Isobaric Vapor−Liquid Equilibria for Water + Ethanol + Ethyl Acetate + 1-Butyl-3-methylimidazolium Acetate at Low Water Mole Fractions

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Isobaric T, x, y data were measured for the quaternary system water + ethanol + ethyl acetate + 1-butyl-3-methylimidazolium acetate at low water mole fractions and at $p = 100$ kPa. By a procedure presented in this work for systems composed of three volatile components and a nonvolatile ionic liquid (IL), the vapor-phase compositions were obtained by analytical methods and the liquid-phase compositions were calculated with the aid of mass balances. Activity coefficients of the volatile components were obtained without the need of a thermodynamic model of the liquid phase. Enhancement of the relative volatilities by addition of the IL was related with the effect of the IL on the activity coefficients. With the addition of the IL, the activity coefficients of water and ethanol decreased, while the activity coefficient of ethyl acetate increased. The reversed effect of the IL on the activity coefficients resulted in a consistent effect on the relative volatility. At an IL mass fraction of 0.7, the relative volatilities reach appreciable values of 14 for ethyl acetate to ethanol, 84.1 for ethyl acetate to water, and 11.3 for ethanol to water. The VLE data were correlated by the NRTL equation.

Introduction

Ethanol and ethyl acetate form, at atmospheric pressure, a minimum boiling azeotrope when ethyl acetate has a mole fraction of 0.538.[1] For extractive distillation of the azeotropic mixture, vapor−liquid equilibria (VLE) of ethanol + ethyl acetate with the addition of various salts have been studied. The salts that have been studied include calcium chloride, potassium acetate, and zinc chloride by Hashitani et al.;[2,3] sodium iodide by Yan et al.;[4] calcium chloride by Gu et al.;[5] lithium nitrate by Topphoff et al.;[6] and calcium chloride and lithium chloride by Takamatsu et al.[7] Because of the low solubility of the salts in ethyl acetate, it is difficult to break the azeotrope in the pure ethyl acetate region.[8] Ionic liquids (ILs), which are organic salts composed of relatively large cations and anions, are becoming important alternatives for separation of azeotropic or close boiling mixtures.[9,10] Recently, Orchilles et al.[8] studied the influence of an IL, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][CF_3SO_3]), on the phase behavior of ethanol + ethyl acetate. This IL was selected because it is completely miscible in both ethanol and ethyl acetate. The authors reported isobaric VLE data for systems containing ethanol, ethyl acetate, and [emim][CF_3SO_3] at $p =$ 100 kPa. Results showed that the azeotrope is removed when [emim][CF_3SO_3] has a mole fraction of 0.20.

In this work, we have studied the influence of 1-butyl-3-methylimidazolium acetate ([bmim][OAc]) on the phase behavior of ethanol + ethyl acetate. Although the solubility of this IL in ethyl acetate is very low, ethyl acetate has appreciable solubility in the IL. On the other hand, this IL is completely miscible in ethanol, indicating relatively strong affinity between ethanol and the IL. Thus, it may be expected that the use of the IL would effectively increase the relative volatility of ethyl acetate to ethanol. Owing to the significant solubility of ethyl acetate in the IL, the IL may be a candidate as an entrainer for the separation of ethanol and ethyl acetate. Moreover, there is inevitably water existing in the separation process of ethanol and ethyl acetate. The effect of water needs to be studied, as for example water may form a ternary azeotrope with ethanol and ethyl acetate. Therefore, we have measured the isobaric VLE for the quaternary system water (1) + ethanol (2) + ethyl acetate (3) + [bmim][OAc] (4) at low water mole fractions.

Experimental Section

Materials. Ethanol and ethyl acetate were analytical grade reagents and were purified by fractional distillation. Final purities were checked by GC, and the results were > 99.9 % for ethanol and 99.8 % for ethyl acetate. Karl Fischer analysis indicated a water mass fraction of $3.2 \cdot 10^{-4}$ for ethanol and $2.8 \cdot 10^{-4}$ for ethyl acetate. For preparation of [bmim][OAc], 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) was first synthesized by reacting 1-methylimidazole with 1-chlorobutane under a nitrogen atmosphere. Purification of [bmim][Cl] was by recrystallization in a mixture of ethyl acetate + acetonitrile. Consequently, [bmim][OAc] was prepared by a patented anion metathesis procedure, in which ethanol was used as solvent and potassium acetate was used as the source of anion.[11] Before use, the IL was dried for 24 h under vacuum at 340 K to remove volatile impurities. Karl Fischer analysis showed typically a water mass fraction of $7.9 \cdot 10^{-3}$ in the IL. The IL appears to be very hydrophilic.

Experimental Apparatus. VLE were measured by an ebulliometer, which was described in detail in our previous work.[12] 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. The uncertainty of the resistance measurement was ± 8 mΩ, which is equivalent to ± 0.08 K for the temperature measurement.

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10.1021/je8001392 CCC: $40.75

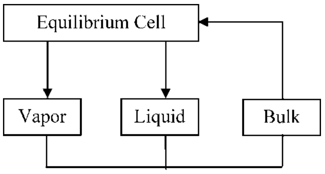

Figure 1. Simplified schematic diagram of an ebulliometer with double circulation. Vapor−liquid equilibrium is established in the equilibrium cell. The terms bulk, liquid, and vapor stand for the three typical compositions.

Determination of Vapor-Phase Composition. As the IL has only a negligible vapor pressure, the vapor-phase samples are ternary mixtures of water (1) + ethanol (2) + ethyl acetate (3). Samples were analyzed by gas chromatography (Fuli 9790J), equipped with a 2 m column of Porapak-Q (80/100). Oven temperature was at 433.2 K. The carrier gas was hydrogen, and detection was by TCD at 453.2 K. The result of the GC analysis was v_{32}, which is defined as $v_{32} = y_3/(y_2 + y_3)$. A calibration curve was prepared for the GC analysis. Samples were also analyzed by Karl Fischer titration. Water mass fraction, w_1, was obtained. Consequently, vapor-phase mole fractions were calculated by the following formulations

$$\frac{1}{y_1} = 1 + \frac{M_1(1-w_1)}{w_1(M_2 - M_2v_{32} + M_3v_{32})} \tag{1a}$$

$$y_3 = (1 - y_1)v_{32} \tag{1b}$$

$$y_2 = 1 - y_1 - y_3 \tag{1c}$$

where M is the molecular weight. Uncertainties of vapor-phase compositions were ± 0.0001 in mole fraction for y_1 and ± 0.002 in mole fraction for y_2, y_3, and v_{32}.

Calculation of Liquid-Phase Composition. In our previous work,[13] we presented a procedure for calculation of the liquid composition. Formulations were presented for ternary systems composed of two volatile components and a nonvolatile ionic liquid. In this work, the calculational procedure was extended to quaternary systems composed of three volatile components and a nonvolatile ionic liquid. In the following formulation, the volatile components are denoted as component i, where i = 1, 2, 3, and the IL is denoted as the component 4.

A simplified schematic diagram of the ebulliometer was shown in Figure 1. There are typically three compositions in the ebulliometer: vapor, liquid, and bulk. The vapor and liquid compositions are what we measured for the vapor−liquid equilibrium. In the following description, we use the term of *vapor material* for anything in the ebulliometer having the vapor composition. Similarly, the terms of *liquid material* and *bulk material* denote anything in the ebulliometer having, respectively, liquid and bulk compositions. Bulk material exists mainly in the boiler. Vapor material may exist as vapor in the equilibrium cell or as condensate adhered on the wall of the cooling jacket or contained in the vapor sampling chamber. Liquid material has only a small amount, existing mainly in the flow path in the equilibrium cell before mixing of the vapor and liquid circulation. On the other hand, the liquid composition is very close to the bulk composition. Therefore, we neglect the term of liquid material and we have

$$m_{\mathrm{b,\,i}} = m_{\mathrm{s,\,i}} - m_{\mathrm{v,\,i}} \tag{2a}$$

$$m_{\mathrm{b,\,4}} = m_{\mathrm{s,\,4}} \tag{2b}$$

where m is the mass and subscripts v, b, and s denote vapor, bulk, and overall synthetic, respectively. Equation 2 is a formulation of the *static* mass balance in the ebulliometer. The mass of each volatile component of the vapor material is calculated by the volume of vapor material (supposed to be in the form of vapor condensate) V, density of the vapor condensate ρ, vapor-phase compositions y_{i}, and the molecular weight M, by

$$m_{\mathrm{v,i}} = V\rho\frac{y_{\mathrm{i}}M_{\mathrm{i}}}{(y_1M_1 + y_2M_2 + y_3M_3)} \tag{3}$$

Having the mass of each component for the bulk material, we can calculate the mass fraction of ionic liquid $w_{\mathrm{b,4}}$ and mole fraction of the volatile components on an IL-free basis ($x'_{\mathrm{b,i}}$), by

$$w_{\mathrm{b,4}} = \frac{m_{\mathrm{b,4}}}{m_{\mathrm{b,1}} + m_{\mathrm{b,2}} + m_{\mathrm{b,3}} + m_{\mathrm{b,4}}} \tag{4a}$$

$$x'_{\mathrm{b,i}} = \frac{m_{\mathrm{b,i}}/M_{\mathrm{i}}}{m_{\mathrm{b,1}}/M_1 + m_{\mathrm{b,2}}/M_2 + m_{\mathrm{b,3}}/M_3} \tag{4b}$$

For calculation of the liquid compositions, the *dynamic* mass balance for the flow of bulk, liquid, and vapor material is written as

$$x'_{\mathrm{l,\,i}}(\dot{n}_{\mathrm{b}} - \dot{n}_{\mathrm{v}}) + y_{\mathrm{i}}\dot{n}_{\mathrm{v}} = x'_{\mathrm{b,\,i}}\dot{n}_{\mathrm{b}} \tag{5a}$$

$$w_{\mathrm{l,4}}(\dot{m}_{\mathrm{b}} - \dot{m}_{\mathrm{v}}) = w_{\mathrm{b,4}}\dot{m}_{\mathrm{b}} \tag{5b}$$

where $\dot{n}$ and $\dot{m}$ are, respectively, the molar and mass flow rate and subscript l denotes liquid. A prime symbol indicates that the quantity is on an IL-free basis.

The vapor-to-liquid circulation ratio, β, can be expressed in molar (β_n) or mass (β_m) quantities and on IL-free or IL-containing basis. Because the liquid flow rate is normally very close to the bulk flow rate, we can have the following relations

$$\beta_m = \frac{\dot{m}_{\mathrm{v}}}{\dot{m}_{\mathrm{l}}} \approx \frac{\dot{m}_{\mathrm{v}}}{\dot{m}_{\mathrm{b}}} \tag{6a}$$

$$\beta'_m = \frac{\dot{m}_{\mathrm{v}}}{\dot{m}_{\mathrm{l}}} \approx \frac{\dot{m}_{\mathrm{v}}}{\dot{m}_{\mathrm{b}}} = \frac{\beta_m}{1 - w_{\mathrm{b,4}}} \tag{6b}$$

$$\beta'_n = \frac{\dot{n}_{\mathrm{v}}}{\dot{n}_{\mathrm{l}}} \approx \frac{\dot{n}_{\mathrm{v}}}{\dot{n}_{\mathrm{b}}} = \beta'_m\frac{x'_{\mathrm{b,1}}M_1 + x'_{\mathrm{b,2}}M_2 + x'_{\mathrm{b,3}}M_3}{y_1M_1 + y_2M_2 + y_3M_3} \tag{6c}$$

Equation 5 can now be rewritten as

$$x'_{\mathrm{l},i} = \frac{x'_{\mathrm{b},i} - \beta'_n y_i}{1 - \beta'_n} \tag{7a}$$

$$w_{\mathrm{l,4}} = \frac{w_{\mathrm{b,4}}}{1 - \beta_m} \tag{7b}$$

For calculation of activity coefficients, we need liquid compositions on an IL-containing basis, which can be calculated by

$$x_{\mathrm{l},i} = \frac{x'_{\mathrm{l},i}}{x'_{\mathrm{l,1}} + x'_{\mathrm{l,2}} + x'_{\mathrm{l,3}} + \dfrac{w_{\mathrm{l,4}}}{1 - w_{\mathrm{l,4}}} \cdot \dfrac{x'_{\mathrm{l,1}}M_1 + x'_{\mathrm{l,2}}M_2 + x'_{\mathrm{l,3}}M_3}{M_4}} \tag{7c}$$

In eqs 2 to 7, i = 1, 2, 3.

Experimental Procedure. The VLE measurements for the quaternary systems were performed in a way in which the IL mass fraction, w_4, changed from high to low, while l_{32}, defined as $l_{32} = x_3/(x_2 + x_3)$, remained almost unchanged. At the beginning of the measurement, samples of ethanol, ethyl acetate, and [bmim][OAc] were introduced into the ebulliometer. The water contents of the samples 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. Liquid compositions were calculated. The next measurement was carried out by replacement of a certain amount of the mixture in the boiler with the IL-free mixture of ethanol + ethyl acetate to reduce w_4 and keep l_{32} almost unchanged. The measurement was repeated until w_4 became close to 0.1 or phase splitting occurred in the boiler.

In the measurements, temperature stability was better than 0.02 K. Liquid-phase circulation was enhanced by a pump-like stirrer and had a value of approximately 500 $\text{cm}^3\cdot\text{min}^{-1}$. Vapor-phase circulation was maintained at approximately 1 $\text{cm}^3\cdot\text{min}^{-1}$ by adjustment of heating power. Neglecting the density difference of the vapor condensate and the liquid-phase mixture, β_m had a value of 0.002. In the measurements, the vapor condensate was cooled to 275 K. The volume of vapor condensate in the vapor sampling chamber is 1.5 cm^3. Taking into account gas-state vapor material and vapor condensate adhered on the wall of the cooling jacket, the volume of vapor material in eq 3 is estimated to be 1.7 cm^3, very small compared to the total sample volume of 270 cm^3 in the ebulliometer. In the calculation of density of the vapor condensate ρ, excess volume of the ternary mixture was neglected. Therefore

$$\frac{y_1M_1 + y_2M_2 + y_3M_3}{\rho} = \frac{y_1M_1}{\rho_1} + \frac{y_2M_2}{\rho_2} + \frac{y_3M_3}{\rho_3} \tag{8}$$

In eq 8, ρ_1, ρ_2, and ρ_3 are densities of pure liquids of water, ethanol, and ethyl acetate, all at 275 K. These densities were calculated from parameters presented in the literature.[14]

Results and Discussion

VLE data for the system water (1) + ethanol (2) + ethyl acetate (3) + [bmim][OAc] (4) were measured at low water mole fractions and at p = 100 kPa. Complete T, x, y data were obtained. Results are shown in Table 1. The liquid-phase compositions are reported in x'_1, l_{32}, and w_4. Here, we use the variable l_{32} for better demonstration of the experimental results, which we will show later. Taking into account the repeated samplings and additions to the ebulliometer in the process of measurement, uncertainties of liquid-phase compositions were estimated[12] to be relatively ± 2 % for x'_1, ± 0.002 for l_{32}, and ± 0.003 for w_4. The vapor-phase compositions are reported in y_1 and v_{32}. The measurements were performed in a way in which w_4 changed from high to low, while l_{32} was kept approximately unchanged at 0.1, 0.3, 0.5, 0.7, 0.9, 0.98, or 1. The water mole fraction was low in the measurements and became much lower as w_4 decreased. For $l_{32} \approx 0.1$, 0.3, 0.5, or 0.7, the liquid mixtures are completely miscible at all w_4. Thus the measurements were performed at $w_4 \approx 0.7$ to 0.1, decreasing with an interval of 0.1. For $l_{32} \approx 0.9$, 0.98, and 1, the liquid mixtures are homogeneous for $w_4 \geq 0.7$, while a miscibility gap appears in the lower w_4 region and the solubility of ethyl acetate in the IL decreases with increasing l_{32}. The measurements were stopped when the liquid mixtures became heterogeneous. In Table 1, activity coefficients of the volatile components are also reported. In the calculation of the activity coefficients, the vapor phase was regarded as ideal gas, and the vapor pressures were calculated by parameters in the literature.[15]

Table 1. Vapor−Liquid Equilibrium Data for the System Water (1) + Ethanol (2) + Ethyl Acetate (3) + [bmim][OAc] (4) at Low Water Mole Fractions and at p = 100 kPa

w_4[a]	x'_1[b]	l_{32}[c]	y_1	v_{32}[d]	T/K	γ_1	γ_2	γ_3
$l_{32} \approx 0.1$								
0.701	0.0401	0.082	0.0092	0.403	378.99	0.29	0.38	3.32
0.652	0.0329	0.089	0.0085	0.405	374.41	0.35	0.42	3.24
0.601	0.0270	0.092	0.0078	0.382	369.52	0.44	0.48	3.18
0.497	0.0187	0.095	0.0070	0.339	361.68	0.70	0.61	3.10
0.400	0.0134	0.097	0.0061	0.297	356.22	1.00	0.75	2.93
0.300	0.0095	0.098	0.0053	0.268	352.46	1.34	0.85	2.79
0.200	0.0065	0.099	0.0045	0.246	350.09	1.76	0.93	2.62
0.099	0.0042	0.100	0.0035	0.219	348.84	2.17	0.97	2.34
$l_{32} \approx 0.3$								
0.706	0.0486	0.273	0.0044	0.786	367.83	0.18	0.28	2.88
0.604	0.0324	0.287	0.0046	0.741	361.50	0.31	0.36	2.64
0.500	0.0224	0.292	0.0049	0.682	356.63	0.51	0.48	2.46
0.401	0.0160	0.295	0.0050	0.615	352.58	0.81	0.62	2.30
0.298	0.0112	0.297	0.0049	0.544	349.21	1.23	0.79	2.11
0.201	0.0077	0.299	0.0046	0.493	347.34	1.71	0.90	1.93
0.101	0.0049	0.299	0.0042	0.445	346.05	2.48	1.00	1.74
$l_{32} \approx 0.5$								
0.710	0.0521	0.475	0.0022	0.927	360.18	0.12	0.18	2.63
0.602	0.0339	0.489	0.0024	0.905	356.23	0.20	0.23	2.33
0.502	0.0236	0.493	0.0031	0.867	353.71	0.36	0.32	2.11
0.401	0.0166	0.495	0.0039	0.819	351.49	0.66	0.44	1.94
0.301	0.0116	0.498	0.0045	0.748	349.25	1.10	0.62	1.77
0.201	0.0078	0.499	0.0044	0.670	347.22	1.63	0.84	1.59
0.100	0.0049	0.501	0.0043	0.581	345.80	2.62	1.08	1.38
$l_{32} \approx 0.7$								
0.702	0.0466	0.691	0.0012	0.956	355.99	0.09	0.23	2.21
0.602	0.0314	0.695	0.0013	0.951	352.98	0.14	0.24	1.99
0.503	0.0223	0.697	0.0015	0.938	351.44	0.22	0.28	1.80
0.405	0.0161	0.699	0.0022	0.916	350.50	0.40	0.36	1.63
0.307	0.0116	0.700	0.0030	0.879	349.54	0.73	0.51	1.49
0.208	0.0082	0.702	0.0042	0.820	348.26	1.46	0.74	1.36
0.108	0.0055	0.703	0.0052	0.738	346.65	2.76	1.10	1.22
$l_{32} \approx 0.9$								
0.833	0.0965	0.890	0.0010	0.985	359.79	0.05	0.32	2.63
0.803	0.0801	0.894	0.0009	0.985	357.35	0.05	0.32	2.45
0.783	0.0717	0.894	0.0008	0.985	355.96	0.05	0.30	2.37
0.703	0.0486	0.896	0.0008	0.986	352.39	0.07	0.27	2.08
0.597	0.0316	0.898	0.0007	0.985	350.43	0.09	0.25	1.79
$l_{32} \approx 0.98$								
0.806	0.0680	0.978	0.0005	0.997	355.16	0.04	0.38	2.51
0.755	0.0514	0.979	0.0006	0.997	352.51	0.05	0.34	2.26
0.703	0.0402	0.979	0.0006	0.997	350.78	0.07	0.33	2.06
$l_{32} = 1$								
0.814	0.0699	1.000	0.0006	1.000	355.43	0.05	—	2.54
0.744	0.0476	1.000	0.0006	1.000	352.10	0.06	—	2.18
0.702	0.0393	1.000	0.0005	1.000	350.92	0.06	—	2.02

[a] IL mass fraction. [b] Mole fraction on an IL-free basis. [c] $l_{32} = x_3/(x_2 + x_3)$. [d] $v_{32} = y_3/(y_2 + y_3)$.

The influence of the ionic liquid on the phase behavior of ethanol and ethyl acetate is shown in Figure 2, in which the T, l_{32}, and v_{32} relations are given at w_4 = 0.1 to 0.7, with an interval of 0.1. The value of x'_1 stays approximately unchanged at each w_4. There are three diagrams in Figure 2: T, l_{32} diagram (bubble lines), T, v_{32} diagram (dew lines), and v_{32}, l_{32} diagram. The equilibrium temperature has a significant dependence on both w_4 and l_{32}. At high ethanol mole fractions (when l_{32} is small), the temperature increases rapidly with increasing w_4. When l_{32} becomes larger, the temperature changes more slowly with the increase of w_4. At $w_4 \geq 0.4$, on the other hand, the bubble point temperature simply decreases with increasing l_{32}. However, a temperature minimum is observed in each bubble line or dew line for w_4 = 0.1, 0.2, or 0.3. These temperature minima are

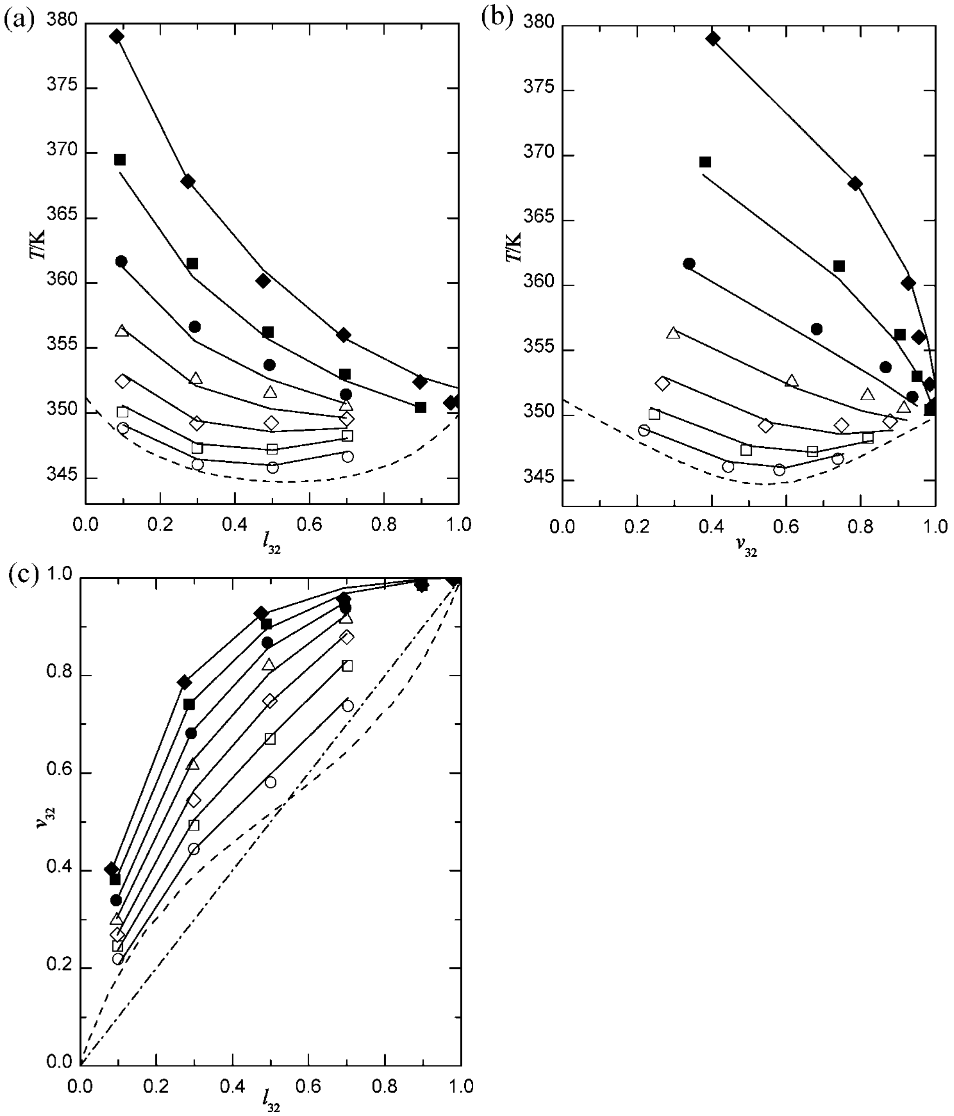

Figure 2. (a) T, l_{32} diagram, (b) T, v_{32} diagram, and (c) v_{32}, l_{32} diagram for the system water (1) + ethanol (2) + ethyl acetate (3) + [bmim][OAc] (4) at several w_4 and at p = 100 kPa: ○, $w_4 \approx 0.1$ and $x'_1 \approx 0.005$; □, $w_4 \approx 0.2$ and $x'_1 \approx 0.007$; ◇, $w_4 \approx 0.3$ and $x'_1 \approx 0.01$; Δ, $w_4 \approx 0.4$ and $x'_1 \approx 0.016$; ●, $w_4 \approx 0.5$ and $x'_1 \approx 0.02$; ■, $w_4 \approx 0.6$ and $x'_1 \approx 0.03$; ♦, $w_4 \approx 0.7$ and $x'_1 \approx 0.04$; solid lines, calculated by the NRTL parameters in Table 2 at p = 100 kPa and at experimental liquid compositions of $w_4 \approx$ 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7, respectively; dashed line, literature data for the system ethyl acetate + ethanol;[8] dash dotted line, $v_{32} = l_{32}$. By definitions, $l_{32} = x_3/(x_2 + x_3)$, $v_{32} = y_3/(y_2 + y_3)$.

not related with azeotropes because it is clear from the v_{32}, l_{32} diagram that the azeotrope of ethanol and ethyl acetate has been removed at the conditions of measurement. A significant increase of v_{32} can be observed with the increase of w_4, indicating a rapid increase of relative volatility of ethyl acetate to ethanol by addition of the IL.

The effects of IL on the relative volatilities of ethyl acetate to ethanol (α_{32}), ethyl acetate to water (α_{31}), and ethanol to water (α_{21}) are shown in Figure 3. By definition, we have $\alpha_{jk} = (y_j/x'_j)/(y_k/x'_k)$, in which the jk pair represents 32, 31, or 21. The relative volatilities are related with the activity coefficients of the volatile components by $\alpha_{jk} = (\gamma_j/\gamma_k)\cdot(p_j^{sat}/p_k^{sat})$, in which the ratio of saturated vapor pressure, p_j^{sat}/p_k^{sat}, is a weak function of temperature. For the temperatures in the present measurement changing from (379 to 345.8) K, the vapor pressure ratio has only a small change of 2.21 to 2.32 for p_2^{sat}/p_1^{sat}, while having a relatively large increase of 0.87 to 1.08 for p_3^{sat}/p_2^{sat} or 1.93 to 2.50 for p_3^{sat}/p_1^{sat}. The fact that the vapor pressure ratio increases with decreasing temperature indicates that the relatively low equilibrium temperature in the high l_{32} region is beneficial for enhancement of the relative volatilities. Generally speaking, the relative volatilities are mainly decided by the activity coefficients of the volatile components. Thus, the effect of IL on the relative volatilities can be illustrated by the effect of IL on the activity coefficients. The effect of IL on the activity coefficients of water (γ_1), ethanol (γ_2), and ethyl acetate (γ_3) is shown in Figure 4.

Table 2. Energy Parameters, Δg_{ij} and Δg_{ji}, and Nonrandomness Factors, α_{ij}, for the NRTL Model Obtained from Correlation of Quaternary VLE Data of Water (1) + Ethanol (2) + Ethyl Acetate (3) + [bmim][OAc] (4) at p = 100 kPa

binary parameters[a]				
component i	component j	Δg_{ij}/J·mol^{-1}	Δg_{ji}/J·mol^{-1}	α_{ij}
water	[bmim][OAc]	−4733.8	−8367.2	0.3
ethanol	[bmim][OAc]	−2969.3	−6605.5	0.5
ethyl acetate	[bmim][OAc]	9098.0	−168.08	0.3

[a] Binary parameters for water (1) + ethanol (2) + ethyl acetate (3) were taken from ref 17 and were fixed as Δg_{12}/J·mol^{-1} = 3698.8 + 4.2758·(T/K), Δg_{21}/J·mol^{-1} = −2216.0 + 6.7055·(T/K), α_{12} = 0.4; Δg_{13}/J·mol^{-1} = −36.820 + 32.041·(T/K), Δg_{31}/J·mol^{-1} = 10728 − 19.501·(T/K), α_{13} = 0.3643; Δg_{23}/J·mol^{-1} = −3502.6 + 15.109·(T/K), Δg_{32}/J·mol^{-1} = 13421 − 36.689·(T/K), α_{23} = 0.1. The objective function used in the optimization was shown in eq 9.

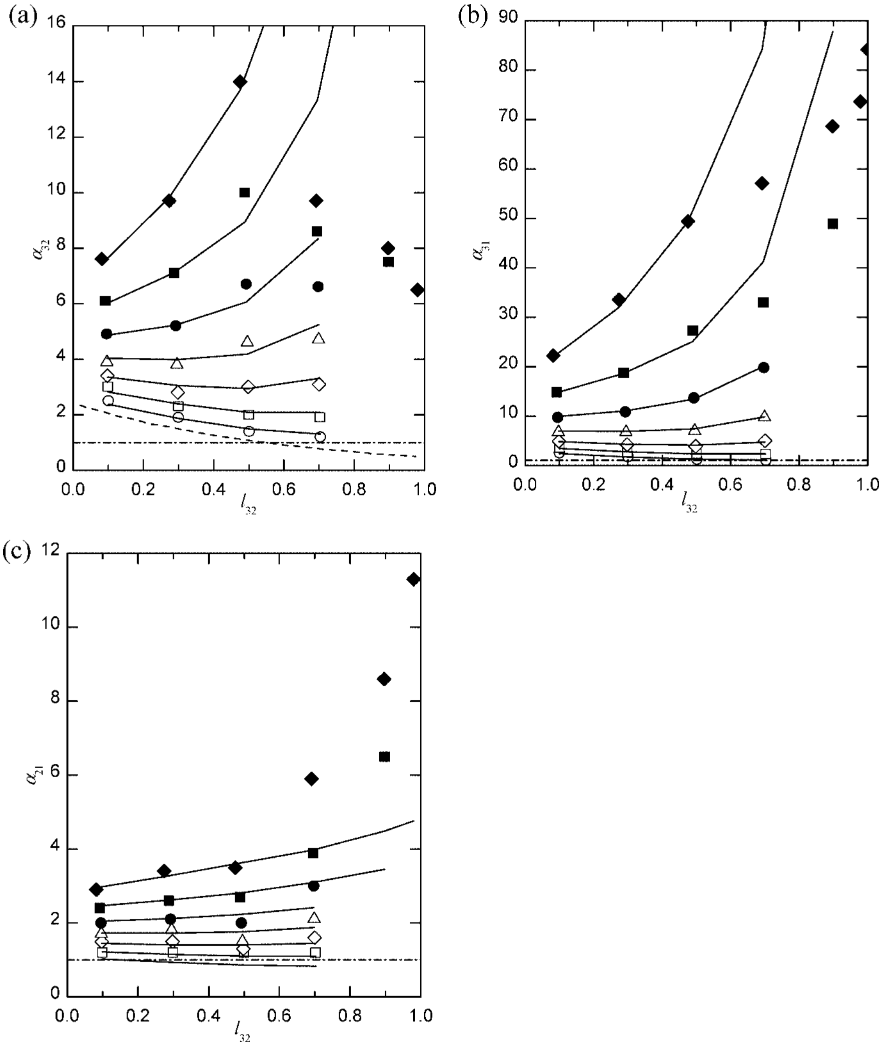

Figure 3. Relative volatilities of (a) α_{32}, (b) α_{31}, and (c) α_{21} in relation with l_{32}, defined as $l_{32} = x_3/(x_2 + x_3)$, for the system water (1) + ethanol (2) + ethyl acetate (3) + [bmim][OAc] (4) at several w_4 and at $p = 100$ kPa: ○, $w_4 \approx 0.1$ and $x'_1 \approx 0.005$; □, $w_4 \approx 0.2$ and $x'_1 \approx 0.007$; ◇, $w_4 \approx 0.3$ and $x'_1 \approx 0.01$; Δ, $w_4 \approx 0.4$ and $x'_1 \approx 0.0016$; ●, $w_4 \approx 0.5$ and $x'_1 \approx 0.02$; ■, $w_4 \approx 0.6$ and $x'_1 \approx 0.03$; ♦, $w_4 \approx 0.7$ and $x'_1 \approx 0.04$; solid lines, calculated by the NRTL parameters in Table 2 at $p = 100$ kPa and at experimental liquid compositions of $w_4 \approx 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7, respectively; dash dotted line, relative volatility at 1; dashed line, literature data for the system ethyl acetate + ethanol.[8]

The activity coefficients are related with the condition of saturated liquid at $p = 100$ kPa.

As shown in Figure 4, the IL has an inversed effect on γ_3 as compared with the effect on γ_1 and γ_2. With the increase of w_4, a decrease of γ_1 and γ_2 is observed, while γ_3 increases. The reversed effect on the activity coefficients results in a consistent effect on the relative volatility. Therefore, α_{32} and α_{31} increase rapidly with increasing w_4 (Figure 3). It can be observed that α_{32} has an appreciable value of 14 at $w_4 = 0.7$ and $l_{32} = 0.5$. Owing to the relatively larger value of $p_3^{\text{sat}}/p_1^{\text{sat}}$ and relatively much more rapid decrease of γ_1, α_{31} is even larger than α_{32}, reaching a very high value of 84.1 at $w_4 = 0.7$ and $l_{32} = 1$. It is thus not surprising that α_{21} also increases with increasing w_4. At $w_4 = 0.7$ and $l_{32} = 0.98$, α_{21} has a value of 11.3.

In Figures 3 and 4, trends of the relative volatilities and activity coefficients are shown in relation with l_{32}. At all IL mass fractions studied, γ_3 decreases with increasing l_{32}. However, the change of γ_2 in relation with l_{32} is rather complicated. When IL concentration is low, namely, $w_4 = 0.1$, γ_2 increases with increasing l_{32}. As w_4 becomes larger, γ_2 tends to decrease with increasing l_{32}. At $w_4 = 0.6$ or 0.7, γ_2 reaches a minimum at $l_{32} = 0.5$ and increases rapidly as l_{32} increases further. It seems that the interaction between ethanol and [bmim][OAc] shows some kind of saturation. At a fixed w_4, the increase of l_{32} results in an effectively larger concentration of the IL as compared with the concentration of ethanol. Thus, a decrease of γ_2 is first observed for $w_4 \geq 0.2$. When the amount of the IL and the amount of ethanol reaches a certain ratio, as shown in the present measurement while $w_4 = 0.6$ or 0.7 and $l_{32} = 0.5$, the effect of the IL is somewhat saturated and the effect of ethyl acetate on γ_2 becomes more important. Further, an increase of l_{32} causes the increase of γ_2 in a way similar to the behavior of the IL-free mixture. The complicated trend of γ_2 in relation with w_4 and l_{32} accounts for the complicated trends of α_{32}. When IL mass fraction is low, namely, $w_4 = 0.1$ or 0.2, α_{32} decreases with increasing l_{32}. As w_4 becomes larger, α_{32} tends to increase with increasing l_{32}. For $w_4 = 0.6$ or 0.7, however, α_{32} reaches a maximum at $l_{32} = 0.5$ and decreases with further increase of l_{32}. On the other hand, the trend of γ_1 in relation with w_4 and l_{32} is generally similar to that of γ_2, showing an increase at $w_4 = 0.1$ and a decrease at $w_4 \geq 0.2$, with the increase of l_{32}. However, the affinity of water and the IL appears to be much stronger. At high IL concentrations, γ_1 decreases steadily with the increase of l_{32}, reaching a very low

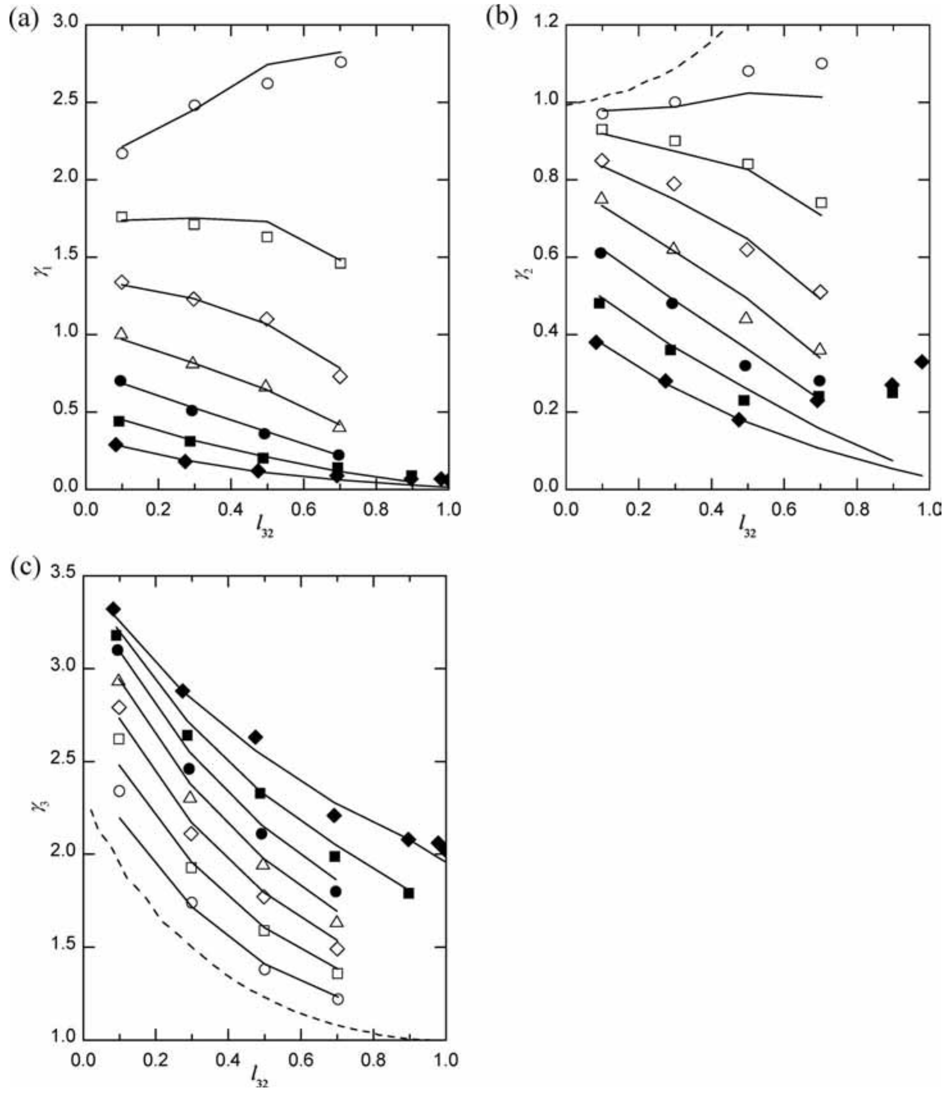

Figure 4. Activity coefficients of (a) water, γ_1, (b) ethanol, γ_2, and (c) ethyl acetate, γ_3, in relation with l_{32}, defined as $l_{32} = x_3/(x_2 + x_3)$, in the saturated liquid mixtures of water (1) + ethanol (2) + ethyl acetate (3) + [bmim][OAc] (4) at several w_4 and at $p = 100$ kPa: ○, $w_4 \approx 0.1$ and $x'_1 \approx 0.005$; □, $w_4 \approx 0.2$ and $x'_1 \approx 0.007$; ◇, $w_4 \approx 0.3$ and $x'_1 \approx 0.01$; Δ, $w_4 \approx 0.4$ and $x'_1 \approx 0.016$; ●, $w_4 \approx 0.5$ and $x'_1 \approx 0.02$; ■, $w_4 \approx 0.6$ and $x'_1 \approx 0.03$; ♦, $w_4 \approx 0.7$ and $x'_1 \approx 0.04$; solid lines, calculated by the NRTL parameters in Table 2 at $p = 100$ kPa and at experimental liquid compositions of $w_4 \approx 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7, respectively; dashed line, literature data for the system ethyl acetate + ethanol.[8]

value of 0.06 at $w_4 = 0.7$ and $l_{32} = 1$. Small γ_1 results in large α_{31} and α_{21} in the region of high w_4 and l_{32}, as can be observed in Figure 3.

The experimental VLE data were correlated with the NRTL equation.[16] For correlation of the quaternary system water (1) + ethanol (2) + ethyl acetate (3) + [bmim][OAc] (4), the binary parameters for water, ethanol, and ethyl acetate were taken from the literature.[17] For the simplicity of application, the energy parameters of Δg_{14}, Δg_{41}, Δg_{24}, Δg_{42}, Δg_{34}, and Δg_{43} were regarded as temperature independent. By giving certain values for the nonrandomness factors of α_{14}, α_{24}, and α_{34}, the six energy parameters were fitted by optimization of the following objective function

$$F = \sum_{n=1}^{N} |T_{\text{calcd}}/\text{K} - T_{\text{exptl}}/\text{K}|/N + \sum_{n=1}^{N} \sum_{i=1}^{3} Q_i |y_{i,\text{calcd}} - y_{i,\text{exptl}}|/N \quad (9)$$

where N is the number of data points. For the y_i terms, we used weight factors Q_i, which were assigned the values $Q_1 = 800$, $Q_2 = 20$, and $Q_3 = 20$. These values are used so that the contribution of temperature and vapor concentration to the objective function is similar. Different values of α_{14}, α_{24}, and α_{34} were used in the correlations. For every combination of values of the nonrandomness factors, several initial values were tested in minimization of the objective function. The minimization is not sensitive to the values of α_{14} and α_{34}, but is significantly affected by the value of α_{24}. In a range of 0.1 to 0.5, a larger value of α_{24} provides better correlation. For $\alpha_{24} > 0.5$, further increase of α_{24} has little effect on the optimization. Thus α_{24} was set at 0.5 in the correlations. On the other hand, the best optimization is obtained when α_{14} and α_{34} have values around 0.3. Therefore, α_{14} and α_{34} were set at 0.3. Results for the optimized parameters and deviations in the correlations are summarized in Tables 2 and 3. The calculated equilibrium temperature, vapor-phase compositions, relative volatilities, and activity coefficients are also shown in Figures 2 to 4. When l_{32} is no more than 0.5, the NRTL equation provides generally reasonable correlations for the activity coefficients of water, ethanol, and ethyl acetate. At $w_4 = 0.1$, however, the reported parameters slightly underestimate γ_2 and slightly overestimate γ_1, resulting in the underestimation of the relative volatility α_{21}.

Table 3. Mean Absolute Deviations, δT and δy_i, in the Correlation by the NRTL Model for Water (1) + Ethanol (2) + Ethyl Acetate (3) + [bmim][OAc] (4) at p = 100 kPa

deviations[a]			
δT/K	δy_1	δy_2	δy_3
0.54	0.0002	0.0083	0.0083

[a] $\delta T/\mathrm{K} = \sum|T_{\mathrm{calcd}}/\mathrm{K} - T_{\mathrm{exptl}}/\mathrm{K}|/N$, $\delta y_i = \sum|y_{i,\mathrm{calcd}} - y_{i,\mathrm{exptl}}|/N$.

Moreover, the present correlation failed to reproduce correctly the trend of increase of γ_2 with the increase of l_{32} at $l_{32} > 0.5$ and $w_4 = 0.6$ and 0.7. Thus, γ_2 is significantly underestimated in these conditions. This should be the reason for the underestimation of α_{21} and overestimation of α_{32}. Similarly, γ_1 is also somewhat underestimated in the same conditions. This should be responsible for the relevant overestimation of α_{31}.

Conclusions

Complete T, x, y data were obtained for water (1) + ethanol (2) + ethyl acetate (3) + [bmim][OAc] (4) at low water mole fractions and at p = 100 kPa. The liquid-phase compositions were obtained by preparing mixtures synthetically, coupled with mass balances. Activity coefficients of the volatile components, as well as relative volatilities, were obtained without the need of a thermodynamic model of the liquid phase. Trends of the activity coefficients and relative volatilities were obtained in relation with w_4 and l_{32}, in which w_4 = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 and l_{32} = 0.1, 0.3, 0.5, 0.7, 0.9, 0.98, and 1, as long as the liquid phase remains homogeneous. The effect of the IL on the relative volatilities was illustrated by effect of the IL on the activity coefficients. With the increase of w_4, γ_1 and γ_2 decrease, while γ_3 increases. The reversed effect on the activity coefficients results in a consistent effect on the relative volatility. At w_4 = 0.7, the relative volatilities reach appreciable values, which are 14 for α_{32}, 84.1 for α_{31}, and 11.3 for α_{21}, respectively. The VLE data were correlated by the NRTL equation.

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Received for review February 24, 2008. Accepted April 3, 2008. The authors gratefully appreciate the financial support by the National Natural Science Foundation of China (20776132) and by the Science Foundation of Zhejiang Province (Z405507).

JE8001392