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Isobaric Vapor−Liquid Equilibrium for (Propan-2-ol + Water + 1-Butyl-3-methylimidazolium Tetrafluoroborate)[†]

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Isobaric vapor−liquid equilibrium (VLE) data for {propan-2-ol (1) + water (2) + 1-butyl-3-methylimidazolium tetrafluoroborate(3)} where 3 is an ionic liquid ($[BMIM]^+[BF_4]^-$) at atmospheric pressure (101.32 kPa) were measured with a modified Othmer still. The results showed that the ionic liquid studied can transfer the azeotropic point and eliminate the azeotropic phenomena when its concentration is up to $x_3 = 0.20$. This means that $[BMIM]^+[BF_4]^-$ can be used as a promising entrainer in the application of extractive distillation. However, the comparison of the salting-out effect of $[BMIM]^+[BF_4]^-$ with that of 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMIM]^+[BF_4]^-$) was conducted. The measured ternary data were correlated using the NRTL equation.

Introduction

Azeotropic or close boiling-point mixtures are complicated, nonideal mixtures that need high energy to be separated. Among all of the separation techniques toward the above mixtures such as azeotropic distillation, reactive distillation, adsorptive distillation, membrane distillation, and so on, extractive distillation behaves the most effectively.[1−3] However, the selection of entrainer that acts to increase the relative volatility of the mixtures is still a handicap for the further application of extractive distillation. The salt may deposit in the distillation column and corrode the sieve plate. Organic solvent will not only give rise to volatile organic compound (VOC) emission but also demand high energy, which does not meet the requirement of green chemistry. As a class of green solvents with negligible vapor pressure and excellent solvation properties, ionic liquids can avoid atmospheric contamination and flammable substances handling. At present, ionic liquids are becoming a kind of promising solvent used in the special separation processes.[4−9] However, further measurements of the thermodynamic data of the ionic-liquid-containing systems are still important, which will be necessary for the design of separation process.

Propan-2-ol is a basic chemical material and solvent used in the production of many chemicals and intermediates. However, at atmospheric pressure (101.32 kPa), the existence of azeotropic temperature for the mixture of propan-2-ol and water makes the separation process depend on special distillation. To select a suitable entrainer for the extractive distillation, the measurements of VLE of the azeotropic system added entrainers have to be done. In our previous work,[10] the vapor−liquid equilibrium (VLE) of {propan-2-ol (1) + water (2) + 1-ethyl-3-methylimidazolium tetrafluoroborate(3)}, where the latter is ($[EMIM]^+[BF_4]^-$), was measured at 101.32 kPa, and the obvious salting-out effect of $[EMIM]^+[BF_4]^-$ was observed. This work is to extend the measurement for the ternary system of {propan-2-ol (1) + water (2) + 1-butyl-3-methylimidazolium tetrafluoroborate(3)}, where the latter is ($[BMIM]^+[BF_4]^-$), and to compare the salting-out effect of $[BMIM]^+[BF_4]^-$ with that of $[EMIM]^+[BF_4]^-$ on the basis of the results of the vapor−liquid equilibria, which will be essential for the selection of ionic liquids for the separation of propan-2-ol and water and the design of the extractive distillation column.

Experimental Section

Chemicals. $[BMIM]^+[BF_4]^-$ was supplied by the Chemical Engineering Institute of the Normal University of Hebei (China) with a mass fraction purity of > 0.098 that was verified by liquid chromatography. Furthermore, the ionic liquid was dried for 48 h at (363 to 383) K under a vacuum by the rotary evaporator to remove the volatile impurity and water before experiments. Also, ionic liquid was reused after the volatile byproducts and water were separated by rotary evaporation. The water mass fraction in ionic liquid determined by Karl Fisher titration was less than 0.005. Propan-2-ol was purchased from Tianjin Chemical Reagents Company (China) with a mass purity of greater than 0.998. Distilled water was degassed and filtered using a 0.2 μm Millipore filter to remove dust. The purity of reagents was checked by gas chromatography (GC 4000A, China), and they were not further purified before experiments.

Apparatus and Procedure. The VLE data were measured by a circulation vapor−liquid equilibrium still (a modified Othmer still) at 101.32 kPa. A detailed description of the apparatus and the uncertainty analysis of equilibrium temperature, pressure, and composition is available in our previous publications.[10,11]

Results and Discussion

The VLE data for the binary azeotropic of {propan-2-ol (1) + water (2)} were measured at 101.32 kPa and listed in Table 1. Figure 1 shows that the VLE data obtained in this work were in good agreement with those reported by Li et al.[10] and Marzal

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Table 1. Vapor−Liquid Equilibrium Data for Propan-2-ol (1) + Water (2) System at P = 101.32 kPa

T/K	x_1	y_1
373.15	0.000	0.000
356.62	0.082	0.487
355.04	0.168	0.500
354.69	0.262	0.532
354.04	0.354	0.554
353.74	0.452	0.574
353.34	0.558	0.608
353.55	0.655	0.662
353.76	0.759	0.739
354.15	0.884	0.835
354.25	0.911	0.874
355.65	1.000	1.000

et al.[12] with the maximum absolute deviations, Δy_1, between the calculated and measured mole fractions of propan-2-ol in the vapor phase less than 0.025, thus verifying that our apparatus and experiment method were reliable.

On this basis, the VLE data for {propan-2-ol (1) + water (2) + $[\mathrm{BMIM}]^+[\mathrm{BF_4}]^-$ (3)} were measured at 101.32 kPa, and the ionic liquid concentrations added to the system were kept at $x_3 = 0.10$, 0.20, and 0.30. The experimental results are listed in Table 2, which comprises the equilibrium mole fractions of liquid and vapor phases (x_3, x_1', y_1), equilibrium temperature (T), activity coefficients of propan-2-ol (1) and water (2) (γ_1, γ_2), and relative volatility (α_{12}). It should be mentioned that x_1' is the mole fraction of propan-2-ol in the liquid phase on an ionic-liquid-free basis.

The activity coefficients of component i and relative volatility of {propan-2-ol (1) to water (2)} could be calculated by the following equations

$$\gamma_i = \frac{y_i P}{x_i P_i^{\mathrm{s}}} \tag{1}$$

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \tag{2}$$

where y_i represents mole fraction of component i in the vapor phase; x_i represents the mole fraction of component i in the liquid phase containing ionic liquid; P represents the total pressure of the equilibrium system, 101.32 kPa; and P_i^{s} represents the vapor pressure of pure component i at system temperature, which could be calculated by the Antoine equation using the Antoine constants from the literature.[13]

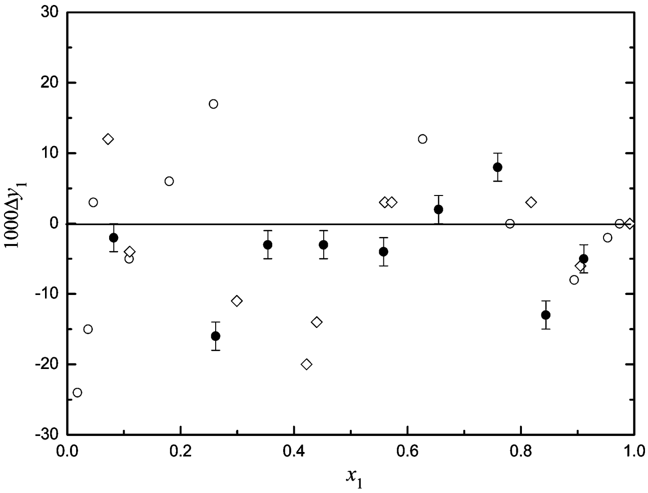

Figure 1. Absolute deviation $\Delta y_1 = y(\mathrm{exptl}) - y(\mathrm{calcd})$ between the calculated and measured mole fractions of propan-2-ol in the vapor phase for the binary system of propan-2-ol (1) + water (2) at 101.32 kPa: ●, this work with error bars representing the extended uncertainty; ◇, ref 10; ○, ref 12.

Table 2. Vapor−Liquid Equilibrium Data for the Ternary System of Propan-2-ol (1) + Water (2) + $[\mathrm{BMIM}]^+[\mathrm{BF4}]^-$ (3) at P = 101.32 kPa

$100x_3$	T/K	x_1'	y_1	γ_1	γ_2	α_{12}
9.951	367.98	0.017	0.170	6.831	1.128	11.8433
10.000	364.43	0.062	0.316	3.976	1.112	6.989
10.001	359.75	0.142	0.423	2.779	1.226	4.430
9.975	357.17	0.245	0.524	2.207	1.272	3.392
9.999	356.46	0.285	0.531	1.978	1.361	2.840
10.035	355.44	0.451	0.620	1.520	1.496	1.986
10.035	355.06	0.599	0.673	1.262	1.790	1.378
9.940	355.07	0.699	0.734	1.177	1.937	1.188
10.014	355.25	0.766	0.787	1.145	1.982	1.129
9.987	355.57	0.877	0.852	1.068	2.586	0.807
9.971	355.90	0.946	0.924	1.060	2.985	0.694
19.734	369.80	0.035	0.187	3.830	1.181	6.342
19.801	365.23	0.127	0.337	2.254	1.261	3.494
19.666	361.84	0.294	0.440	1.443	1.495	1.887
19.702	358.56	0.409	0.528	1.414	1.710	1.616
19.982	358.10	0.474	0.586	1.383	1.722	1.571
19.961	356.46	0.561	0.632	1.345	1.956	1.344
20.014	356.28	0.633	0.698	1.326	1.935	1.340
19.953	356.41	0.705	0.760	1.289	1.902	1.325
19.959	356.65	0.863	0.889	1.220	1.876	1.271
19.755	356.97	0.918	0.932	1.174	2.114	1.224
29.934	370.94	0.055	0.214	3.066	1.281	4.678
29.961	367.36	0.126	0.382	2.724	1.242	4.288
29.728	363.51	0.202	0.476	2.437	1.328	3.589
29.915	361.06	0.272	0.571	2.391	1.312	3.562
29.697	359.97	0.372	0.655	2.085	1.272	3.205
29.990	359.74	0.473	0.710	1.801	1.291	2.728
29.666	358.86	0.562	0.768	1.689	1.280	2.580
29.953	358.50	0.750	0.857	1.438	1.407	1.998
29.834	359.15	0.784	0.868	1.356	1.463	1.812
29.922	359.34	0.933	0.951	1.241	1.740	1.394

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

i component	j component	α_{ij}	Δg_{ij} / $\mathrm{J{\cdot}mol^{-1}}$	Δg_{ji} / $\mathrm{J{\cdot}mol^{-1}}$
propan-2-ol (1)	water (2)	0.300	−259.05	7633.49
propan-2-ol (1)	$[\mathrm{BMIM}]^+[\mathrm{BF_4}]^-$ (3)	0.118	15 577.55	−8971.89
water (2)	$[\mathrm{BMIM}]^+[\mathrm{BF_4}]^-$ (3)	0.283	21 966.33	−5954.31
propan-2-ol (1)	$[\mathrm{EMIM}]^+[\mathrm{BF_4}]^-$ (3)	0.174	17 097.04	−9204.33
water (2)	$[\mathrm{EMIM}]^+[\mathrm{BF_4}]^-$ (3)	0.297	34 790.24	−7423.83

As suggested in previous works,[6,7] the binary interaction parameters of the NRTL model were first obtained from the VLE data of {propan-2-ol (1) + water (2)}, and then other binary interaction parameters were obtained from ternary VLE data. The Marquardt method was used for data correlation, and the correlated results are given in Table 3, where the average relative deviation (ARD) is defined as

$$\mathrm{ARD}(\%) = \frac{1}{n}\sum_{n}\left|\frac{\gamma_i^{\mathrm{exptl}} - \gamma_i^{\mathrm{calcd}}}{\gamma_i^{\mathrm{exptl}}}\right|\cdot 100 \tag{3}$$

In the NRTL model, only the nonrandomness parameter, α, for the {propan-2-ol (1) + water (2)} system was set to be 0.30, taken from refs 10 and 14. In this case, the ARD is 2.32 % for {propan-2-ol (1) + water (2)}, 7.97 % for {propan-2-ol (1) + water (2) + $[\mathrm{BMIM}]^+[\mathrm{BF_4}]^-$ (3)}, and 5.49 % for {propan-2-ol (1) + water (2) + $[\mathrm{EMIM}]^+[\mathrm{BF_4}]^-$ (3)}, which was not yet correlated in our previous work.

The ionic liquid investigated increased the relative volatility of propan-2-ol to water, and thus showed a salting-out effect for propan-2-ol, as shown in Figures 2, 3, and 4. In general, the increasing mole fraction of ionic liquid will enhance the

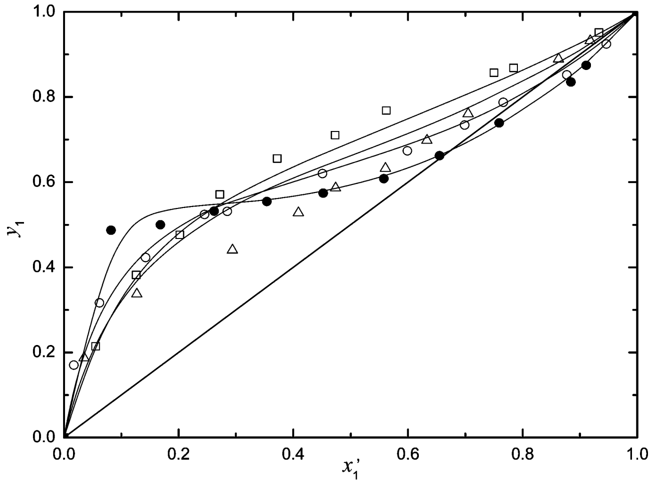

Figure 2. Isobaric VLE diagram for propan-2-ol (1) + water (2) + $[BMIM]^+[BF_4]^-$ (3) system at 101.32 kPa: ●, $x_3 = 0$; ○, $x_3 = 0.10$; △, $x_3 = 0.20$; □, $x_3 = 0.30$; solid lines, correlated using the NRTL model.

relative volatility of the mixtures more quickly when the ionic liquid has a good solubility in the components to be separated. However, we found the inverse effect from Figure 2; the lower ionic liquid mole fraction has a better salting-out effect than the higher ionic liquid mole fraction when the mole fraction of propan-2-ol is below 0.2 (on ionic-liquid-free basis). The {propan-2-ol (1) + water (2) + $[BMIM]^+[BF_4]^-$ (3)} system exhibits a trend similar to that of {propan-2-ol (1) + water (2) + $[EMIM]^+[BF_4]^-$ (3)}, as reported by Li et al.[10] We relate it to liquid−liquid demixing, which is brought out by more ionic liquid added to the system in the water-rich region and thus leads to the complex effect of ionic liquid on the VLE. With the increase in the mole fraction of propan-2-ol in the propan-2-ol-rich region, the salting-out effect tends to follow the expected order of $x_3 = 0.30 > x_3 = 0.20 > x_3 = 0.10$, because in this case, $[BMIM]^+[BF_4]^-$ has a good solubility with {propan-2-ol + water}. In addition, Figure 2 demonstrates that $[BMIM]^+[BF_4]^-$ can obviously shift the azeotropic point formed by {propan-2-ol + water}. When the mole fraction of $[BMIM]^+[BF_4]^-$ is up to $x_3 = 0.20$, the azeotropic point disappears. Therefore, the ionic liquid $[BMIM]^+[BF_4]^-$ may be a promising entrainer used for the purification of propan-2-ol.

This work compares the salting-out effect of $[BMIM]^+[BF_4]^-$ with that of $[EMIM]^+[BF_4]^-$, as shown in Figure 3. The relative volatility of propan-2-ol to water with $[EMIM]^+[BF_4]^-$ as entrainer is higher than that with $[BMIM]^+[BF_4]^-$ at the same concentration. Moreover, $[EMIM]^+[BF_4]^-$ can eliminate the azeotropic point at $x_3 = 0.10$, whereas $[BMIM]^+[BF_4]^-$ can eliminate the azeotropic point at $x_3 = 0.20$. As we know, for a given anion, the polarity of ionic liquids depends on the length of carbon chain. Therefore, $[EMIM]^+[BF_4]^-$ with a short carbon chain on the cation has stronger polarity than $[BMIM]^+[BF_4]^-$, which makes the salting-out effect of $[EMIM]^+[BF_4]^-$ toward the azeotropic system more intense than that of $[BMIM]^+[BF_4]^-$.

The *T*, *x*, *y* diagram for {propan-2-ol (1) + water (2) + $[BMIM]^+[BF_4]^-$ (3)} is shown in Figure 4. Figure 4 shows that the equilibrium temperatures increase with the increase in the amount of $[BMIM]^+[BF_4]^-$ added to the system, which indicates that the heat duty of the extractive distillation column will increase. Meanwhile, the column that is used to recover the entrainer will also need more heat. The equilibrium temperature of {propan-2-ol (1) + water (2) + $[BMIM]^+[BF_4]^-$ (3)} is higher than that of {propan-2-ol (1) + water (2) + $[EMIM]^+[BF_4]^-$ (3)} at the same concentration. This means that the energy demand for extractive distillation with $[BMIM]^+[BF_4]^-$ as entrainer may be larger than that with $[EMIM]^+[BF_4]^-$ as entrainer.

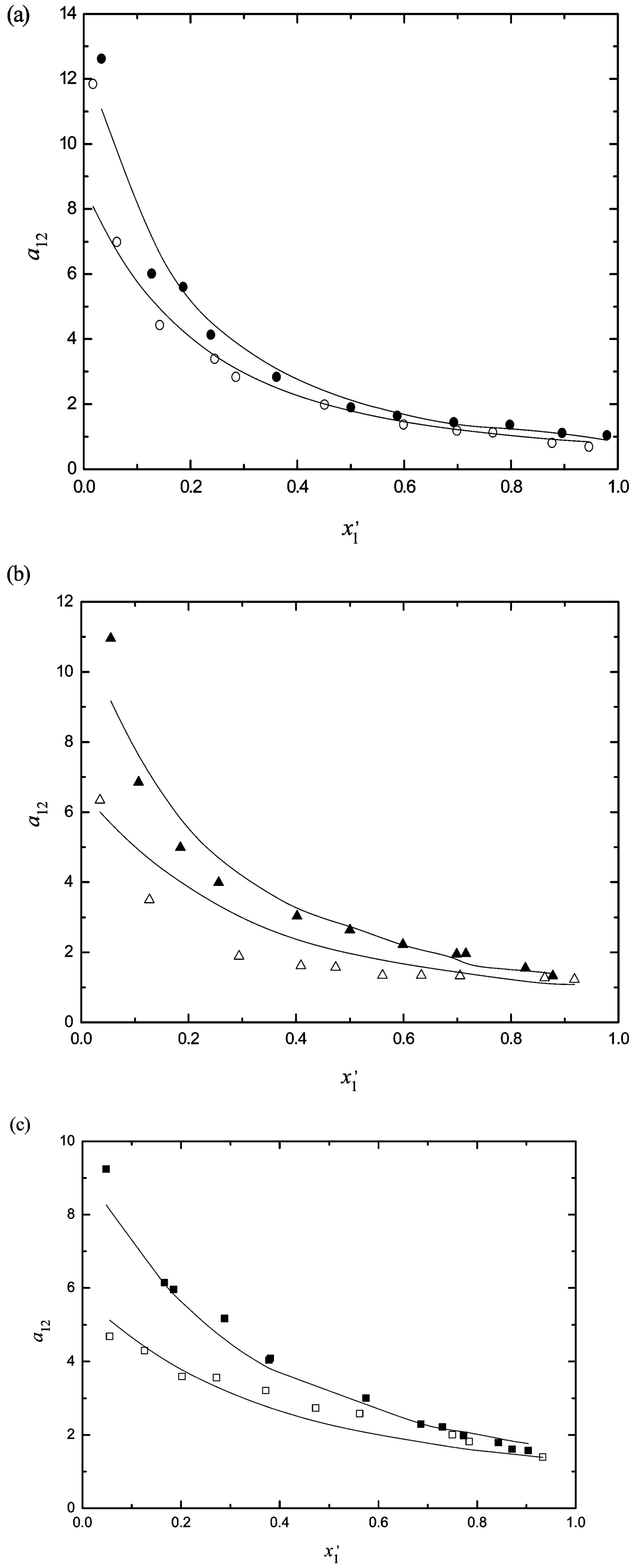

Figure 3. Relative volatility of propan-2-ol (1) to water (2) at 101.32 kPa: (a) $x_3 = 0.1$: ●, $[EMIM]^+[BF_4]^-$; ○, $[BMIM]^+[BF_4]^-$; (b) $x_3=0.20$: ▲, $[EMIM]^+[BF_4]^-$; △, $[BMIM]^+[BF_4]^-$; (c) $x_3 = 0.30$: ■, $[EMIM]^+[BF_4]^-$; □, $[BMIM]^+[BF_4]^-$; solid lines, correlated using the NRTL model.

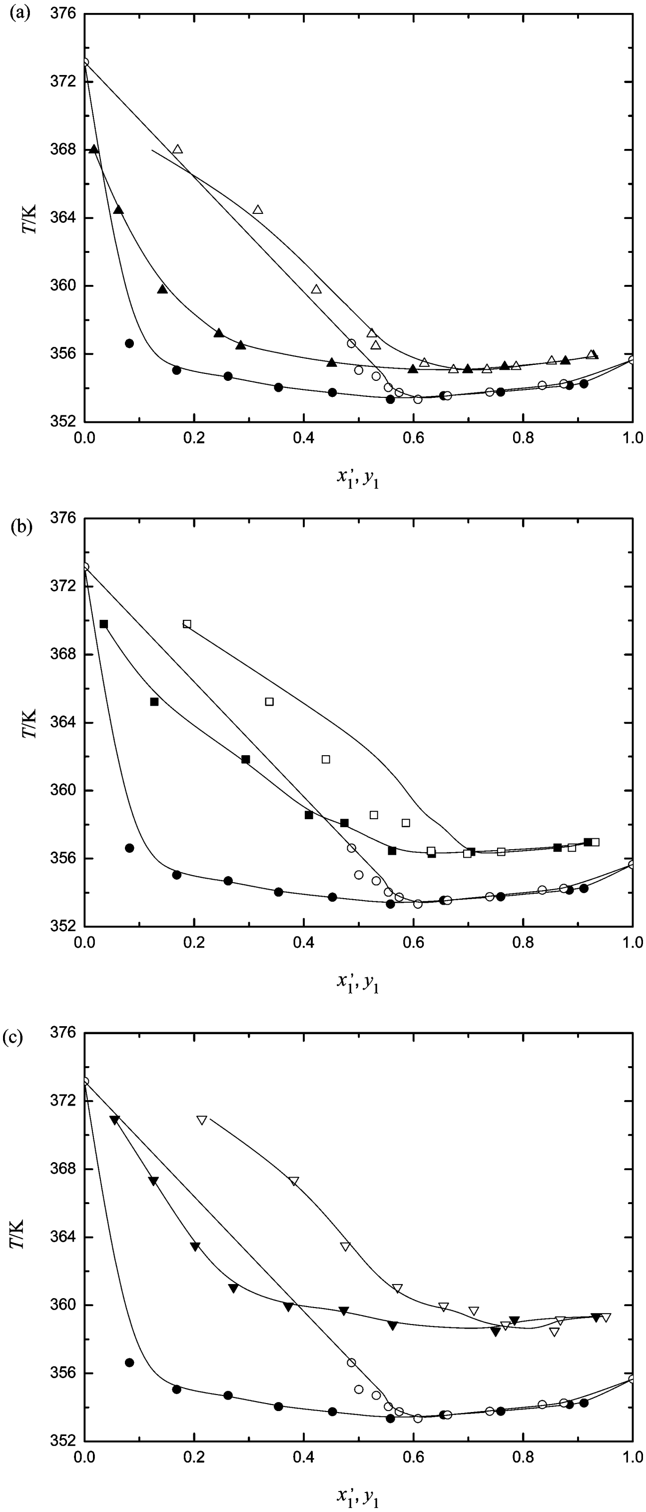

Figure 4. *T*, *x*, *y* diagram for the ternary system of propan-2-ol (1) + water (2) containing $[BMIM]^+[BF_4]^-$ (3) at different contents of IL: ●, x_1' ($x_3 = 0$); ○, y_1 ($x_3 = 0$); (a) ▲, x_1' ($x_3 = 0.10$); △, y_1 ($x_3 = 0.10$); (b) ■, x_1' ($x_3 = 0.20$); □, y_1 ($x_3 = 0.20$); (c) ▼, x_1' ($x_3 = 0.30$); ▽, y_1 ($x_3 = 0.30$); solid lines, correlated using the NRTL model.

Conclusions

The isobaric VLE data for {propan-2-ol (1) + water (2) + $[BMIM]^+[BF_4]^-$ (3)} were measured at 101.32 kPa. The experimental results showed that the ionic liquid $[BMIM]^+[BF_4]^-$ can eliminate the azeotropic point at $x_3 = 0.20$. In the propan-2-ol-rich region, the salting-out effect of $[BMIM]^+[BF_4]^-$ tends to follow the order of $x_3 = 0.30 > x_3 = 0.20 > x_3 = 0.10$, whereas in the water-rich region, the effect of ionic liquid on the VLE is complicated because of the liquid−liquid demixing. The salting-out effect of $[BMIM]^+[BF_4]^-$ with that of $[EMIM]^+[BF_4]^-$ was compared in this work, and it was found that $[EMIM]^+[BF_4]^-$ has a higher salting-out effect than $[BMIM]^+[BF_4]^-$ because its carbon chain on the cation is shorter. The VLE data, along with {propan-2-ol (1) + water (2) + $[EMIM]^+[BF_4]^-$ (3)}, were correlated using the NRTL model with the ARD of 2.32 % for the {propan-2-ol (1) + water (2)} system, 7.97 % for the {propan-2-ol (1) + water (2) + $[BMIM]^+[BF_4]^-$ (3)} system, and 5.49 % for the {propan-2-ol (1) + water (2) + $[EMIM]^+[BF_4]^-$ (3)} system. The binary interaction parameters obtained in this work will be useful for the distillation design with such simulation software as Aspen Plus, HYSYS, and PROII.

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