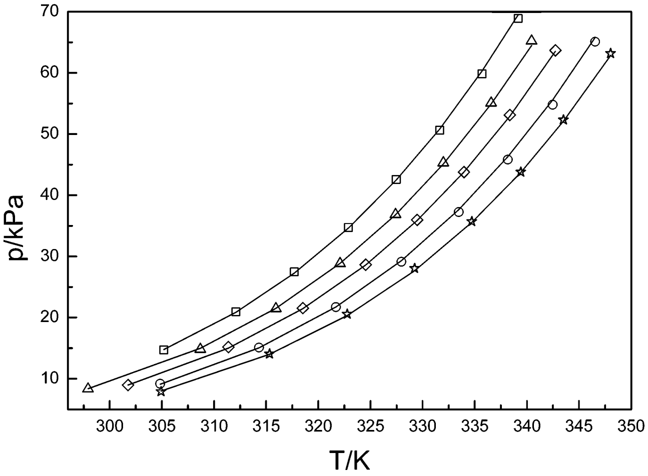

Figure 2. Experimental and correlative vapor pressure p for ethanol (1) + methanol (2) + [MMIM][DMP] (3) system at different temperature T and compositions: □, $x_1 = 0.1284$; △, $x_1 = 0.3186$; ◇, $x_1 = 0.4688$; ○, $x_1 = 0.6375$; ☆, $x_1 = 0.7837$; −, NRTL.

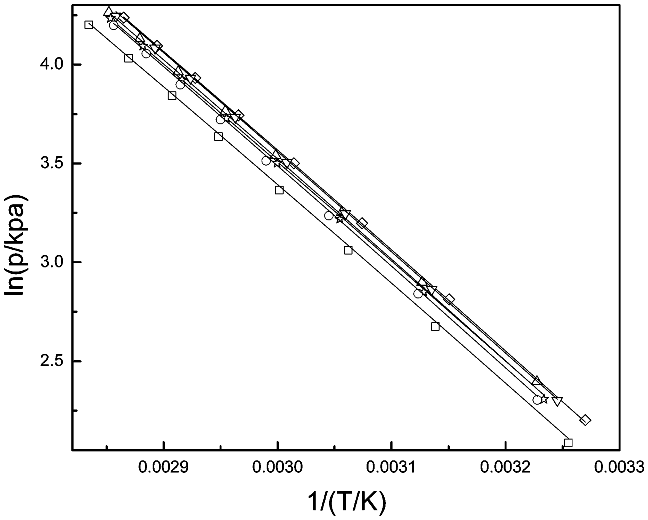

Figure 3. Experimental and correlative vapor pressure p for ethanol (1) + water (2) + [MMIM][DMP] (3) system at different temperature T and compositions: □, $x_1 = 0.1003$; △, $x_1 = 0.1866$; ◇, $x_1 = 0.3798$; ▽, $x_1 = 0.5266$; ☆, $x_1 = 0.6906$; ○, $x_1 = 0.7912$; −, NRTL.

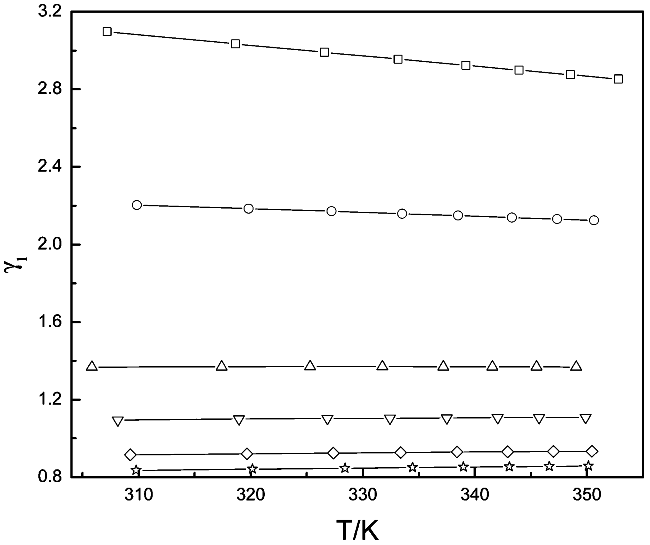

Figure 4. Calculated activity coefficient γ_1 of ethanol in ethanol (1) + water (2) + [MMIM][DMP] (3) system at different temperature T and compositions: □, $x_1 = 0.1003$; ○, $x_1 = 0.1866$; △, $x_1 = 0.3798$; ▽, $x_1 = 0.5266$; ◇, $x_1 = 0.6906$; ☆, $x_1 = 0.7912$.

for nonelectrolyte solution[15] is employed to describe activity coefficients in this work. The NRTL binary parameters α_{ij} and $(g_{ij} - g_{jj})$ were obtained by fitting the experimental vapor pressure data in the whole temperature and composition range with least-squares method. The fitted interaction parameters of NRTL equation along with the average absolute relative deviations (ARD) and root mean square deviations (RMSDs) of vapor pressure, as defined by eqs 2 and 3, are listed in Table 7:

$$\text{ARD} = \left(\frac{1}{n}\sum_{i=1}^{n} |p^{\text{cal}} - p^{\text{exp}}|/p^{\text{exp}}\right) \tag{2}$$

$$\text{RMSDs} = \sqrt{\frac{1}{n}\sum_{n}\left(\frac{p^{\text{exp}} - p^{\text{cal}}}{p^{\text{exp}}}\right)^2} \tag{3}$$

where p^{exp} and p^{cal} are the experimental and calculated vapor pressure, respectively; n is the number of data points. As shown in Table 7, the vapor pressure can be correlated by the NRTL model with satisfying accuracy, and the maximum ARD was found for the ethanol (1) + water (2) + [MMIM][DMP] (3) system within 1.7 %.

The nonideality of a solution can be reflected by the activity coefficient of component i, which is obtained as an intermediate in the fitting process of vapor pressure. As an example, the activity coefficients of ethanol, γ_1, in the ternary system ethanol (1) + water (2) + [MMIM][DMP] (3) at different temperatures and compositions are plotted in Figure 4. It was found from Figure 4 that the activity coefficient of ethanol was mainly affected by the liquid-phase composition, while its temperature dependence was marginal.

For a ternary system solvent (1) + solvent (2) + IL (3), the vapor-phase mole fraction of component i at VLE can be calculated with eq 4:[15]

$$y_i = \frac{p_i^{s} x_i \gamma_i}{\sum_{i=1}^{2} p_i^{s} x_i \gamma_i} \quad i = 1, 2 \tag{4}$$

To investigate the salt effect of IL on the VLE of the ethanol + methanol and ethanol + water systems, the vapor-phase mole fraction of ethanol at 320 K and IL mass fraction of 50 % was predicted by using the NRTL parameters listed in Table 7, and the isothermal VLE diagram, y_1 versus x_1' was plotted in Figures 5 and 6. x_1' is the liquid-phase mole fraction of ethanol on the IL-free basis. It is shown that the IL has a remarkable influence on the VLE of the ethanol + methanol and ethanol + water systems. For the former system, the VLE curve of y_1 versus x_1' was changed from under the diagonal to above the diagonal, which means that methanol is effectively converted from a light component to a heavy one in the presence of IL. For the latter system, the azeotropic phenomenon is completely removed by the IL added. This suggests that both methanol and water in the ethanol + methanol + water system can be extracted down to the bottom of a distillation tower by the IL added from the overhead. The salting-out effect of the ILs on ethanol follows the order of [EMIM][DEP] > [MMIM][DMP] > [BMIM][DBP] for the ethanol + methanol system. This result can be ascribed to the affinity difference between different ILs and solvents. Although the vapor pressure of methanol, ethanol, and water are all lowered by the hydrophilic ILs added, the degrees of lowering are different, leading to the variation in relative volatility of the components involved.

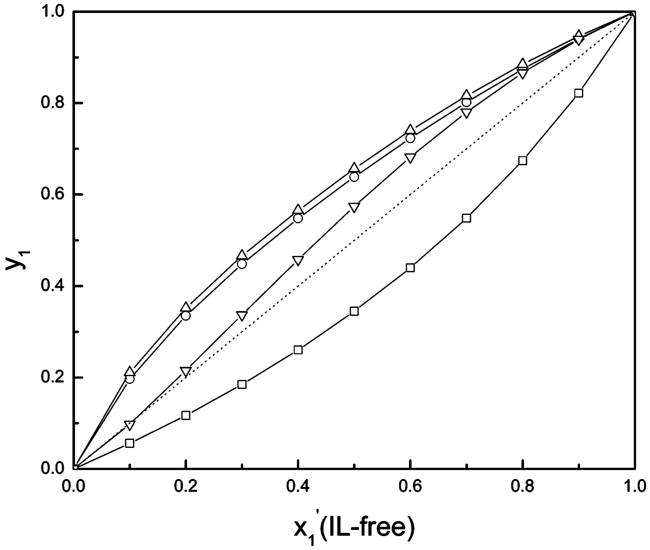

Figure 5. Influence of ILs on VLE of ethanol (1) + methanol (2) system at 320 K and IL mass fraction of 50 % □, IL-free; ○, [MMIM][DMP]; △, [EMIM][DEP]; ▽, [BMIM][DBP].

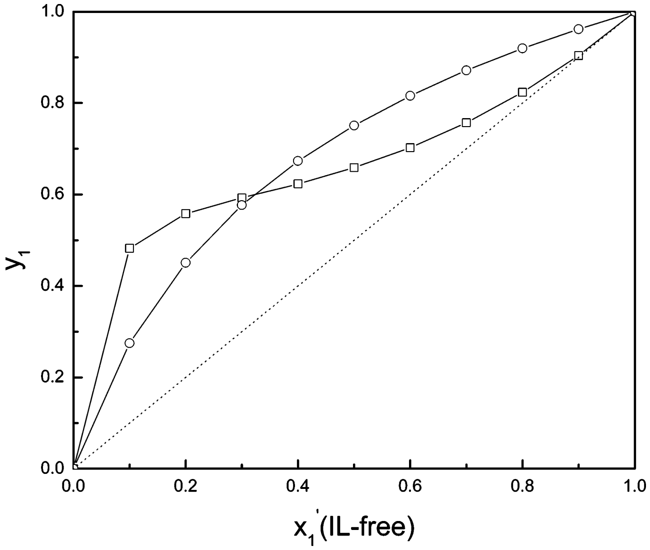

Figure 6. Influence of [MMIM][DMP] on VLE of ethanol (1) + water (2) system at 320 K and IL mass fraction of 50 % □, IL-free; ○, [MMIM]-[DMP].

Conclusion

Vapor pressure data for ternary systems containing an IL [MMIM][DMP], [EMIM][DEP], or [BMIM][DBP] were measured and correlated using the nonelectrolyte NRTL model with satisfying accuracy. The hydrophilic IL had a remarkable influence on the VLE behavior of the ethanol + methanol and ethanol + water systems as indicated by the conversion of methanol from a light component to a heavy one in the ethanol + methanol system and the disappearance of azeotropic phenomenon for the ethanol + water system. The salting-out effect of IL on ethanol followed the order of [EMIM][DEP] > [MMIM][DMP] > [BMIM][DBP] for the ethanol + methanol system. As a result, the separation of methanol and water from ethanol is facilitated by the addition of phosphoric IL.

Literature Cited

(1) Kong, X. Q. Study on removing water and methyl alcohol from edible alcohol with natural zeolite. *Ind. Miner. Process* **2004**, *4*, 12−13 (in Chinese).

(2) Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R. Room temperature ionic liquids and their mixtures—a review. *Fluid Phase Equilib.* **2004**, *219*, 93−98.

(3) Wei, G. T.; Yang, Z.; Chen, C. J. Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions. *Anal. Chim. Acta* **2003**, *488*, 183−192.

(4) Matsumoto, M.; Mochiduki, K.; Fukunishi, K.; Kondo, K. Extraction of organic acids using imidazolium-based ionic liquids and their toxicity to *Lactobacillus rhamnosus*. *Sep. Purif. Technol.* **2004**, *40*, 97−101.

(5) Gmehling, J.; Krummen, M. Separation of aromatic hydrocarbons from non-aromatic hydrocarbons, comprises using a selective solvent selected from liquid onium salts. Patent DE10154052-A1, November 2, 2001.

(6) 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.

(7) Safarov, J.; Verevkin, S. P.; Bich, E.; Heintz, A. Vapor pressures and activity coefficients of *n*-alcohols and benzene in binary mixtures with 1-methyl-3-butylimidazolium octyl sulfate and 1-methyl-3-octylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 518−525.

(8) Döker, M.; Gmehling, J. Measurement and prediction of vapor−liquid equilibria of ternary systems containing ionic liquids. *Fluid Phase Equilib.* **2005**, *227*, 255−266.

(9) Kim, K. S.; Shin, B. K.; Lee, H.; Ziegler, F. Refractive index and heat capacity of 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium tetrafluoroborate, and vapor pressure of binary systems for 1-butyl-3-methylimidazolium bromide + trifluoroethanol and 1-butyl-3-methylimidazolium tetrafluoroborate + trifluoroethanol. *Fluid Phase Equilib.* **2004**, *218*, 215−220.

(10) Riddick, A.; Bunger, W. B.; Sakano, T. K. *Organic Slovents, Physical Properties and Method of Purification*; Wiley-Interscience: New York, 1986.

(11) Zhou, Y. H.; Robertson, A. J.; Hillhouse, J. H. Phosphonium and imidazolium salts and methods of their preparation. Patent WO2004/016631, February 26, 2004.

(12) Sun, H. Y.; Fang, W. J.; Guo, Y. S.; Lin, R. S. Investigation of bubble-point vapor pressures for mixtures of an endothermic hydrocarbon fuel with ethanol. *Fuel* **2005**, *84*, 825−831.

(13) Xu, Y. J.; Li, H. R.; Wang, C. M.; Wang, Y.; Han, S. J. Bubble points measurement for (triethyl orthoformate + diethyl malonate). *J. Chem. Thermodyn.* **2004**, *36*, 971−976.

(14) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, 1977; pp 41, 154.

(15) Sandler, S. I. *Chemical and Engineering Thermodynamics*; John Wiley & Sons: Singapore, 1989; pp 372, 383.

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