Experimental Measurement and Modeling of Vapor−Liquid Equilibrium for the Ternary System Water + Ethanol + 1-Butyl-3-methylimidazolium Chloride

Wei Geng, Lianzhong Zhang,* Dongshun Deng, Yun Ge, and Jianbing Ji

College of Chemical Engineering and Material Science, Zhejiang University of Technology, Hangzhou 310014, China

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Vapor−liquid equilibrium (VLE) data were measured for the ternary system water (1) + ethanol (2) + 1-butyl-3-methylimidazolium chloride ([bmim]Cl) (3). Complete *T*, *x*, and *y* data were obtained in a relatively wide range of ionic liquid (IL) mass fractions up to 0.8 and in a relatively complete composition range for the volatile binary pair. The nonrandom two-liquid (NRTL) equation was used for correlation and was revealed to be adequate for the ternary system in the experimental composition range. The ternary VLE behavior was also modeled by the correlation of two data sets, in which the ethanol mole fraction on IL-free basis is respectively at 0.1 and 0.98. In this way, the six data sets were reproduced satisfactorily, with root-mean-square deviations of 0.40 K for temperature and 0.0070 for vapor-phase mole fractions. Owing to the regular distribution of the experimental data, a good agreement between the experiment and the calculation was graphically presented. The effect of the IL on the VLE behavior of the volatile components was also illustrated.

Introduction

In recent years, ionic liquids (ILs) have received considerable attention for their use in the chemical industry and are considered to be potential solvents for extractive distillation.[1,2] With the addition of an IL, the activity coefficients of the components to be separated change their values to a different extent. It is desirable that the changes in activity coefficients result in an increase of relative volatility. Therefore, the performance of an IL depends mainly on the composition dependence of the activity coefficients in the IL-containing mixture. At the present stage, such information is mainly obtained from experimental measurement and by correlation using a model of excess Gibbs energy.[3−8]

In our previous work,[9] we presented an procedure for the experimental measurement and modeling of vapor−liquid equilibrium of ternary systems containing ionic liquid, taking the system water + ethanol + 1-hexyl-3-methylimidazolium chloride as a case study. Six sets of complete *T*, *x*, and *y* data were measured, in which two data sets were used for correlation of the nonrandom two-liquid (NRTL) model[10] and the other four data sets were used for checking the model. On the basis of detailed discussion, the modeling of vapor−liquid equilibrium (VLE) behavior of a ternary system containing ILs has been generally recommended by the correlation of two ternary data sets, which are measured at a relatively wide range of IL mass fraction, while the mole fractions of the volatile quasi-binary pair are distributed respectively in the two diluted ends.

In this work, we have extended the experimental measurement and modeling to the system water (1) + ethanol (2) + 1-butyl-3-methylimidazolium chloride ([bmim]Cl) (3). The modeling was based on *T*, *x*, and *y* data in a relatively wide range of IL mass fraction up to 0.8 and in a relatively complete composition range for the volatile binary pair. This system has been studied by Jork et al.[8] The headspace technique was used in the measurements. Therefore, only *x* and *y* data were reported. Zhao et al.,[5] Calvar et al.,[7] and Ge et al.[11] have reported *T*, *x*, and *y* data for the system. However, the measurements were generally limited to a relatively small range of IL mass fraction, especially in the ethanol-rich region.

Experimental Section

Materials. Water was double-distilled. Ethanol was an analytical grade reagent and was used without further purification. The purity of ethanol was checked by gas chromatography (GC), and the result was 99.9 %, while Karl Fischer analysis indicated a water mass fraction of $4.3 \cdot 10^{-4}$. [bmim]Cl was synthesized by the reaction of 1-chlorobutane with 1-methylimidazole under a nitrogen atmosphere. The purification of [bmim][Cl] was by recrystallization in a mixture of ethyl acetate + acetonitrile. Before use, the IL was dried for 24 h under vacuum at 353 K to remove volatile impurities. Karl Fischer analysis showed typically a water mass fraction of $1.2 \cdot 10^{-3}$ in the IL. The IL was also checked by electrospray ionization mass spectrometry (ESI-MS), showing a single positive ion, $m/z = 139$ ([bmim]).

Apparatus and Procedure. VLE data were measured by an ebulliometer, which was described in detail in previous work.[12,13] In the measurements, liquid-phase circulation was enhanced by a pump-like stirrer and had a value of approximately 200 $\text{cm}^3 \cdot \text{min}^{-1}$. Vapor-phase circulation was maintained at approximately 1 $\text{cm}^3 \cdot \text{min}^{-1}$, while the vapor-to-liquid circulation ratio calculated on mass basis had a value of 0.005. Vapor condensate was cooled to 275 K. The volume of vapor material is estimated to be 1.7 cm^3, which is very small compared to the total sample volume of 270 cm^3 in the ebulliometer. For more details, please refer to our previous work.[12,13]

Pressure was measured by a precision pressure gauge with an uncertainty of ± 0.04 kPa. A 20 dm^3 glass container was used as a pressure buffer connected to the ebulliometer. Temperature measurement was by a standard platinum thermometer and a 6.5 digit multimeter. The uncertainty of the

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* Corresponding author. Phone: +86 571 88320892. E-mail: zhanglz@zjut.edu.cn.

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resistance measurement was ± 8 mΩ, which is equivalent to ± 0.08 K for the temperature measurement.

The VLE measurements were performed in a way in which the IL mass fraction, w_3, changed from high to low, while x'_2, which is the mole fraction of ethanol on IL-free basis, remained almost unchanged. At high IL mass fractions, namely, at $w_3 =$ 0.6, 0.7, and 0.8, the measurements were performed at subatmospheric pressures. As has been commonly recognized, the activity coefficients in the liquid mixture depend strongly on composition. Often, they depend only weakly on temperature and very weakly on pressure. Therefore, the present measurements will provide mainly the composition dependence of the activity coefficients.

At the beginning of the measurement, samples of water, ethanol, and the IL were introduced into the ebulliometer. The water contents of ethanol and the IL were determined by Karl Fischer analysis. Every sample added in or taken out of the ebulliometer was weighed by an electronic balance (Mettler-Toledo AL204) with an uncertainty of ± 0.0002 g. Masses of water and the other components added in the ebulliometer were calculated. Therefore, we have the overall synthetic masses for the first measurement. When equilibrium was established, the vapor condensate was sampled and analyzed. As the IL is nonvolatile, the vapor phase is composed of water and ethanol. Vapor-phase composition was determined by analyzing the water content using the Karl Fischer method. When the water mole fraction is greater than 0.1, the sample was first mixed with ethanol quantitatively, and the water content of the mixture was analyzed. Vapor-phase composition was then calculated by the ratio of mixing and the result of the water content. The uncertainty of the vapor-phase composition was estimated to be 0.0001 in water mole fraction or relatively 1 %, whichever is the greater. Liquid-phase compositions were calculated on the basis of mass balances, using a procedure presented in previous work.[12,14] The next measurement was carried out by the replacement of a certain amount of the mixture in the boiler with IL-free mixture of water and ethanol to keep x'_2 almost unchanged. The measurement was repeated until w_3 became close to 0.1.

Results and Discussion

The experimental VLE data for the ternary system water (1) + ethanol (2) + [bmim]Cl (3) are listed in Table 1. The measurements were performed in a way in which w_3 varied from 0.8 to 0.1, while x'_2 remained almost unchanged. There are six data sets in Table 1, at respectively $x'_2 = 0.1$, 0.2, 0.4, 0.6, 0.8, and 0.98. The six data sets of forty-eight data points were regularly distributed at eight w_3 and six x'_2. In the measurements the pressure was kept, respectively, at 30 kPa for $w_3 = 0.8$ and 0.7, at 40 kPa for $w_3 = 0.6$, and at 100 kPa for $w_3 = 0.5$ down to 0.1. Therefore, the pressure was practically the same for a given w_3 at different x'_2. Complete T, x, and y data were obtained. The liquid-phase compositions were reported in x'_2 and w_3. Activity coefficients of water (γ_1) and ethanol (γ_2), as well as the relative volatility of ethanol to water ($\alpha_{2,1}$), were also reported. In the calculation of the activity coefficients the vapor phase was regarded as an ideal gas, and the vapor pressures were calculated by parameters in the literature.[15]

In the measurements, the temperature stability was better than 0.04 K. As discussed in our previous work,[9,13] the uncertainty for the reported w_3 was estimated to be ± 0.003. The uncertainty of the molar composition of the volatile binary pair, x'_2 or x'_1, was estimated to be less than relatively 1 %.

Table 1. VLE Data for the Ternary System Water (1) + Ethanol (2) + [bmim]Cl (3)

x'_2	w_3	y_2	p/kPa	T/K	γ_1	γ_2	$\alpha_{2,1}$
			$x'_2 = 0.1$				
0.1031	0.8005	0.4061	30.00	360.15	0.47	1.25	5.95
0.0935	0.6994	0.3855	30.04	349.17	0.65	1.73	6.08
0.0951	0.5999	0.3858	40.00	348.14	0.83	2.19	5.98
0.0961	0.5003	0.3939	100.00	367.56	0.91	2.50	6.11
0.0970	0.4002	0.3977	100.00	364.42	0.98	2.70	6.15
0.0975	0.3002	0.4089	100.00	362.42	1.01	2.89	6.40
0.0980	0.2002	0.4202	100.00	360.95	1.03	3.06	6.67
0.0988	0.1000	0.4343	100.00	359.69	1.04	3.24	7.00
			$x'_2 = 0.2$				
0.2020	0.8002	0.5880	30.00	358.93	0.40	1.01	5.64
0.1927	0.6992	0.5637	30.00	346.23	0.60	1.43	5.41
0.1993	0.6003	0.5602	40.00	344.85	0.79	1.77	5.12
0.2000	0.5004	0.5394	100.00	363.67	0.91	1.92	4.68
0.2000	0.4000	0.5418	100.00	360.51	0.98	2.08	4.73
0.1997	0.3002	0.5318	100.00	358.49	1.06	2.14	4.55
0.1991	0.2000	0.5334	100.00	357.19	1.08	2.21	4.60
0.1990	0.1003	0.5393	100.00	356.32	1.08	2.27	4.71
			$x'_2 = 0.4$				
0.3998	0.8000	0.7746	29.99	359.58	0.31	0.71	5.16
0.3996	0.6997	0.7381	30.00	345.28	0.53	0.99	4.23
0.3997	0.5997	0.7025	40.00	343.32	0.79	1.23	3.55
0.3996	0.5000	0.6798	100.00	361.54	0.94	1.35	3.19
0.3995	0.3996	0.6591	100.00	358.00	1.10	1.42	2.91
0.3997	0.2999	0.6513	100.00	355.85	1.18	1.47	2.81
0.3997	0.2017	0.6397	100.00	354.55	1.25	1.48	2.67
0.4006	0.1000	0.6343	100.00	353.77	1.28	1.47	2.60
			$x'_2 = 0.6$				
0.5979	0.7997	0.8790	30.00	362.02	0.24	0.53	4.88
0.5988	0.6998	0.8472	30.01	347.01	0.46	0.75	3.71
0.6010	0.5999	0.8220	40.00	344.37	0.71	0.95	3.07
0.6011	0.5003	0.7928	100.00	361.81	0.94	1.06	2.54
0.6002	0.4001	0.7769	100.00	357.61	1.12	1.15	2.32
0.6000	0.2999	0.7587	100.00	355.04	1.28	1.19	2.10
0.6002	0.1999	0.7289	100.00	353.42	1.49	1.18	1.79
0.6000	0.0999	0.7074	100.00	352.52	1.62	1.16	1.61
			$x'_2 = 0.8$				
0.8012	0.7996	0.9514	29.98	364.73	0.19	0.41	4.85
0.8003	0.6999	0.9365	30.04	349.89	0.36	0.58	3.68
0.8001	0.6000	0.9161	40.00	346.56	0.63	0.75	2.73
0.7999	0.4999	0.8977	100.00	363.09	0.90	0.88	2.19
0.8000	0.4007	0.8833	100.00	358.19	1.16	0.98	1.89
0.7995	0.2996	0.8686	100.00	355.02	1.41	1.04	1.66
0.7998	0.2000	0.8540	100.00	353.07	1.63	1.06	1.46
0.7994	0.0999	0.8411	100.00	351.86	1.81	1.06	1.33
			$x'_2 = 0.98$				
0.9778	0.8002	0.9953	30.00	367.97	0.15	0.33	4.80
0.9790	0.7001	0.9943	30.00	352.31	0.29	0.47	3.73
0.9794	0.6000	0.9919	40.00	348.71	0.55	0.63	2.58
0.9797	0.5003	0.9889	100.00	364.55	0.93	0.77	1.86
0.9799	0.4001	0.9874	100.00	359.34	1.21	0.87	1.61
0.9797	0.2999	0.9854	100.00	355.48	1.54	0.95	1.40
0.9796	0.1999	0.9834	100.04	353.25	1.82	1.00	1.23
0.9799	0.1000	0.9813	100.00	351.93	2.12	1.01	1.08

Modeling of the ternary VLE was first performed by the correlation of the six data sets, using the NRTL equation.[10] In the correlation, the binary parameters for water + ethanol were taken from literature.[16] The suitability of the binary parameters was discussed in previous work.[9] While the values of nonrandomness factors α_{13} and α_{23} were set as 0.3, binary parameters for water + [bmim]Cl and ethanol + [bmim]Cl were obtained by the minimization of the following objective function:

$$F = \sqrt{\sum_{n=1}^{N} (\gamma_{1,\mathrm{cal}}/\gamma_{1,\mathrm{exp}} - 1)^2/N} + \sqrt{\sum_{n=1}^{N} (\gamma_{2,\mathrm{cal}}/\gamma_{2,\mathrm{exp}} - 1)^2/N} \quad (1)$$

in which N is the number of data points. The obtained parameters were used for the calculation of the ternary VLE

Table 2. Root-Mean-Square Deviations, δT and δy, in the Calculation of VLE Data of Water (1) + Ethanol (2) + [bmim]Cl (3), Based on Correlations by the NRTL Equation

data sets used in correlation	root mean square deviations[a]	
	δT/K[b]	δy[c]
six data sets in Table 1	0.40	0.0062
$x'_2 = 0.1$ and 0.98	0.40	0.0070

[a] Deviations are calculated for the six data sets. [b] $\delta T/\mathrm{K} = (\Sigma(T_{\mathrm{cal}}/\mathrm{K} - T_{\mathrm{exp}}/\mathrm{K})^2/N)^{1/2}$. [c] $\delta y = (\Sigma(y_{2,\mathrm{cal}} - y_{2,\mathrm{exp}})^2/N)^{1/2}$.

Table 3. Energy Parameters, Δg_{ij} and Δg_{ji}, and Nonrandomness Factors, α_{ij}, for the NRTL Model Obtained from the Correlation of Ternary VLE Data of Water (1) + Ethanol (2) + [bmim]Cl (3), Using Data Sets at $x'_2 = 0.1$ and $x'_2 = 0.98$

binary parameters[a]				
		Δg_{ij}	Δg_{ji}	
component i	component j	J·mol^{-1}	J·mol^{-1}	α_{ij}
water	[bmim]Cl	−5270.6	−7372.2	0.3
ethanol	[bmim]Cl	−2449.9	−6457.3	0.3

[a] Binary parameters for water (1) + ethanol (2) were taken from ref 16 and were fixed as $\Delta g_{12}/\mathrm{J\cdot mol^{-1}} = 4458.8 + 8.4420(T/\mathrm{K})$, $\Delta g_{21}/\mathrm{J\cdot mol^{-1}} = -3791.4 + 4.1451(T/\mathrm{K})$, and $\alpha_{12} = 0.1448$. The objective function used in the optimization was shown in eq 1.

data in comparison with experimental values. Results are given in Table 2, in which δT and δy are respectively the root-mean-square deviations of temperature and vapor-phase mole fractions. The NRTL equation, with the nonrandomness factors α_{13} and α_{23} having the most common value of 0.3, appeared suitable for the ternary system in the experimental composition range, with $\delta T = 0.40$ K and $\delta y = 0.0062$.

Following a procedure recommended in previous work[9] for modeling of ternary VLE behavior, two data sets at $x'_2 = 0.1$ and $x'_2 = 0.98$ were correlated. The optimized binary parameters are given in Table 3. The parameters obtained were used for calculation in comparison with the six sets of experimental data. The results were quite good, with $\delta T = 0.40$ K and $\delta y = 0.0070$. These deviations are very close to those by direct correlation of the six data sets. Therefore, the two data sets at $x'_2 = 0.1$ and $x'_2 = 0.98$ appear to be adequate for modeling the VLE behavior in the experimental composition range.

VLE results calculated by using parameters in Table 3 are also shown in Figures 1, 2, and 3, in comparison with the experimental values. In Figure 1, γ_1 and γ_2 are shown in relation with x'_2. As the experimental data were measured regularly at $w_3 = 0.8$ to 0.1, in an interval of 0.1, the calculated activity coefficients, in relation with x'_2, can be compared with the experimental values at several fixed IL mass fractions. Good agreement can be observed. For the best illustration, typical results at $w_3 = 0$ (no IL), 0.1, 0.3, 0.5, 0.6, 0.7, and 0.8 are presented. While γ_2 decreases with increasing x'_2 at all given w_3, γ_1 varies with x'_2 in a more complicated manner. When the IL mass fraction is high, namely, at $w_3 = 0.6$, 0.7, and 0.8, γ_1 decreases rapidly with increasing x'_2. At the same time, γ_1 increases with increasing x'_2 at $w_3 = 0.1$ and 0.3, while having a maximum with changing x'_2 for $w_3 = 0.5$. These trends are similar to those presented for the system water (1) + ethanol (2) + [hmim]Cl.[9] On the other hand, composition dependence of the activity coefficients on the IL mass fraction can also be observed in Figure 1. Generally, both γ_1 and γ_2 decrease with increasing w_3. While the decrease of γ_1 is beneficial for the enhancement of the relative volatility, the decrease of γ_2 is not desirable. The effect of the IL on the relative volatility of ethanol to water, $\alpha_{2,1}$, is shown in Figure 2. While the addition of the IL results in an increase of relative volatility in the ethanol-rich region, showing a salting-out effect, there is a salting-in effect in the water-rich region. Moreover, T, x'_2, and y_2 relations at typically $w_3 = 0.7$ and 0.8 are shown in Figure 3. Such an illustration is realized because we have set the pressure at practically the same value for a given w_3 at different x'_2 in the measurements. While the boiling temperature of water is higher than ethanol, the boiling temperature of water + [bmim]Cl becomes lower than that of ethanol + [bmim]Cl at $w_3 = 0.8$. Although the azeotrope of water + ethanol has been removed by addition of the IL, there is a minimum for respectively the bubble line and the dew line at a given w_3.

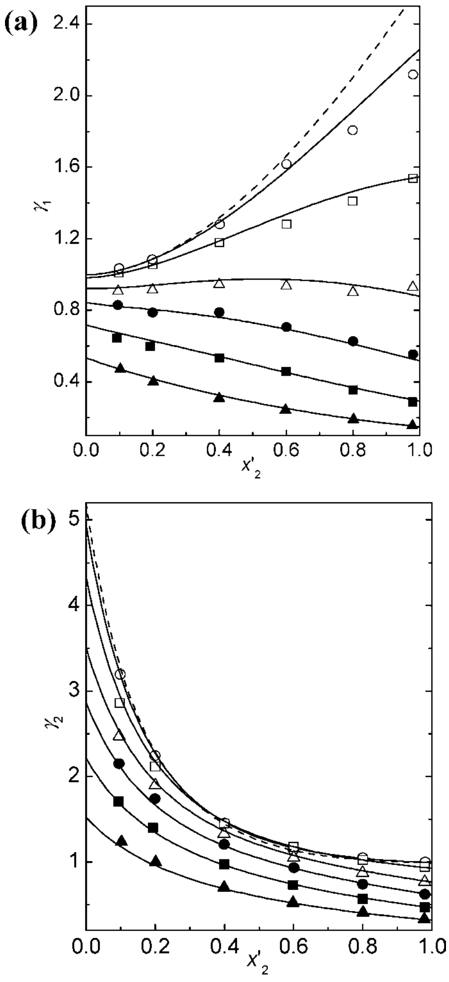

Figure 1. Experimental and calculated activity coefficients of (a) water, γ_1, and (b) ethanol, γ_2, in relation with ethanol mole fraction on IL-free basis, x'_2, for the saturated mixture water (1) + ethanol (2) + [bmim]Cl (3): ○, $w_3 = 0.1$, $p = 100$ kPa; □, $w_3 = 0.3$, $p = 100$ kPa; Δ, $w_3 = 0.5$, $p = 100$ kPa; ●, $w_3 = 0.6$, $p = 40$ kPa; ■, $w_3 = 0.7$, $p = 30$ kPa; ▲, $w_3 = 0.8$, $p = 30$ kPa. Lines were calculated by NRTL parameters in Table 3: solid lines, calculated values at $w_3 = 0.1$, 0.3, 0.5, 0.6, 0.7, and 0.8, respectively, and at relevant pressures; dashed line, calculated values for the system water (1) + ethanol (2) at $p = 100$ kPa.

VLE data for the same ternary system at $p = 101.3$ kPa have been reported by Calvar et al.[7] By using the parameters proposed in Table 3, the literature ternary data were calculated, showing root-mean-square deviations of $\delta T = 2.97$ K and $\delta y = 0.0410$. The calculated temperatures are generally lower than the reported values. In the original literature, all of the nine binary parameters for the ternary mixture were optimized. The reported deviations were $\delta T = 1.18$ K and $\delta y = 0.06$. The reported deviations in vapor mole fractions are larger than those we

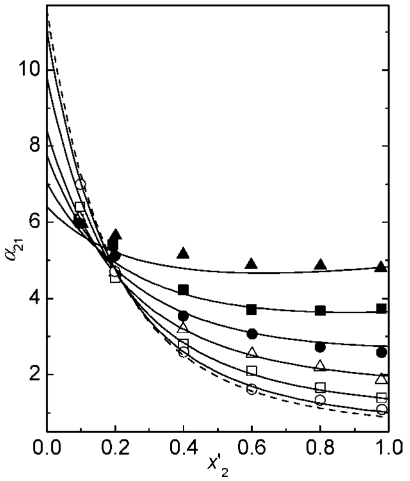

Figure 2. Experimental and calculated relative volatility of ethanol to water, $\alpha_{2,1}$, in relation with ethanol mole fraction on IL-free basis, x'_2, for the saturated mixture water (1) + ethanol (2) + [bmim]Cl (3): ○, $w_3 = 0.1$, $p = 100$ kPa; □, $w_3 = 0.3$, $p = 100$ kPa; △, $w_3 = 0.5$, $p = 100$ kPa; ●, $w_3 = 0.6$, $p = 40$ kPa; ■, $w_3 = 0.7$, $p = 30$ kPa; ▲, $w_3 = 0.8$, $p = 30$ kPa. Lines were calculated by NRTL parameters in Table 3: solid lines, calculated values at $w_3 = 0.1$, 0.3, 0.5, 0.6, 0.7, and 0.8, respectively, and at relevant pressures; dashed line, calculated values for the system water (1) + ethanol (2) at $p = 100$ kPa.

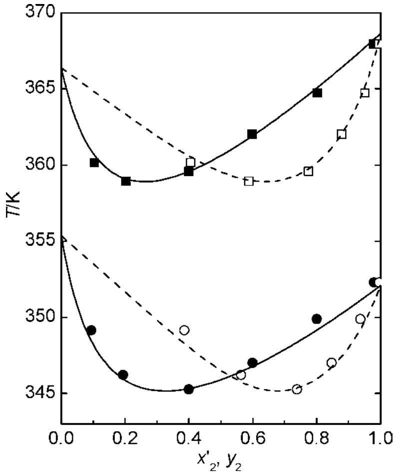

Figure 3. Experimental and calculated relations of the T, x'_2, and y_2 diagram for the system water (1) + ethanol (2) + [bmim]Cl (3) at $p = 30.0$ kPa: ○, ●, $w_3 = 0.7$; □, ■, $w_3 = 0.8$. Lines were calculated by NRTL parameters in Table 3 at $p = 30$ kPa and at $w_3 = 0.7$ and 0.8, respectively: Solid points and solid lines represent the T, x'_2 relation; hollow points and dashed lines represent the T and y_2 relation.

calculated. When, on the other hand, the reported parameters are used for the calculation of the six data sets in this work, the deviations are $\delta T = 3.87$ K and $\delta y = 0.0175$, which appear to be much larger than those we presented by using parameters in Table 3. It should be also noted that the ternary VLE data reported in this work, as compared with the literature data, are in a relatively wide range of IL mass fraction, especially in the ethanol-rich region. The same ternary system has been studied by Zhao et al.,[5] reporting data at $p = 101.32$ kPa and at $w_3 \approx 0.2$ and 0.3. By using parameters proposed in Table 3, the literature data were calculated, showing root-mean-square deviations of $\delta T = 0.54$ K and $\delta y = 0.0460$. The deviations of vapor mole fractions are relatively large in the water-rich region. In our previous work, we have measured VLE data for the same system at $x'_2 = 0.95$ and IL mass fractions up to 0.59. By using the parameters in Table 3, calculations of the VLE data show root-mean-square deviations of $\delta T = 0.55$ K and $\delta y = 0.0013$. The same ternary system has also been studied by Jork et al.[8] using the headspace technique. Vapor compositions were reported at 363.15 K and at three IL mole fractions, namely, at $x_3 = 0.1$, 0.3, and 0.5. The reported uncertainty in vapor mole fractions was 0.015. At low IL mole fractions, namely, at $x_3 = 0.1$, calculations using the parameters in Table 3 show good agreement, with $\delta y = 0.0082$. However, relatively large deviations can be observed at high IL concentration, with $\delta y = 0.0290$ for all of the three IL mole fractions. The calculated vapor mole fractions of ethanol are smaller than the reported values.

Conclusions

T, x, and y data were measured for the ternary system water (1) + ethanol (2) + [bmim]Cl (3). Six data sets of 48 data points were obtained, which were regularly distributed at $w_3 = 0.1$ to 0.8, in an interval of 0.1, and at $x'_2 = 0.1$, 0.2, 0.4, 0.6, 0.8, and 0.98. The pressure was kept, respectively, at 30 kPa for $w_3 = 0.8$ and 0.7, at 40 kPa for $w_3 = 0.6$, and at 100 kPa for $w_3 = 0.5$ down to 0.1. The NRTL equation was used for correlation and was revealed to be adequate for the ternary system in the experimental composition range. By correlating the two data sets respectively at $x'_2 = 0.1$ and 0.98, all of the six data sets were reproduced satisfactorily, with $\delta T = 0.40$ K and $\delta y = 0.0070$. Owing to the regular distribution of the experimental data, a good agreement between the experiment and the calculation was graphically presented. The effect of the IL on the VLE behavior of the volatile components was also illustrated.

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