Experimental Measurement and Modeling of Vapor−Liquid Equilibrium for Ternary Systems Containing Ionic Liquids: A Case Study for the System Water + Ethanol + 1-Hexyl-3-methylimidazolium Chloride

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Vapor−liquid equilibrium (VLE) data were measured for the ternary system water (1) + ethanol (2) + 1-hexyl-3-methylimidazolium chloride ([hmim]Cl) (3) at $p = 100$ kPa. Six sets of complete T, x, y data were reported. While the mole fraction of ethanol on an ionic liquid (IL)-free basis was fixed, respectively, at 0.1, 0.2, 0.4, 0.6, 0.8, and 0.98, measurements were performed in a way in which the IL mass fraction varied from 0.8 to 0.1, in an interval of 0.1. The NRTL equation was used for correlation and was revealed as adequate for the ternary system in the experimental composition range. The quality of correlation appeared to be sensitive to the parameters used for water + ethanol. The ternary VLE behavior was also modeled by correlation of two data sets, in which the ethanol mole fraction on an 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 0.49 K for temperature and 0.0042 for vapor phase mole fraction. Owing to the regular distribution of the experimental compositions, the feasibility of the correlation−prediction procedure was graphically presented, and in some sense visualized, in terms of relative volatility, activity coefficient, and bubble temperature, showing good agreement between experiment and calculation.

Introduction

Ionic liquids (ILs) are generally defined as organic salts that are liquid at temperatures below 373 K, showing negligible vapor pressure and having tunable properties by combination of different anions and cations. In recent years, ILs have received considerable attention for their use in the chemical industry[1] and are considered to be a potential solvent for extractive distillation.[2,3] When an IL is introduced into an azeotropic or close boiling mixture, the components to be separated change their liquid phase nonideality, and the activity coefficients of these components are affected to a different extent. Assuming an ideal vapor phase, the relative volatility of component i to component j, $\alpha_{i,j}$, can be related with the ratio of the activity coefficients by $\alpha_{i,j} = (\gamma_i/\gamma_j)\cdot(p_i^{sat}/p_j^{sat})$.[4] The vapor pressure ratio, p_i^{sat}/p_j^{sat}, is generally a weak function of temperature and is decided by the nature of the pure components. Therefore, the enhancement of relative volatility is mainly decided by the composition dependence of the activity coefficients. At the present stage, such information is mainly obtained from experimental measurement and by correlation using a model of excess Gibbs energy (G^E).

For a binary or ternary system containing volatile components and an IL, the number of independent variables is, respectively, 2 or 3 if the system is at vapor−liquid equilibrium (VLE). When the liquid compositions are given, there is a single variable that remains independent. This can be, for example, temperature or pressure. Any further experimental data can be used for correlation of the G^E model. VLE measurements are generally performed at constant temperature or constant pressure. For isothermal measurements, there are generally two measuring techniques: one is headspace measurement in which the vapor composition is analyzed,[5,6] and another is static measurement in which the total pressure is obtained.[7] For isobaric measurements, which use the dynamic circulation technique, the boiling temperature is obtained,[8−10] and frequently the vapor compositions are also analyzed.[11−16] Local composition models are frequently used for correlation, especially the NRTL equation.[17] It is desirable that the G^E model is correlated on the basis of a few experimental data and then used to predict ternary VLE data in a substantially wide range. It is expected to predict vapor composition from static measurement or boiling temperature measurement or to predict total pressure from headspace measurement. As the G^E models generally contain only binary parameters, it is also desirable that ternary VLE behavior can be predicted by measurement of constituent binary pairs. Strict verification of these correlation-prediction procedures requires reliable T, x, y data of ternary systems at constant pressure.

In our previous work,[18−20] we presented an ebulliometer for measurement of T, x, y data at constant pressure, in which the vapor phase compositions were obtained by analytical methods while the liquid phase compositions were calculated with the aid of mass balances. While the mole fraction of a volatile component on an IL-free basis is kept unchanged, composition dependence of the activity coefficients can be directly measured at several IL mass fractions. The experimental procedure eliminates the need for liquid phase analysis, which would require generally tedious procedures. Effects of several ILs on the azeotropic mixtures of water + 2-propanol,[19] water + ethanol,[21] and water + 2-methyl-2-propanol[22] have been studied by this technique.

In this work we have measured T, x, y data for a ternary system water (1) + ethanol (2) + 1-hexyl-3-methylimidazolium chloride ([hmim]Cl) (3) in a relatively wide range of IL mass fractions up to 0.8 and in a relatively complete composition range for the volatile binary pair. On the basis of the

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experimental data obtained, several prediction-correlation procedures were evaluated. A procedure is proposed for experimental measurement and modeling of VLE behaviors for ternary systems containing ionic liquid.

Experimental Section

Materials. Water was double distilled. Ethanol was analytical grade reagent and was used without further purification. The purity of ethanol was checked by GC, and the result was 99.9 %, while Karl Fischer analysis indicated a water mass fraction of $5.2 \cdot 10^{-4}$. [hmim]Cl was synthesized by reaction of 1-chlorohexane with 1-methylimidazole under a nitrogen atmosphere. 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 ESI-MS, showing a single positive ion, $m/z = 167$ ([hmim]).

Apparatus and Procedure. VLE were measured by an ebulliometer, which was described in detail in our previous work.[19] In the measurements, liquid phase circulation was enhanced by a pumplike 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 a 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, very small compared to the total sample volume of 270 cm^3 in the ebulliometer. For more details, please refer to our previous work.[19]

Pressure measurement was by a U-tube filled with water, one end connected to a pressure buffer and another to the atmosphere. Atmospheric pressure was measured by a standard barometer. Uncertainty of the pressure measurement was ± 0.05 kPa. Temperature measurement was by a standard platinum thermometer and a 6-1/2-digit multimeter. Uncertainty of the resistance measurement was ± 8 mΩ, which is equivalent to ± 0.08 K for 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 an IL-free basis, remained almost unchanged. 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. This has also been checked and verified by GC. Vapor phase composition was determined by analyzing the water content using the Karl Fischer method. When 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 water content. Uncertainty of the vapor phase composition was estimated to be 0.0001 in water mole fraction or relatively 1 %, whichever is greater. Liquid phase compositions were calculated on the basis of mass balances, using a procedure presented in previous work.[18] The next measurement was carried out by replacement of a certain amount of the mixture in the boiler with an 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) + [hmim]Cl (3) at $p = 100$ kPa are listed in Table 1. Complete T, x, y data were obtained. The liquid phase compositions were reported in x'_2 and w_3. 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 48 data points were regularly distributed at eight w_3 and six x'_2. 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.[23] Boiling temperature data for the binary system water (1) + [hmim]Cl (3) were also measured at $p = 100$ kPa, and the results are shown in Table 2.

In the measurements, temperature stability was better than 0.04 K. As discussed in our previous work,[19] uncertainty for the reported w_3 was estimated to be ± 0.003. Uncertainty of molar composition of the volatile binary pair, x'_2 or x'_1, was estimated to be less than relatively 1 %.

As a first step of the modeling work, we used the NRTL equation[17] for correlations of the six ternary data sets. Four sets of binary parameters for water + ethanol, which have been proposed and used by several authors in the literature,[2,24−26] were used and compared in the correlations. The parameter sets are: (1) proposed by Gmehling et al.;[24] (2) proposed by Gmehling and Onken[25] and used by Zhao et al.,[8] Jiang et al.,[9] and Wang et at.;[10] (3) proposed and used by Seiler et al.;[2] (4) proposed by Tang et al.[26] and used in our previous work.[21] While the values of nonrandomness factors α_{13} and α_{23} were set to 0.3, binary parameters for water + [hmim]Cl and ethanol + [hmim]Cl were obtained by minimization of the following objective function

$$F_\gamma = \sqrt{\sum_{n=1}^{N} (\gamma_{1,\text{cal}}/\gamma_{1,\text{exp}} - 1)^2/N} + \sqrt{\sum_{n=1}^{N} (\gamma_{2,\text{cal}}/\gamma_{2,\text{exp}} - 1)^2/N} \qquad (1)$$

in which N is the number of data points. The obtained parameters were used for calculation of the ternary VLE data in comparison with experimental values. Results are summarized in Table 3, in which δT and δy are, respectively, root-mean-square deviations of temperature and vapor phase composition.

As shown in Table 3, the best results were obtained using binary parameters for water + ethanol recommended by Gmehling et al.,[24] with $\delta T = 0.42$ K and $\delta y = 0.0040$. By using the other parameter sets, the deviations are larger, although the results are generally acceptable. For example, by using the parameters proposed by Tang et al.,[26] which have been used in our previous work,[21] the deviations are $\delta T = 0.63$ K and $\delta y = 0.0073$. The quality of correlation appeared to be sensitive to the parameters used for water + ethanol.

Activity coefficients of water and ethanol in water (1) + ethanol (2) were calculated and compared by using the four parameter sets. The main differences appeared in the two diluted

Table 1. Vapor−Liquid Equilibrium Data for the System Water (1) + Ethanol (2) + [hmim]Cl (3) at $p = 100$ kPa

x'_2	w_3	y_2	T/K	γ_1	γ_2	$\alpha_{2,1}$
$x'_2 = 0.1$						
0.0980	0.7987	0.2946	390.15	0.61	1.08	3.84
0.0995	0.6993	0.3213	377.82	0.78	1.51	4.29
0.0990	0.6007	0.3389	371.10	0.90	1.88	4.66
0.0990	0.5005	0.3570	367.10	0.97	2.18	5.05
0.0989	0.4000	0.3740	364.16	1.02	2.46	5.44
0.0991	0.3005	0.3916	362.58	1.03	2.66	5.85
0.0992	0.2000	0.4136	361.27	1.02	2.89	6.41
0.0994	0.1002	0.4261	359.88	1.04	3.09	6.73
$x'_2 = 0.2$						
0.1963	0.8002	0.4489	388.60	0.59	0.90	3.34
0.1960	0.7010	0.4645	376.17	0.75	1.21	3.56
0.1992	0.5987	0.4786	367.89	0.91	1.50	3.69
0.1986	0.5008	0.4861	363.51	1.01	1.70	3.82
0.1984	0.4005	0.5006	360.69	1.05	1.88	4.05
0.1984	0.3005	0.5107	358.82	1.08	2.00	4.22
0.1990	0.2001	0.5251	357.52	1.08	2.11	4.45
0.1992	0.1002	0.5333	356.28	1.10	2.21	4.59
$x'_2 = 0.4$						
0.3983	0.7959	0.6749	390.37	0.46	0.67	3.14
0.4013	0.6967	0.6575	374.75	0.71	0.92	2.86
0.4007	0.6002	0.6448	366.15	0.92	1.11	2.71
0.3989	0.5002	0.6380	361.05	1.06	1.25	2.66
0.3992	0.4004	0.6318	357.83	1.18	1.33	2.58
0.3991	0.3002	0.6277	355.81	1.25	1.39	2.54
0.3995	0.2001	0.6215	354.58	1.30	1.40	2.47
0.3997	0.1002	0.6185	353.80	1.33	1.41	2.43
$x'_2 = 0.6$						
0.5985	0.7987	0.8054	393.73	0.40	0.52	2.78
0.5992	0.7012	0.7772	376.79	0.68	0.71	2.33
0.5999	0.6005	0.7655	366.76	0.92	0.89	2.18
0.6003	0.5002	0.7508	360.72	1.14	1.01	2.01
0.6003	0.4005	0.7395	356.96	1.32	1.09	1.89
0.6001	0.3003	0.7288	354.66	1.45	1.13	1.79
0.6000	0.2000	0.7210	353.23	1.53	1.15	1.72
0.6003	0.1003	0.7129	352.39	1.59	1.15	1.65
$x'_2 = 0.8$						
0.7999	0.8005	0.9211	396.94	0.32	0.43	2.92
0.8007	0.7008	0.8999	379.64	0.58	0.59	2.24
0.8005	0.6001	0.8849	368.35	0.88	0.75	1.92
0.7997	0.4999	0.8734	361.55	1.15	0.88	1.73
0.7995	0.4000	0.8601	358.05	1.37	0.93	1.54
0.8000	0.3003	0.8511	354.23	1.63	1.02	1.43
0.8003	0.2002	0.8416	352.90	1.78	1.03	1.33
0.8004	0.1000	0.8256	351.65	2.00	1.03	1.18
$x'_2 = 0.98$						
0.9798	0.8008	0.9935	400.40	0.25	0.36	3.15
0.9799	0.7006	0.9917	381.77	0.46	0.51	2.46
0.9801	0.6006	0.9895	370.39	0.77	0.66	1.92
0.9802	0.5006	0.9876	363.04	1.10	0.78	1.61
0.9803	0.4004	0.9860	357.93	1.43	0.89	1.41
0.9805	0.3003	0.9846	354.80	1.71	0.95	1.27
0.9804	0.2002	0.9827	352.90	1.98	0.98	1.14
0.9802	0.1002	0.9804	351.77	2.27	1.00	1.01

Table 2. Boiling Temperature T in Relation with IL Mass Fractions w_3 for the System Water (1) + [hmim]Cl (3) at $p = 100$ kPa

w_3	T/K	γ_1
0.8007	394.82	0.648
0.6999	384.41	0.807
0.5999	379.47	0.896
0.5003	376.62	0.950
0.3997	375.05	0.977
0.2998	374.2	0.986
0.2000	373.62	0.992
0.1000	373.19	0.995

ends. Comparison of the four parameter sets in the ethanol-rich region was presented in Figure 1a. It can be observed that γ_1 calculated by the parameters of Gmehling et al.[24] are generally in good agreement with the experimental values of Arce et al.[27] and Kurihara et al.,[28] as well as the limiting activity coefficients at 351.45 K by Kojima and Tochigi, which was cited in a review by Kojima et al. [29] The calculated values of γ_1 are also consistent with our experimental results, which are given in Table 4. The other three parameter sets provide somewhat smaller γ_1 in this region.

When x'_2 is kept unchanged for the ternary system containing IL, the VLE behavior should change continuously with the IL mass fractions changing from high to low, and finally to zero, which relates to the IL-free binary pair. Therefore, deviations caused by binary parameters of water + ethanol can not always be compensated by adjustment of the parameters of water + [hmim]Cl and ethanol + [hmim]Cl, which are optimized in the correlations. Correlations using the four-parameter sets were also

Table 3. Root Mean Square Deviations, δT and δy, in the Calculation of VLE Data of Water (1) + Ethanol (2) + [hmim]Cl (3), Based on Correlations by the NRTL Equation and by Using Several Binary Parameters for Water + Ethanol, Several Sets of Experimental Data, And Several Objective Functions

source of binary parameters for water + ethanol	objective function	data sets used in correlation[a]	root mean square deviations[b]	
			δT/K[c]	δy[d]
Gmehling et al.[e]	eq 1	six data sets	0.42	0.0040
Gmehling and Onken[f]	eq 1	six data sets	0.54	0.0054
Seiler et al.[g]	eq 1	six data sets	0.62	0.0065
Tang et al.[h]	eq 1	six data sets	0.63	0.0073
Gmehling et al.[e]	eq 1	$x'_2 = 0.1$ and 0.98	0.49	0.0042
Gmehling et al.[e]	eq 2	six data sets	0.27	0.0275
Gmehling et al.[e]	eq 3	six data sets	4.69	0.0036
Gmehling et al.[e]	eq 4a	see footnote[i]	1.00	0.0249

[a] The six data sets are, respectively, at $x'_2 = 0.1$, 0.2, 0.4, 0.6, 0.8, and 0.98, as shown in Table 1. [b] Deviations are calculated for the six data sets. [c] $\delta T/\mathrm{K} = [\sum (T_{\mathrm{cal}}/\mathrm{K} - T_{\mathrm{exp}}/\mathrm{K})^2/N]^{1/2}$. [d] $\delta y = [\sum (y_{2,\mathrm{cal}} - y_{2,\mathrm{exp}})^2/N]^{1/2}$. [e] Ref 24, in which the proposed energy parameters, Δg_{12} and Δg_{21}, and nonrandomness factor, α_{12}, are: $\Delta g_{12}/\mathrm{J \cdot mol^{-1}} = 4458.8 + 8.4420 \cdot (T/\mathrm{K})$, $\Delta g_{21}/\mathrm{J \cdot mol^{-1}} = -3791.4 + 4.1451 \cdot (T/\mathrm{K})$, $\alpha_{12} = 0.1448$. [f] Ref 25, $\Delta g_{12}/\mathrm{J \cdot mol^{-1}} = 5612.08$, $\Delta g_{21}/\mathrm{J \cdot mol^{-1}} = -510.81$, $\alpha_{12} = 0.3008$. [g] Ref 2, $\Delta g_{12}/\mathrm{J \cdot mol^{-1}} = -7631.0 + 37.7 \cdot (T/\mathrm{K})$, $\Delta g_{21}/\mathrm{J \cdot mol^{-1}} = 5686.0 - 17.9 \cdot (T/\mathrm{K})$, $\alpha_{12} = 0.3$. [h] Ref 26, $\Delta g_{12}/\mathrm{J \cdot mol^{-1}} = 3698.8 + 4.2758 \cdot (T/\mathrm{K})$, $\Delta g_{21}/\mathrm{J \cdot mol^{-1}} = -2216.0 + 6.7055 \cdot (T/\mathrm{K})$, $\alpha_{12} = 0.4$. [i] Using γ_1 from binary boiling temperature data in Table 2 and γ_2 from the ternary data set at $x'_2 = 0.98$.

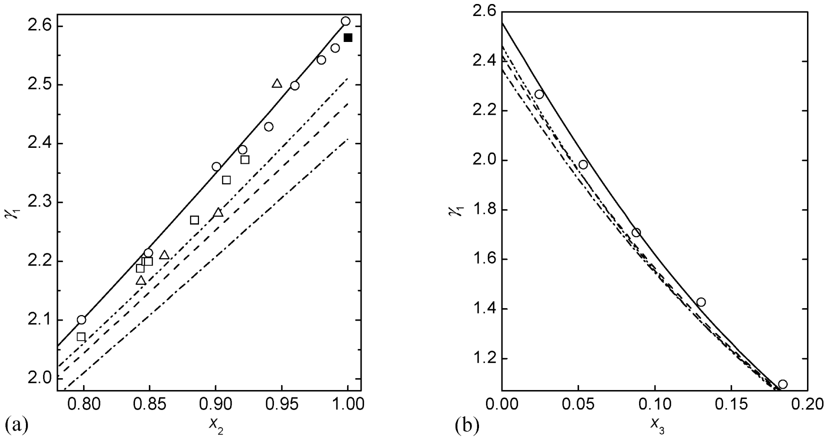

Figure 1. Influence of binary parameters of water + ethanol on the correlation of the ternary system water (1) + ethanol (2) + [hmim]Cl (3): experimental and calculated activity coefficients of water, γ_1, in (a) a binary mixture of water (1) + ethanol (2) and (b) a ternary mixture of water (1) + ethanol (2) + [hmim]Cl (3) at $x'_2 = 0.98$, all at $p = 100$ kPa: ○, by this work; Δ, by Arce et al. (ref 27); □, by Kurihara et al. (ref 28); ■, limiting activity coefficient at 351.45 K by Kojima and Tochigi (1970, cited in ref 29). Lines were calculated by the binary parameters of water + ethanol and the binary parameters obtained from the correlation described in Table 3: solid lines, Gmehling et al. (ref 24); dash line, Gmehling and Onken (ref 25); dash dot line, Seiler et al. (ref 2); dash dot dot line, Tang et al. (ref 26).

Table 4. Vapor−Liquid Equilibrium Data for the System Water (1) + Ethanol (2) at $p = 100$ kPa

x_2	y_2	T/K	γ_1
0.99837	0.99815	351.07	2.61
0.99051	0.9894	351.11	2.56
0.9801	0.9780	351.08	2.54
0.9598	0.9563	351.07	2.50
0.9401	0.9368	351.04	2.43
0.9204	0.9175	350.96	2.39
0.9006	0.8983	350.99	2.36
0.8491	0.8552	350.99	2.21
0.7985	0.8160	351.07	2.10

Table 5. Energy Parameters, Δg_{ij} and Δg_{ji}, and Nonrandomness Factors, α_{ij}, for the NRTL Model Obtained from Correlation of Ternary VLE Data of Water (1) + Ethanol (2) + [hmim]Cl (3) at $p = 100$ kPa, Using Data Sets at $x'_2 = 0.1$ and $x'_2 = 0.98$

binary parameters[a]				
component i	component j	$\Delta g_{ij}/\mathrm{J \cdot mol^{-1}}$	$\Delta g_{ji}/\mathrm{J \cdot mol^{-1}}$	α_{ij}
water	[hmim]Cl	−5500.5	−6594.2	0.3
ethanol	[hmim]Cl	−1982.5	−7436.3	0.3

[a] Binary parameters for water (1) + ethanol (2) were taken from ref 24 and were fixed as $\Delta g_{12}/\mathrm{J \cdot mol^{-1}} = 4458.8 + 8.4420 \cdot (T/\mathrm{K})$, $\Delta g_{21}/\mathrm{J \cdot mol^{-1}} = -3791.4 + 4.1451 \cdot (T/\mathrm{K})$, and $\alpha_{12} = 0.1448$. The objective function used in the optimization was shown in eq 1.

compared in Figure 1b. The best consistency can be obtained using parameters of Gmehling et al.,[24] while correlations by the other three parameter sets provide a smaller value of γ_1, as compared with the experimental data.

Comparisons as shown in Figure 1a and 1b may be regarded as a tool for analyzing the deviations in correlation. The deviations may result from the experiment. In correlation and modeling of VLE data, such comparisons may be used for checking the suitability of the parameters chosen for the volatile binary pair. In this sense, the parameters of Gmehling et al.[24] appeared to be the most suitable.

The success correlation of the six data sets also indicated that the NRTL equation is suitable for the ternary system in the experimental composition range. Also, it appears adequate if the nonrandomness factors α_{13} and α_{23} are set at the most common value of 0.3.

With the aim to obtain model parameters using much less experimental data, two data sets at $x'_2 = 0.1$ and $x'_2 = 0.98$ were correlated. The optimized binary parameters are given in Table 5. The parameters obtained were used for calculation in comparison with the six sets of experimental data. The results were quite good, with $\delta T = 0.49$ K and $\delta y = 0.0042$. 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.

Moreover, the feasibility of predicting vapor compositions from T, x data was tested by correlation of the six data sets by the objective function

$$F_T = \sqrt{\sum_{n=1}^{N} (T_{\mathrm{cal}} - T_{\mathrm{exp}})^2/N} \qquad (2)$$

The ternary VLE data were calculated, and the deviations were also shown in Table 3. While the deviation of temperature is very small ($\delta T = 0.27$ K), the deviation of vapor composition is appreciable ($\delta y = 0.0275$).

Similarly, x, y data were correlated using the objective function

$$F_y = \sqrt{\sum_{n=1}^{N} (y_{2,\mathrm{cal}} - y_{2,\mathrm{exp}})^2/N} \qquad (3)$$

The six data sets were used in the correlation. Results were shown in Table 3. The deviation of vapor composition is small, with $\delta y = 0.0036$. However, the temperatures predicted deviate significantly from experimental values, with $\delta T = 4.69$ K.

Further, correlation was performed using the objective function

$$F_{\mathrm{WE}} = F_{\mathrm{W}} + F_{\mathrm{E}} \qquad (4a)$$

$$F_{\mathrm{W}} = \sqrt{\sum_{n=1}^{L} (\gamma_{1,\mathrm{cal}}/\gamma_{1,\mathrm{exp}} - 1)^2/L} \qquad (4b)$$

$$F_{\mathrm{E}} = \sqrt{\sum_{n=1}^{M} (\gamma_{2,\mathrm{cal}}/\gamma_{2,\mathrm{exp}} - 1)^2/M} \qquad (4c)$$

Here, F_{W} takes into account the activity coefficient of water, γ_1, of water (1) + [hmim]Cl (3) in Table 2. At the same time, F_{E} uses the activity coefficient of ethanol, γ_2, of water (1) + ethanol (2) + [hmim]Cl (3) at $x'_2 = 0.98$. The purpose of this correlation was to test the modeling of the ternary system by boiling temperature measurement of the constituent binary pairs. As water cannot be completely removed from ethanol and the IL, we used the data of γ_2 at $x'_2 = 0.98$ instead of the activity coefficient of ethanol in ethanol (2) + [hmim]Cl (3). As shown in Table 3, the result is not good ($\delta T = 1$ K, $\delta y = 0.0249$). When, on the other hand, the binary parameters in Table 3 were used for calculation of boiling temperatures of water (1) + [hmim]Cl (3), the root-mean-square deviation is $\delta T = 0.43$ K.

It has been commonly accepted that vapor compositions can be predicted from total pressure data and that ternary VLE can be predicted by data of the constituent binary pairs. The predictions have generally acceptable precision. However, as shown above, the predictions for the present IL-containing system could not always be successful. The reasons might be as follows: (1) the experimental IL mole fraction is only in a very small range, especially when the dynamic circulation method is used, as presented in this work. For all the six ternary data sets in Table 1 and the binary data in Table 2, $x_3 < 0.5$, although the IL mass fraction reached a relatively high value of 0.8. (2) The activity coefficient of the IL is not available from direct experimental measurement because the IL is undetectable in the vapor phase. (3) It is not clear if the behavior of the IL-containing ternary mixtures can be modeled based only on the behaviors of the binary pairs. (4) The binary parameters lack theoretical significance. Frequently, several different parameter sets may be obtained starting from different initial values. Therefore, extrapolation of behaviors of binary pairs over a wide composition range cannot always be successful.

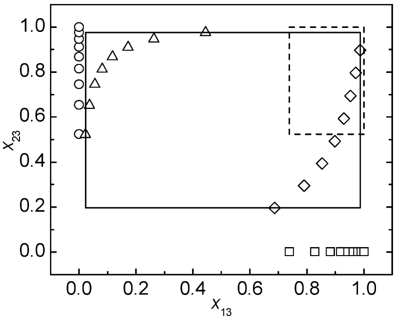

Figure 2. Composition range covered by two experimental procedures for the ternary mixture of water (1) + ethanol (2) + [hmim]Cl (3): □, T, x measurement of water (1) + [hmim]Cl (3); ○, T, x measurement of ethanol (2) + [hmim]Cl (3); ◇, T, x, y measurement of water (1) + ethanol (2) + [hmim]Cl (3) at $x'_2 = 0.1$; Δ, T, x, y measurement of water (1) + ethanol (2) + [hmim]Cl (3) at $x'_2 = 0.98$; dashed rectangle, composition range covered by T, x measurement of water (1) + [hmim]Cl (3) and ethanol (2) + [hmim]Cl (3); solid rectangle, composition range covered by T, x, y measurement of water (1) + ethanol (2) + [hmim]Cl (3) at $x'_2 = 0.1$ and 0.98. All measurements were performed at $w_3 = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8. By definition, $x_{13} = x_1/(x_1 + x_3)$ and $x_{23} = x_2/(x_2 + x_3)$.

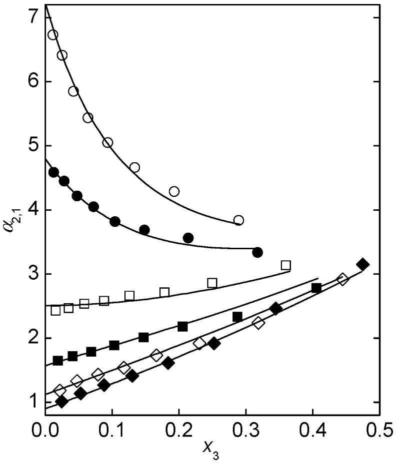

Figure 3. Experimental and calculated relative volatility of ethanol to water, $\alpha_{2,1}$, in relation with IL mole fraction, x_3, for the saturated mixture water (1) + ethanol (2) + [hmim]Cl (3) at $p = 100$ kPa: ○, $x'_2 = 0.1$; ●, $x'_2 = 0.2$; □, $x'_2 = 0.4$; ■, $x'_2 = 0.6$; ◇, $x'_2 = 0.8$; ◆, $x'_2 = 0.98$; Lines were calculated by NRTL parameters in Table 5 at $p = 100$ kPa and at $x'_2 = 0.1$, 0.2, 0.4, 0.6, 0.8, and 0.98, respectively.

The feasibility of modeling the ternary mixture by VLE measurements at $x'_2 = 0.1$ and $x'_2 = 0.98$ can be recognized by the experimental composition range shown in Figure 2. Compositions of the ternary system were described in terms of mole fractions of two quasi-binary pairs, x_{13} and x_{23}. By definition, $x_{13} = x_1/(x_1 + x_3)$ and $x_{23} = x_2/(x_2 + x_3)$. The solid rectangle in Figure 2 represents the composition range covered by T, x, y measurements at $x'_2 = 0.1$ and $x'_2 = 0.98$. In such a view, calculation of VLE for all the six data sets may be regarded as *interpolation*, and good results can be expected.

On the other hand, the composition range covered by the boiling temperature measurement of the binary pairs is very limited, as indicated by the dashed rectangle in Figure 2.

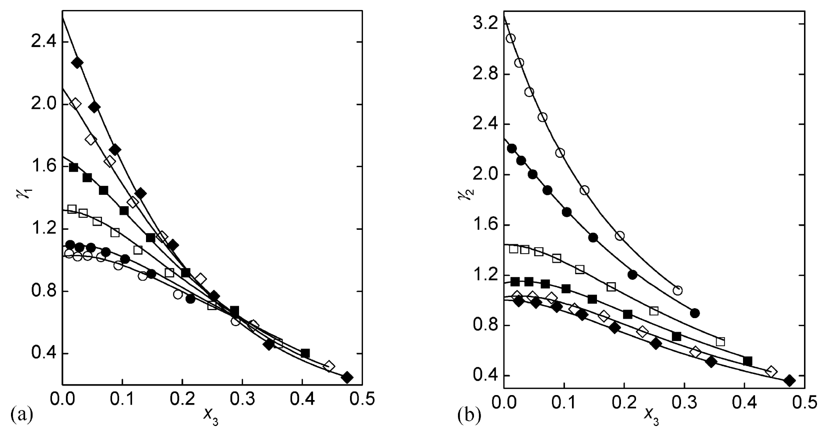

Figure 4. Experimental and calculated activity coefficients of (a) water, γ_1, and (b) ethanol, γ_2, in relation with IL mole fraction, x_3, for the saturated mixture water (1) + ethanol (2) + [hmim]Cl (3) at $p = 100$ kPa: ○, $x'_2 = 0.1$; ●, $x'_2 = 0.2$; □, $x'_2 = 0.4$; ■, $x'_2 = 0.6$; ◇, $x'_2 = 0.8$; ◆, $x'_2 = 0.98$; Lines were calculated by NRTL parameters in Table 5 at $p = 100$ kPa and at $x'_2 = 0.1$, 0.2, 0.4, 0.6, 0.8, and 0.98, respectively.

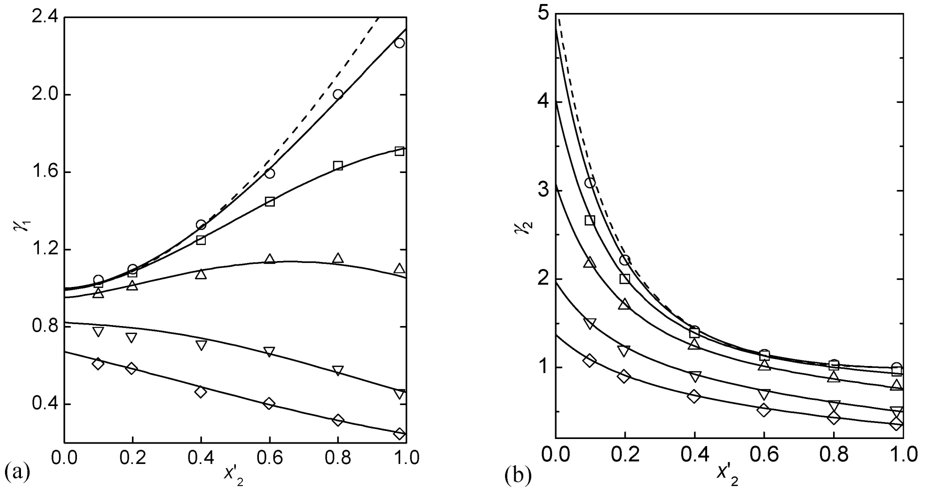

Figure 5. Experimental and calculated activity coefficients of (a) water, γ_1, and (b) ethanol, γ_2, in relation with ethanol mole fraction on an IL-free basis, x'_2, for the saturated mixture water (1) + ethanol (2) + [hmim]Cl (3) at $p = 100$ kPa: ○, $w_3 = 0.1$; □, $w_3 = 0.3$; Δ, $w_3 = 0.5$; ▽, $w_3 = 0.7$; ◇, $w_3 = 0.8$. Lines were calculated by NRTL parameters in Table 5 at $p = 100$ kPa: solid lines, calculated values at $w_3 = 0.1$, 0.3, 0.5, 0.7, and 0.8, respectively; dashed line, calculated values for the system water (1) + ethanol (2).

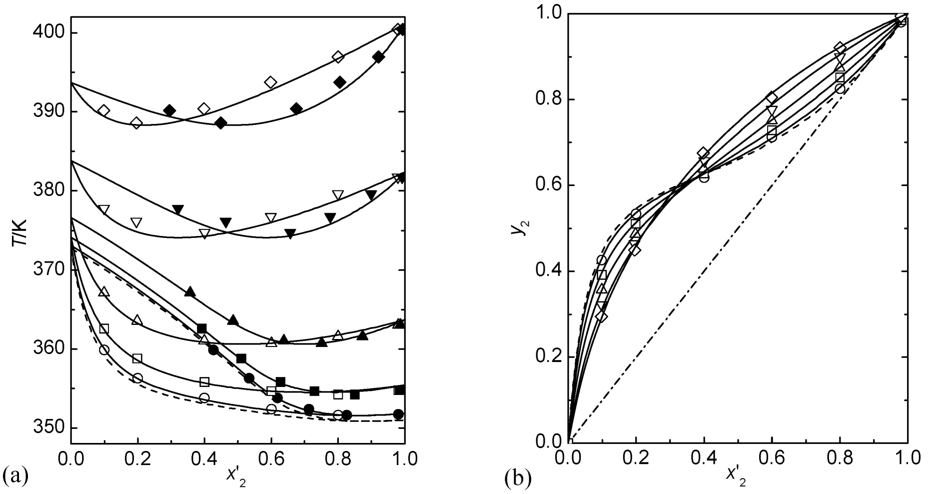

Figure 6. Experimental and calculated relations of (a) T, x'_2, y_2 diagram and (b) y_2, x'_2 diagram for the system water (1) + ethanol (2) + [hmim]Cl (3) at $p = 100$ kPa: ○, ●, $w_3 = 0.1$; □, ■, $w_3 = 0.3$; Δ, ▲, $w_3 = 0.5$; ▽, ▼, $w_3 = 0.7$; ◇, ◆, $w_3 = 0.8$. Lines were calculated by NRTL parameters in Table 5 at $p = 100$ kPa: solid lines, calculated values at $w_3 = 0.1$, 0.3, 0.5, 0.7, and 0.8, respectively; dashed line, calculated values for the system water (1) + ethanol (2); dash dot line, $y_2 = x'_2$.

For example, all data of water (1) + [hmim]Cl (3) in Table 2 have $x_1 > 0.7$. In this case $x_{13} = x_1$. On the contrary, ternary data at $x'_2 = 0.98$ for the system water (1) + ethanol (2) + [hmim]Cl (3) have a minimum value of 0.0218 for x_{13}. Therefore, extensive *extrapolation* would be required if the ternary VLE data were calculated using parameters correlated from data of the constituent binary pairs. Here, we have restricted the IL mass fraction by 0.8. For dynamic circulation measurements, such a value of IL mass fraction should be considerably high.

As described in the previous section, the experimental procedure for measurements at fixed x'_2 is quite convenient. Therefore, the modeling of VLE behavior of a ternary system containing IL is generally recommended by correlation of two ternary data sets, which are measured at a relatively wide range of IL mass fractions, while the mole fractions of the volatile quasi-binary pair are distributed, respectively, in the two diluted ends. In this work, with consideration of having the best reliability for experimental data, x'_2 in the diluted ends were chosen to be 0.1 and 0.98. Consequently, the other four data sets at $x'_2 = 0.2$, 0.4, 0.6, and 0.8 can be used for checking the model.

VLE results calculated by using parameters in Table 5 are also shown in Figures 3 to 6, in comparison with the experimental values. Owing to the regular distribution of the six sets of experimental data, which are at eight w_3 and six x'_2, the feasibility of the recommended correlation-prediction procedure was graphically presented, and in some sense visualized, in terms of relative volatility, activity coefficient, and bubble temperature. Good agreement can be observed between experiment and calculation. Effects of the IL on the phase behavior are also illustrated in these figures. In Figure 3, the relative volatility of ethanol to water, $\alpha_{2,1}$, is shown in relation with the IL mole fraction, x_3, showing the effect of the ILs on a molar basis. At high ethanol mole fractions, namely, at $x'_2 = 0.98$, 0.8, 0.6, and 0.4, enhancement of $\alpha_{2,1}$ can be observed by addition of the IL. However, at $x'_2 = 0.1$ and 0.2, $\alpha_{2,1}$ decreases with increasing x_3. The effect of the IL on $\alpha_{2,1}$ can be separately depicted by its effect on γ_1 and γ_2 with the relation $\alpha_{2,1} = (\gamma_2/\gamma_1)\cdot(p_2^{\text{sat}}/p_1^{\text{sat}})$. The ratio of vapor pressures, $p_2^{\text{sat}}/p_1^{\text{sat}}$, is insensitive to temperature and is in a range of 2.1 to 2.3 in the present measurement. Therefore the effect of IL on $\alpha_{2,1}$ is mainly decided by the ratio of the activity coefficients affected by addition of the IL. As shown in Figure 4, both the activity coefficients of water and ethanol decrease with increasing x_3. While the decrease of γ_1 is beneficial for enhancement of the relative volatility, the decrease of γ_2 is not desirable. This accounts for the trend that $\alpha_{2,1}$ decreases with increasing x_3 at $x'_2 = 0.1$ and 0.2. In Figure 5, γ_1 and γ_2 are also 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. 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 IL mass fraction is high, for example at $w_3 = 0.7$ 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 $w_3 = 0.5$. Moreover, T, x'_2, y_2 and y_2, x'_2 diagrams were shown in Figure 6. While the boiling temperature of water is higher than ethanol, the boiling temperature of water + [hmim]Cl becomes lower than that of ethanol + [hmim]Cl at $w_3 = 0.8$. Although the azeotrope of water + ethanol was removed by addition of the IL at $w_3 = 0.1$, there is a minimum for, respectively, the bubble line and the dew line at a given w_3. As can be observed in the y_2, x'_2 diagram, y_2 increases with addition of the IL at given x'_2 in the ethanol-rich region, showing a salting-out effect. On the contrary, there is a salting-in effect in the water-rich region. These are consistent with the trend of $\alpha_{2,1}$ as shown in Figure 3.

VLE data for the same ternary system at $p = 101.3$ kPa have been reported by Calvar et al.[15] By using parameters proposed in Table 5, the literature ternary data were calculated, showing root-mean-square deviations of $\delta T = 1.82$ K and $\delta y = 0.0688$. These deviations appeared to be very close to those by direct correlation of the literature data, using eq 1 as an objective function and having deviations of $\delta T = 1.64$ K and $\delta y = 0.0625$. In the original literature, all nine binary parameters for the ternary mixture were optimized. Negative values (−0.351 and −0.131) and a very large positive value (0.725) were used for the nonrandomness factors. In this case, the reported deviations are $\delta T = 1.11$ K and $\delta y = 0.057$. When, on the other hand, these reported parameters were used for calculation of the six data sets in this work, the deviations were $\delta T = 1.69$ K and $\delta y = 0.0534$, which appeared to be much larger than those we presented by using parameters in Table 5. 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 fractions, especially in the ethanol-rich region.

Conclusions

T, x, y data were measured for the ternary system water (1) + ethanol (2) + [hmim]Cl (3) at $p = 100$ kPa. 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 NRTL equation was used for correlation and revealed to be adequate for the ternary system in the experimental composition range. The quality of correlation appeared to be sensitive to the parameters used for water + ethanol. 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 $\delta T = 0.49$ K and $\delta y = 0.0042$. As a result, the modeling of VLE behavior of a ternary system containing ILs is generally recommended by correlation of two ternary data sets, which are measured at a relatively wide range of IL mass fractions, while the mole fractions of the volatile quasi-binary pair are distributed, respectively, in the two diluted ends.

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