

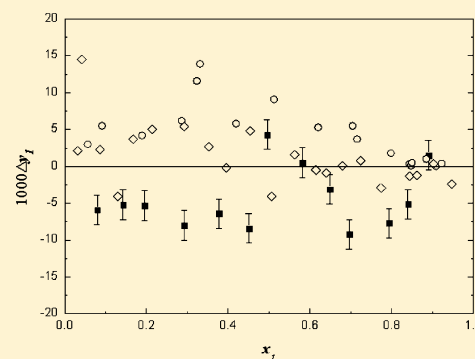
Isobaric Vapor–Liquid Equilibrium for the Ethanol + Water + 1,3-Dimethylimidazolium Dimethylphosphate System at 101.3 kPa

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ABSTRACT: Isobaric vapor–liquid equilibrium (VLE) data were measured for the ternary system {ethanol (1) + water (2) + 1,3-dimethylimidazolium dimethylphosphate (3) ([MMIM]⁺DMP⁻)} at atmospheric pressure (101.3 kPa). The measurement was performed with a modified Othmer still. The results indicated that the VLE of the {ethanol (1) + water (2) + [MMIM]⁺DMP⁻ (3)} ternary system was clearly different from that of the {ethanol (1) + water (2)} binary system. The IL studied showed a slight crossover salt effect, which led to a change of the relative volatility of ethanol to water and even to the elimination of the azeotropic phenomenon of ethanol and water. The measured ternary VLE data were correlated using NRTL.



INTRODUCTION

Extractive distillation with ionic liquid (IL) as the separating agent is a very new process for producing high-purity products.^{1–6} This process integrates the advantages of liquid solvent and solid salt. However, compared with extractive distillation with the combination of liquid solvent and solid salt, it has no problem of entrainment of the solvent into the top product of the column. Besides, thermodynamic data for ionic-liquid-containing systems are essential for understanding the thermodynamic behavior and predicting VLE for the IL-containing system.

The vapor–liquid equilibrium of the {ethanol (1) + water (2)} system may be one of the most studied binary systems owing to its industrial importance and the promising applications. Nevertheless, the presence of the azeotropic phenomenon of {ethanol (1) + water (2)} at atmospheric pressure makes it difficult to obtain high-purity ethanol from the mixture by ordinary distillation or rectification methods. Several ILs have been reportedly used as entrainers to move or break the ethanol + water azeotropic point,^{7–20} and [MMIM]⁺DMP⁻ was one of them.

To understand the thermodynamic behavior of the {ethanol (1) + water (2) + [MMIM]⁺DMP⁻ (3)} ternary system better, in this work, isobaric VLE data for the {ethanol (1) + water (2)} system containing [MMIM]⁺[DMP]⁻ are measured at atmospheric pressure (101.3 kPa), and the effects of [MMIM]⁺[DMP]⁻ on the VLE of the {ethanol (1) + water (2)} system are also discussed.

EXPERIMENTAL SECTION

Chemicals. The chemical reagents used in this work were ethanol, redistilled water, and IL. AR grade ethanol with mass fraction >99.6 % was obtained from Beijing Chemical Reagents

Company (China). Purities of ethanol and water were checked by GC (SP6890, China). Redistilled water was further purified using a 0.2 μm Millipore filter. The IL, [MMIM]⁺[DMP]⁻, was purchased from Shanghai Cheng Jie Chemical Co. LTD (China). The mass fraction purity of IL, $x_w > 98\%$, was checked by liquid chromatography. The water mass fraction in the ionic liquid, $x_w < 0.054\%$, was determined by Karl Fisher titration. Good agreement of the physical properties was found between the measured and literature values as shown in Table 1. Refractive indices were measured by a WZS-I Abbe refractometer, Shanghai Optical Instruments Factory (China), with an uncertainty of ± 0.0001 . Densities were measured by a DMA-4100 densimeter, AntoPaar GmbH (Germany), with an uncertainty of $\pm 0.0001\text{ g}\cdot\text{cm}^{-3}$. Furthermore, the IL used was dried for 48 h under a vacuum by rotary evaporation (Shanghai Shen Shun Biotechnology Co. Ltd., China) at 383 K which was used to separate the volatile components from IL before the experiments. The IL was reused using rotary evaporation after experiments and characterized by NMR spectroscopy.

Apparatus and Procedure. All vapor–liquid equilibrium data were measured in a modified Othmer still at atmospheric pressure (101.3 kPa). The equilibrium still used in this work was detailed in our previous publications.^{21,22}

The equilibrium compositions of ethanol and water in the vapor and liquid phase of samples were analyzed by gas chromatography (GC). All samples were directly injected into the GC without any pretreatment. The glass linear of GC was filled with glass wool which can trap the IL and protect the GC column. The GC (SP6900, China) was equipped with a thermal conductivity detector. The GC was packed with

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Table 1. Densities (d), Refractive Indices (n_D), and Antoine's Constants (A , B , C) for the Chemicals

compound	d (298.15 K) $\text{g}\cdot\text{cm}^{-3}$		n_D (298.15 K)		A	B	C
	exp.	lit.	exp.	lit.			
water	0.9971	0.99705 ²⁴	1.3324	1.33250 ²⁴	7.23255	1750.286	235.000
ethanol	0.7849	0.78504 ²⁴	1.3591	1.35941 ²⁴	7.16879	1552.601	222.419
[MMIM] ⁺ [DMP] ⁻	1.2857	1.2853 ²⁵ 1.314 ²⁶	1.4858	-	-	-	-

Table 2. VLE Data for the Ethanol (1) + Water (2) Binary System at 101.3 kPa

T/K	x_1	y_1
373.2	0.000	0.000
360.5	0.079	0.407
357.5	0.143	0.493
356.6	0.195	0.530
354.8	0.292	0.570
354.2	0.378	0.602
353.4	0.450	0.626
353.1	0.495	0.657
352.3	0.581	0.691
352.0	0.648	0.721
351.8	0.696	0.742
351.5	0.794	0.807
351.4	0.840	0.844
351.2	0.890	0.893
351.6	1.000	1.000

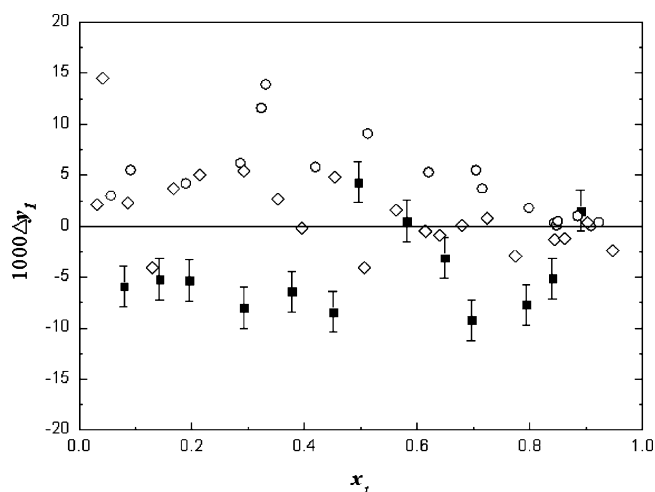


Figure 1. Absolute deviations $\Delta y_1 = y(\text{exptl}) - y(\text{calcd})$ between the values calculated using the NRTL model and the measured mole fractions of ethanol in the vapor phase for the binary system of ethanol (1) + water (2) at 101.3 kPa: ■, this work with error bars representing the extended uncertainty; ○, ref 23; ◇, ref 24.

Porapak-Q column (3 m × 0.3 mm). The carrier gas was hydrogen with a flow rate of 45 $\text{cm}^3\cdot\text{min}^{-1}$. The GC operating conditions were as follows: the injector temperature at 423 K, the oven temperature at 353 K, and the detector temperature at 453 K, respectively. The equilibrium temperature was measured by a calibrated mercury thermometer which has an uncertainty of 0.1 K, and the equilibrium pressure of the whole system was kept constant using an on-off pressure controller with a standard uncertainty of 0.10 kPa.

The standard solutions were prepared gravimetrically by an electronic balance (Satorius) with an uncertainty of ± 0.1 mg.

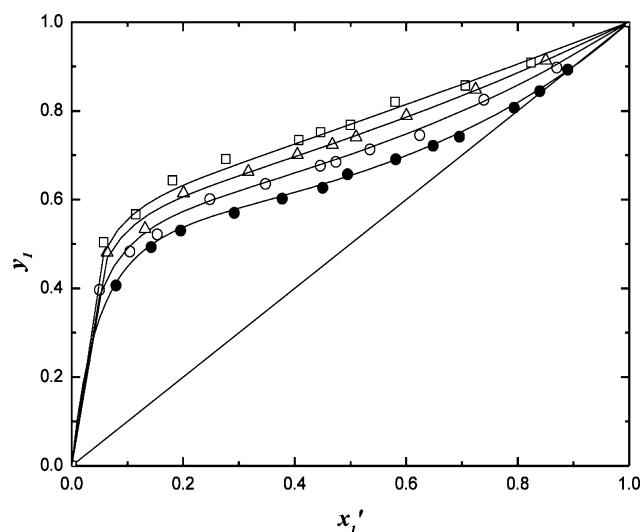


Figure 2. Isobaric VLE diagram for the ethanol (1) + water (2) + [MMIM]⁺[DMP]⁻ (3) system at 101.3 kPa: ●, $x_3 = 0$; ○, $x_3 = 0.05$; △, $x_3 = 0.10$; □, $x_3 = 0.15$; solid lines, correlated using the NRTL model.

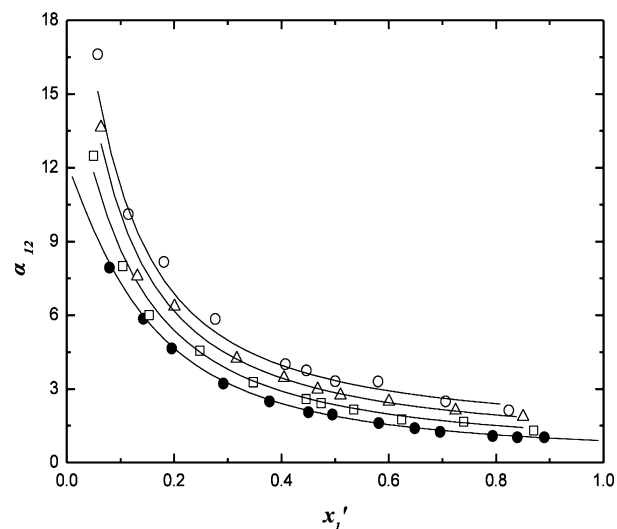


Figure 3. Relative volatility of ethanol (1) + water (2) at 101.3 kPa: ●, $x_3 = 0$ (IL-free); □, $x_3 = 0.05$ ([MMIM]⁺[DMP]⁻); △, $x_3 = 0.10$ ([MMIM]⁺[DMP]⁻); ○, $x_3 = 0.15$ ([MMIM]⁺[DMP]⁻); solid lines, correlated using the NRTL model.

The amounts of ethanol and water in the samples were quantified using a calibration correction factor which was acquired from a set of standard solutions. In this case, the uncertainty of mole fraction of the ethanol and water in the liquid and vapor phase of samples was 0.002. The IL concentrations in the liquid phase of samples were determined

by measuring the mass difference of standard solutions with and without solvents.

RESULTS AND DISCUSSION

The VLE data for the binary azeotrope of {ethanol (1) + water (2)} were measured at atmospheric pressure (101.3 kPa), and the results are listed in Table 2. Figure 1 indicates that the VLE data obtained in our work were quite consistent with those reported by Kurihara et al.²³ and Arce et al.²⁴ and shows the maximum absolute deviation (Δy_1) between the calculated, using the NRTL model, and measured mole fraction of ethanol in the vapor phase (y_1) was less than 0.010. Hence the experimental apparatus can be used to investigate the effect of the IL on the VLE of the {ethanol (1) + water (2)} system at atmospheric pressure (101.3 kPa).

In the same way, the vapor–liquid equilibrium data for the ternary system of {ethanol (1) + water (2) + [MMIM]⁺[DMP]⁻ (3)} were measured at atmospheric pressure. The IL concentrations (x_3) added to the system were 0.05, 0.10, and 0.15, respectively. The experimental results are listed in Table 3, which includes the mole fraction of IL in

Table 3. VLE Data for the Ethanol (1) + Water (2) + [MMIM]⁺[DMP]⁻ (3) System at 101.3 kPa

100 x_3	T/K	x_1'	y_1	γ_1	γ_2	α_{12}
5.321	364.0	0.050	0.397	5.186	0.937	12.485
5.289	360.2	0.105	0.483	3.474	0.986	7.995
5.311	358.5	0.153	0.521	2.724	1.032	6.004
5.276	356.3	0.248	0.601	2.109	1.056	4.555
5.321	355.3	0.347	0.635	1.653	1.154	3.273
5.213	354.5	0.446	0.676	1.415	1.250	2.589
5.277	354.3	0.474	0.685	1.358	1.288	2.412
5.314	354.1	0.535	0.713	1.262	1.341	2.153
5.229	353.9	0.624	0.745	1.139	1.485	1.756
5.289	353.7	0.740	0.825	1.076	1.485	1.659
5.274	353.6	0.870	0.897	0.999	1.759	1.301
9.878	366.6	0.064	0.481	4.754	0.784	13.641
9.823	364.1	0.131	0.534	2.793	0.831	7.585
9.910	361.4	0.201	0.615	2.324	0.829	6.355
9.874	359.6	0.317	0.662	1.696	0.909	4.237
9.856	358.5	0.405	0.701	1.464	0.966	3.447
9.823	358.1	0.468	0.724	1.328	1.013	2.984
9.846	358.0	0.510	0.741	1.253	1.039	2.745
9.901	357.5	0.600	0.789	1.154	1.054	2.495
9.875	357.3	0.725	0.848	1.037	1.113	2.123
9.876	357.0	0.851	0.914	0.963	1.171	1.875
15.214	374.1	0.058	0.504	4.466	0.598	16.609
15.222	370.7	0.115	0.567	2.844	0.629	10.107
15.199	367.3	0.181	0.643	2.307	0.635	8.164
15.243	365.1	0.277	0.691	1.751	0.675	5.847
15.237	364.1	0.407	0.734	1.309	0.738	4.004
15.246	363.7	0.447	0.752	1.243	0.749	3.749
15.232	363.5	0.500	0.768	1.144	0.781	3.310
15.201	362.8	0.580	0.820	1.078	0.738	3.303
15.267	362.1	0.706	0.857	0.951	0.863	2.493
15.213	361.4	0.824	0.908	0.886	0.947	2.117

the liquid phase (x_3), the equilibrium temperature (T), the mole fraction of ethanol in the liquid phase on an IL-free basis (x_1'), the mole fraction of ethanol in the vapor phase (y_1), the activity coefficient of ethanol (γ_1), the activity coefficient of water (γ_2), and the relative volatility of ethanol to water (α_{12}).

Table 4. Calculated Values of NRTL Parameters, Δg_{ij} and Δg_{ji}

i component	j component	α_{ij}	$\Delta g_{ij}/\text{J}\cdot\text{mol}^{-1}$	$\Delta g_{ji}/\text{J}\cdot\text{mol}^{-1}$
ethanol (1)	water (2)	0.4000	212.0	5076.5
ethanol (1)	[MMIM] ⁺ [DMP] ⁻ (3)	0.1208	-59354.1	-12122.3
water (2)	[MMIM] ⁺ [DMP] ⁻ (3)	0.0365	-70954.2	-17837.1

The activity coefficient of ethanol and water (γ_1, γ_2) and relative volatility of ethanol to water (α_{12}) were computed by the following equations

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

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

where y_i presents vapor-phase mole fraction of component i ; x_i presents liquid-phase containing IL mole fraction of component i ; P is the total pressure of the whole system, which equals to 101.3 kPa; and P_i^S is the vapor pressure of pure component i at equilibrium temperature and was computed by the Antoine equation using the Antoine coefficients given in Table 1.

The NRTL, Wilson, UNIQUAC,^{27,28} and electrolyte NRTL²⁰ models are commonly used to correlate the VLE data of the systems containing ILs. As suggested in our previous works, the NRTL model was used to correlate the vapor–liquid equilibrium of the ternary system in this work. The Levenberg–Marquardt method was used for data correlation. The objective function is defined as

$$\text{ARD} (\%) = \frac{1}{n} \sum_n \left| \frac{\gamma_i^{\text{exptl}} - \gamma_i^{\text{calcd}}}{\gamma_i^{\text{exptl}}} \right| \cdot 100 \quad (3)$$

which is the average relative deviation between the calculated and experimental activity coefficients of ethanol and water. The correlated results are given in Table 4.

In the NRTL model, only the nonrandomness parameter for the {ethanol (1) + water (2)} system, α_{12} , was set to be 0.40, which was the same as ref 23. The 1–2 binary interaction parameters of the NRTL model were first obtained from the VLE data of the {ethanol (1) + water (2)} system. The 1–3 and 2–3 binary interaction parameters were calculated from ternary VLE data. In this case, the ARD is 1.57 % for the {ethanol (1) + water (2)} binary system and 2.49 % for the {ethanol (1) + water (2) + [MMIM]⁺[DMP]⁻ (3)} ternary system.

The IL investigated could increase the relative volatility of ethanol to water and thus performed a salting-out effect for ethanol, as observed in Figures 2, 3, and 4. Besides, the azeotropic phenomena of the {ethanol (1) + water (2)} azeotrope could be totally eliminated when the IL concentration is equal to or greater than 5 %, and the azeotropic point at $x_1 \approx 0.90$ is shifted upward with the increase of IL concentration.

The [MMIM]⁺[DMP]⁻ produces a slight crossover salt effect in the {ethanol (1) + water (2)} system which can be observed in Figure 2, where at lower composition ($x_1' < 0.07$) the x_1, y_1 curve remains almost unchanged, whatever the ionic

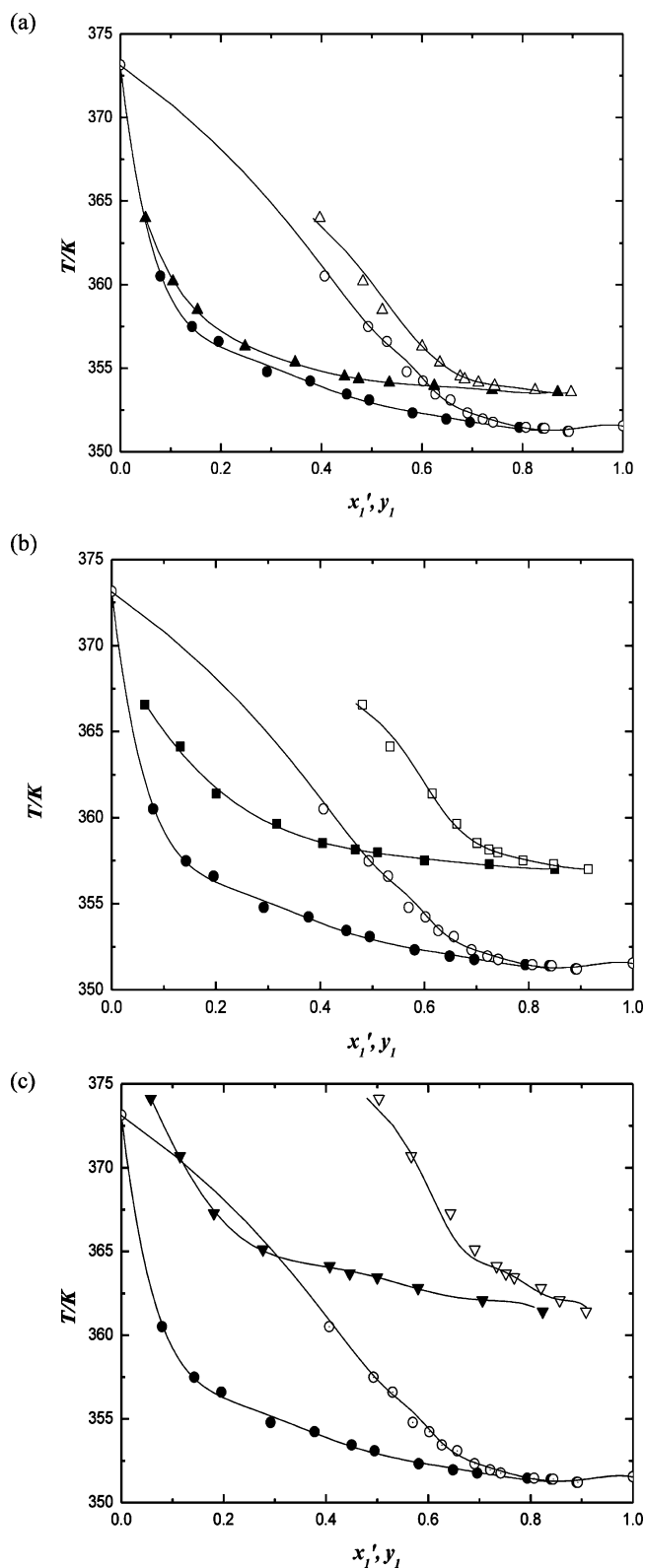


Figure 4. T, x, y diagram for the ternary system of ethanol (1) + water (2) containing $[\text{MMIM}]^+[\text{DMP}]^-$ (3) at different contents of IL: ●, x_1' ($x_3 = 0$); ○, y_1 ($x_3 = 0$); (a) ▲, x_1' ($x_3 = 0.05$); △, y_1 ($x_3 = 0.05$); (b) ■, x_1' ($x_3 = 0.10$); □, y_1 ($x_3 = 0.10$); (c) ▼, x_1' ($x_3 = 0.15$); ▽, y_1 ($x_3 = 0.15$); solid lines, correlated using the NRTL model.

liquid concentration is. This phenomena may be due to the interaction difference between $[\text{MMIM}]^+[\text{DMP}]^-$ and the solvent molecule.

Figure 3 indicates that an increase of IL mole fraction leads to the higher ethanol mole fraction in the vapor phase and the larger relative volatility of ethanol to water, and the salting-out effect follows the order: 15 % > 10 % > 5 %.

The T, x, y diagram of {ethanol (1) + water (2) + $[\text{MMIM}]^+[\text{DMP}]^-$ (3)} is shown in Figure 4. Figure 4 indicates that the higher the mole fraction of ionic liquid in the liquid phase, the higher the equilibrium temperatures of the whole system. That means that when a new equilibrium at higher mole fraction of ionic liquid is reached a new higher reboiler temperature is needed in the extractive distillation process. However, for a given purity in the extractive distillation, the corresponding reflux ratio can be reduced when the relative volatility of ethanol to water becomes higher. Though the heat demand needed in the above process decreases, the heat quality increases.

CONCLUSIONS

Ionic liquid could become an alternative entrainer in extractive distillation. The isobaric VLE data for {ethanol (1) + water (2) + $[\text{MMIM}]^+[\text{DMP}]^-$ (3)} were measured at 101.3 kPa. The experimental results showed that the ionic liquid $[\text{MMIM}]^+[\text{DMP}]^-$ can eliminate the azeotropic phenomenon, and the salting-out effect of $[\text{MMIM}]^+[\text{DMP}]^-$ follows the order of $x_3 = 0.15 > x_3 = 0.10 > x_3 = 0.05$. Therefore, the results further confirmed that $[\text{MMIM}]^+[\text{DMP}]^-$ can be used as new alternative entrainers for the {ethanol (1) + water (2)} system in extractive distillation. Moreover, compared with classic entrainers, $[\text{MMIM}]^+[\text{DMP}]^-$ has a notable salt effect and excellent properties, such as high chemical stability, non-volatility, and less causticity. The VLE data were correlated using the NRTL model with the ARD of 1.57 % for the {ethanol (1) + water (2)} binary system and of 2.49 % for the {ethanol (1) + water (2) + $[\text{MMIM}]^+[\text{DMP}]^-$ (3)} ternary system. The NRTL parameters obtained in this work can be used for the distillation design in the near future.

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