J. Chem. Eng. Data **2007,** *52,* 1401−1407

Isobaric Vapor−Liquid Equilibria for Three Ternary Systems: Water + 2-Propanol + 1-Ethyl-3-methylimidazolium Tetrafluoroborate, Water + 1-Propanol + 1-Ethyl-3-methylimidazolium Tetrafluoroborate, and Water + 1-Propanol + 1-Butyl-3-methylimidazolium Tetrafluoroborate

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Isobaric vapor−liquid equilibrium (VLE) data were measured for three ternary systems containing ionic liquids (ILs): water + 2-propanol + 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), water + 1-propanol + [emim][BF_4], and water + 1-propanol + 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]). The measurements were performed at $P = 100$ kPa and at several constant IL mass fractions. Activity coefficients of the volatile components were obtained without the need of a thermodynamic model of the liquid phase. The effect of the ILs on the relative volatility of the volatile components was depicted separately by their effect on the activity coefficients. Results of the activity coefficients showed that $[emim]^+$ has a stronger interaction with water than $[bmim]^+$; however, it has a weaker interaction with 1-propanol or 2-propanol. Boiling temperature data were also measured at 100 kPa for the six binary systems containing ILs. Ternary VLE data were also calculated from binary NRTL parameters, which were obtained from correlations of the binary boiling temperature data.

Introduction

Ionic liquids (ILs) are becoming an important alternative for separation of azeotropic or close boiling mixtures.[1−7] In our previous work,[8] we presented an ebulliometer for measurement of *T*, *x*, *y* data at constant pressure by continuous synthesis. The design of the ebulliometer ensured reliability of the vapor-phase composition when hold-up and circulation of the vapor material are relatively small. A procedure was presented for the calculation of liquid-phase composition. The tedious procedure for liquid-phase analysis was avoided. The ebulliometer and the calculation procedure were verified in the measurement of a ternary system composed of water + 2-propanol + 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]). Activity coefficients of the volatile components were obtained without the need of a thermodynamic model of the liquid phase. The activity coefficients obtained are useful for thermodynamic analysis of the effect of ILs on the volatile mixture.

In this work, we extend the measurement to three ternary systems containing ILs, namely, water + 2-propanol + 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), water + 1-propanol + [bmim][BF_4], and water + 1-propanol + [emim][BF_4]. Together with the ternary system we have measured previously,[8] the four ternary systems were composed of water, 1-propanol or 2-propanol, and [emim][BF_4] or [bmim][BF_4]. The ILs investigated in the measurements have the same anion and a different length of alkyl substitution on the cation. 1-Propanol and 2-propanol are isomers, and the aqueous mixtures studied are important for their production and recovery. Boiling temperature data of the six corresponding binary systems containing ILs were also measured.

Experimental Section

Materials. Water was double distilled. 1-Propanol and 2-propanol were analytical grade reagents and were used without further purification. Purities of 1-propanol and 2-propanol were checked by GC, and the results were > 99.9 %. Karl Fischer analysis indicated water contents of 480 ppm for 1-propanol and 230 ppm for 2-propanol. The preparation of [bmim][BF_4] has been described in our previous work.[8] Similarly, [emim][BF_4] was prepared by anion metathesis in water using $AgBF_4$. After removal of water, the ILs were dissolved in 1,2-dichloroethane and refrigerated to 255 K. The IL product was obtained after filtration and distilling off the solvent. Before use, the ILs were dried for 6 h under vacuum at 380 K to remove volatile impurities. Water contents analyzed by Karl Fischer analysis were 40 ppm for [bmim][BF_4] and 60 ppm for [emim][BF_4].

Apparatus and Procedure. VLE were measured by an ebulliometer made of quartz glass featuring vapor-phase sampling and synthetic liquid composition.[8] The pressure was measured by a U-tube filled with water, with one end connected to a pressure buffer and another to the atmosphere. Atmospheric pressure was measured by a standard barometer. The uncertainty of the pressure measurement was ± 0.05 kPa. The temperature was measured 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.

The VLE measurements for the ternary systems were performed in a way of continuous synthesis. At the beginning of the measurement, certain amounts of 2-propanol (or 1-propanol) and [bmim][BF_4] (or [emim][BF_4]) were introduced into the ebulliometer to form the first synthesis. The water contents of the samples in the first synthesis were determined by Karl Fischer analysis, with a relative error of ± 0.5 %. Every sample

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10.1021/je700092d CCC: $37.00

Table 1. Vapor−Liquid Equilibrium Data for the System Water (1) + 2-Propanol (2) + [emim][BF$_4$] (3) at 100 kPa and IL Mass Fractions w_3 = 0.300, 0.400, 0.600, and 0.800

$x'_2{}^{a,b}$	y_2	T/K	$x_1{}^{a,c}$	$x_2{}^{a,c}$	γ_1	γ_2	$x'_2{}^{a,b}$	y_2	T/K	$x_1{}^{a,c}$	$x_2{}^{a,c}$	γ_1	γ_2
$w_3 = 0.300$													
0.9879	0.9869	355.37	0.0108	0.8750	2.36	1.11	0.5941	0.7105	354.01	0.3714	0.5435	1.59	1.36
0.9574	0.9559	355.08	0.0378	0.8501	2.28	1.12	0.4955	0.6673	354.11	0.4654	0.4570	1.45	1.51
0.9439	0.9430	355.05	0.0499	0.8390	2.23	1.12	0.3921	0.6397	354.43	0.5656	0.3649	1.28	1.79
0.8869	0.8914	354.75	0.1010	0.7920	2.13	1.13	0.2893	0.6219	354.82	0.6671	0.2715	1.12	2.30
0.8235	0.8435	354.44	0.1584	0.7392	1.98	1.16	0.1840	0.5917	355.89	0.7729	0.1742	1.00	3.27
0.7583	0.7966	354.18	0.2182	0.6843	1.89	1.20	0.1163	0.5730	357.37	0.8420	0.1108	0.90	4.69
0.6776	0.7498	354.04	0.2929	0.6156	1.74	1.26							
$w_3 = 0.400$													
0.9980	0.9981	355.46	0.0016	0.8302	2.20	1.18	0.6409	0.7550	354.25	0.3119	0.5566	1.59	1.39
0.9800	0.9811	355.35	0.0167	0.8169	2.18	1.18	0.5961	0.7286	354.24	0.3527	0.5206	1.55	1.44
0.9505	0.9549	355.17	0.0414	0.7952	2.12	1.19	0.5564	0.7096	354.26	0.3893	0.4882	1.50	1.49
0.9006	0.9125	354.92	0.0837	0.7579	2.06	1.20	0.4642	0.6781	354.43	0.4756	0.4121	1.36	1.68
0.8498	0.8767	354.72	0.1272	0.7195	1.92	1.23	0.3706	0.6424	354.79	0.5654	0.3329	1.25	1.94
0.8004	0.8433	354.53	0.1700	0.6817	1.84	1.26	0.2711	0.6179	355.48	0.6632	0.2466	1.11	2.45
0.7467	0.8108	354.40	0.2171	0.6402	1.75	1.29	0.1689	0.5971	356.94	0.7663	0.1557	0.95	3.54
0.6893	0.7794	354.30	0.2682	0.5951	1.66	1.34	0.1116	0.5786	358.80	0.8252	0.1037	0.86	4.79
$w_3 = 0.600$													
0.9905	0.9942	355.60	0.0066	0.6820	1.68	1.42	0.5689	0.7606	355.23	0.3271	0.4317	1.42	1.74
0.9677	0.9806	355.54	0.0224	0.6697	1.66	1.43	0.4632	0.7187	355.54	0.4180	0.3607	1.29	1.94
0.9126	0.9476	355.44	0.0612	0.6394	1.65	1.45	0.3688	0.6787	356.08	0.5033	0.2941	1.20	2.20
0.8502	0.9103	355.33	0.1064	0.6040	1.63	1.48	0.2457	0.6370	357.54	0.6209	0.2022	1.04	2.84
0.7647	0.8670	355.21	0.1705	0.5540	1.52	1.55	0.1596	0.6100	359.75	0.7077	0.1344	0.90	3.75
0.6737	0.8192	355.16	0.2415	0.4985	1.46	1.63	0.1235	0.5751	361.29	0.7453	0.1050	0.87	4.27
$w_3 = 0.800$													
0.9806	0.9946	358.12	0.0088	0.4462	1.06	1.96	0.6119	0.8555	359.97	0.2060	0.3248	1.13	2.16
0.9483	0.9846	358.36	0.0238	0.4369	1.11	1.97	0.5013	0.7963	360.62	0.2786	0.2800	1.15	2.27
0.9015	0.9697	358.52	0.0462	0.4231	1.12	1.99	0.4025	0.7460	361.48	0.3502	0.2359	1.10	2.45
0.8439	0.9500	358.72	0.0750	0.4054	1.13	2.02	0.2998	0.6857	363.03	0.4325	0.1852	1.04	2.70
0.7734	0.9216	358.94	0.1121	0.3825	1.17	2.06	0.1952	0.5885	365.73	0.5259	0.1275	1.01	3.05
0.6992	0.8928	359.61	0.1536	0.3570	1.14	2.08	0.1433	0.5461	367.87	0.5764	0.0964	0.94	3.46

[a] Compositions reported are of equilibrium liquid. [b] Mole fraction on IL-free basis. [c] Mole fraction on IL-containing basis.

Table 2. Vapor−Liquid Equilibrium Data for the System Water (1) + 1-Propanol (2) + [emim][BF$_4$] (3) at 100 kPa and IL Mass Fractions w_3 = 0.600 and 0.700

$x'_2{}^{a,b}$	y_2	T/K	$x_1{}^{a,c}$	$x_2{}^{a,c}$	γ_1	γ_2	$x'_2{}^{a,b}$	y_2	T/K	$x_1{}^{a,c}$	$x_2{}^{a,c}$	γ_1	γ_2
$w_3 = 0.600$													
0.9756	0.9719	370.95	0.0169	0.6740	1.78	1.38	0.4414	0.5465	365.14	0.4374	0.3455	1.37	1.90
0.9028	0.8909	369.98	0.0682	0.6339	1.77	1.40	0.3428	0.4970	364.72	0.5275	0.2752	1.28	2.20
0.8428	0.8292	369.18	0.1118	0.5998	1.74	1.42	0.2419	0.4487	364.84	0.6246	0.1993	1.18	2.73
0.7353	0.7417	367.79	0.1931	0.5363	1.60	1.49	0.1537	0.4165	365.79	0.7138	0.1297	1.06	3.75
0.6217	0.6580	366.56	0.2834	0.4658	1.51	1.60	0.1218	0.4107	366.55	0.7471	0.1036	0.99	4.50
0.5375	0.5984	365.86	0.3536	0.4109	1.46	1.70							
$w_3 = 0.700$													
0.9925	0.9940	372.09	0.0044	0.5823	1.40	1.57	0.4630	0.5937	367.49	0.3724	0.3211	1.32	2.02
0.9207	0.9368	371.44	0.0475	0.5517	1.40	1.60	0.3687	0.5301	367.09	0.4524	0.2642	1.28	2.23
0.8597	0.8859	370.82	0.0856	0.5246	1.43	1.63	0.2513	0.4627	367.19	0.5599	0.1879	1.18	2.72
0.7643	0.8135	369.88	0.1481	0.4802	1.40	1.69	0.1606	0.4204	368.24	0.6495	0.1243	1.05	3.59
0.6663	0.7423	369.01	0.2163	0.4319	1.37	1.77	0.1238	0.4113	369.30	0.6877	0.0972	0.97	4.32
0.5747	0.6632	368.25	0.2840	0.3838	1.40	1.84							

[a] Compositions reported are of equilibrium liquid. [b] Mole fraction on IL-free basis. [c] Mole fraction on IL-containing basis.

added in or taken out of the ebulliometer was weighed by an electronic balance (Mettler-Toledo AL204) with an uncertainty of ± 0.0002 g. Liquid circulation was enhanced by a pumplike stirrer and was kept at approximately 500 cm^3·min^{-1}. Vapor circulation was maintained at 0.5 cm^3·min^{-1} by adjustment of heating power. Neglecting the influence of density, the vapor−liquid circulation ratio was 0.001. When equilibrium was established, vapor condensate was sampled and analyzed. Vapor-phase compositions were measured by the Karl Fischer method, when the water mole fraction was less than 0.1, or by gas chromatography, when the water mole fraction was greater than 0.1. The uncertainty of the Karl Fischer analysis was ± 0.0001 in water mole fraction or relatively 0.5 %, whichever was greater. The uncertainty of the GC analysis was ± 0.002 in mole fraction. Consequently, the liquid composition was calculated on the basis of synthetic quantities and with regard to vapor-phase composition, quantity of vapor material, and vapor−liquid circulation ratio.[8] The quantity of vapor material was calculated from the volume of the vapor material, which was 0.8 cm^3, and from the density of the vapor condensate, which was calculated on the basis of correlation of literature data at 273.15 K for water + 1-propanol[9] and 275.15 K for water + 2-propanol.[10] Therefore, we had the first point of measurement. The synthesis for the next point of measurement was carried out by adding the same mass of water to compensate the vapor sampling and by replacement of a certain amount of bulk material with an aqueous IL solution having the same IL mass fraction. As a result, the IL mass fraction of the equilibrium liquid phase was kept almost unchanged.

Table 3. Vapor−Liquid Equilibrium Data for the System Water (1) + 1-Propanol (2) + [bmim][BF$_4$] (3) at 100 kPa and IL Mass Fractions w_3 = 0.300, 0.500, and 0.700

$x'_2{}^{a,b}$	y_2	T/K	$x_1^{a,c}$	$x_2^{a,c}$	γ_1	γ_2	$x'_2{}^{a,b}$	y_2	T/K	$x_1^{a,c}$	$x_2^{a,c}$	γ_1	γ_2
						$w_3 = 0.300$							
0.9805	0.9564	370.39	0.0176	0.8813	2.71	1.06	0.5655	0.4787	362.76	0.4025	0.5239	1.87	1.20
0.9602	0.9121	369.76	0.0359	0.8643	2.73	1.06	0.4573	0.4491	362.21	0.5068	0.4271	1.61	1.42
0.9298	0.8543	368.86	0.0634	0.8388	2.65	1.06	0.3589	0.4345	362.04	0.6032	0.3377	1.39	1.74
0.8599	0.7410	367.11	0.1270	0.7797	2.51	1.05	0.2647	0.4247	362.18	0.6967	0.2508	1.22	2.28
0.7726	0.6366	365.32	0.2075	0.7050	2.30	1.07	0.1748	0.4264	362.67	0.7873	0.1668	1.06	3.38
0.6694	0.5428	363.75	0.3039	0.6155	2.10	1.12	0.1139	0.4178	363.70	0.8494	0.1091	0.96	4.85
						$w_3 = 0.500$							
0.9776	0.9613	371.51	0.0178	0.7747	2.28	1.16	0.4115	0.4584	363.73	0.5088	0.3558	1.48	1.63
0.9038	0.8424	369.78	0.0771	0.7241	2.28	1.17	0.3195	0.4408	363.58	0.5972	0.2804	1.31	2.00
0.8107	0.7186	367.92	0.1538	0.6587	2.18	1.17	0.2214	0.4195	363.93	0.6945	0.1975	1.16	2.67
0.7067	0.6134	366.37	0.2421	0.5833	2.02	1.20	0.1394	0.4028	365.14	0.7783	0.1260	1.01	3.83
0.6138	0.5569	365.23	0.3234	0.5140	1.81	1.29	0.0913	0.3977	366.32	0.8285	0.0832	0.92	5.47
0.5078	0.5141	364.35	0.4191	0.4324	1.58	1.47							
						$w_3 = 0.700$							
0.9956	0.9950	374.81	0.0027	0.6149	1.71	1.34	0.4226	0.5014	367.81	0.4214	0.3084	1.42	1.76
0.8640	0.8473	372.97	0.0870	0.5532	1.74	1.36	0.3314	0.4511	367.41	0.5025	0.2491	1.33	1.99
0.7790	0.7531	371.55	0.1449	0.5108	1.78	1.38	0.2456	0.4307	367.32	0.5834	0.1899	1.19	2.50
0.6902	0.6658	370.36	0.2084	0.4643	1.75	1.41	0.1596	0.3978	367.95	0.6692	0.1271	1.07	3.36
0.6031	0.6021	369.38	0.2740	0.4163	1.64	1.47	0.1046	0.3352	369.17	0.7269	0.0849	1.04	4.05
0.5143	0.5371	368.43	0.3445	0.3647	1.57	1.55	0.0702	0.2889	370.56	0.7641	0.0577	1.01	4.87

[a] Compositions reported are of equilibrium liquid. [b] Mole fraction on IL-free basis. [c] Mole fraction on IL-containing basis.

Table 4. Boiling Temperature *T* in Relation to IL Mass Fractions w_2 for Six Binary Mixtures at 100 kPa

w_2	T/K	γ_1	w_2	T/K	γ_1
		Water (1) + [bmim][BF$_4$] (2)			
0.8474	379.19	1.152	0.5892	374.71	1.040
0.7979	377.19	1.125	0.4905	374.27	1.021
0.7324	375.98	1.087	0.3711	373.86	1.007
0.6725	375.45	1.058			
		Water (1) + [emim][BF$_4$] (2)			
0.7826	380.64	1.008	0.4001	374.61	0.993
0.7475	379.35	1.008	0.3276	374.22	0.992
0.6978	377.91	1.010	0.2005	373.68	0.990
0.6043	376.29	1.005	0.1004	373.26	0.993
0.5029	375.30	0.998			
		2-Propanol (1) + [bmim][BF$_4$] (2)			
0.8302	363.56	1.646	0.5376	356.54	1.228
0.7909	361.40	1.557	0.4971	356.31	1.195
0.7300	359.19	1.453	0.4593	356.10	1.170
0.7033	358.43	1.420	0.4234	355.98	1.146
0.6790	358.07	1.380	0.3860	355.88	1.124
0.6554	357.64	1.352	0.3475	355.80	1.102
0.6249	357.40	1.308	0.3006	355.69	1.081
0.5797	356.90	1.264			
		2-Propanol (1) + [emim][BF$_4$] (2)			
0.8068	357.68	2.033	0.5218	355.53	1.299
0.7397	356.76	1.731	0.4180	355.48	1.191
0.6590	355.90	1.526	0.3260	355.45	1.123
0.5979	355.62	1.412			
		1-Propanol (1) + [bmim][BF$_4$] (2)			
0.8190	380.08	1.514	0.4853	371.82	1.160
0.7526	376.19	1.429	0.3683	370.99	1.106
0.6704	373.93	1.322	0.2769	370.74	1.065
0.5857	372.57	1.241	0.2077	370.60	1.039
		1-Propanol (1) + [emim][BF$_4$] (2)			
0.8009	374.77	1.848	0.5663	370.66	1.353
0.6898	371.87	1.551	0.4422	370.11	1.228
0.6276	371.20	1.435			

In the measurements of binary systems composed of a volatile component and an IL, the IL mass fraction was changed by replacing a certain amount of bulk material with a pure sample of the volatile component. As there was only the volatile component in the vapor phase, the data obtained were boiling temperatures of the IL-containing mixtures.

Results and Discussion

The ternary VLE data were measured at 100 kPa and at constant IL mass fractions, w_3. For the system water (1) + 2-propanol (2) + [emim][BF$_4$] (3), data were measured at w_3 = 0.300, 0.400, 0.600, and 0.800. For the system water (1) + 1-propanol (2) + [emim][BF$_4$] (3), data were measured at w_3 = 0.600 and 0.700. For the system water (1) + 1-propanol (2) + [bmim][BF$_4$] (3), data were measured at w_3 = 0.300, 0.500, and 0.700. Results are shown in Tables 1 to 3. Activity coefficients of the volatile components are also reported. In the calculation of the activity coefficients, the vapor phase was regarded as an ideal gas and the vapor pressures were calculated using parameters in the literature.[11] Boiling temperature data were also measured at 100 kPa for the six binary systems containing ILs, namely, water (1) + [bmim][BF$_4$] (2), water (1) + [emim][BF$_4$] (2), 2-propanol (1) + [bmim][BF$_4$] (2), 2-propanol (1) + [emim][BF$_4$] (2), 1-propanol (1) + [bmim][BF$_4$] (2), and 1-propanol (1) + [emim][BF$_4$] (2). Results are shown in Table 4.

It is well-known that [BF$_4$]$^-$ hydrolyzes[12] in the presence of water and that Ag$^+$, which exists as a trace contaminant from the synthesis of [emim][BF$_4$], may catalyze this hydrolysis. The hydrolysis of [BF$_4$]$^-$ produces [BF$_3$OH]$^-$ and HF, and [BF$_3$OH]$^-$ can further hydrolyze and produce more HF. In our VLE measurements, we monitored the formation of HF by checking the pH value of the bulk material, which was taken out of the ebulliometer during the process of bulk material replacement. At the beginning of the measurement, the pH value was around 7. As the VLE measurements proceeded, the bulk material showed slight acidity, indicating slow hydrolysis of [BF$_4$]$^-$. At the end of the measurements, the pH value of the bulk material became 4 to 5, which is equivalent to an activity of H$^+$ of 10^{-4} to 10^{-5}. We have calculated the ratio of H$^+$ activity to IL mole fraction, and results showed that it was less than 0.001. The relation between H$^+$ activity and the mole fraction of HF is not available. We assumed a multiplier of 5 for the calculation of HF mole fraction from H$^+$ activity, and the [BF$_4$]$^-$ hydrolysis during the VLE measurements was estimated to be less than 0.5 %. We have also checked the effect of [BF$_4$]$^-$ hydrolysis

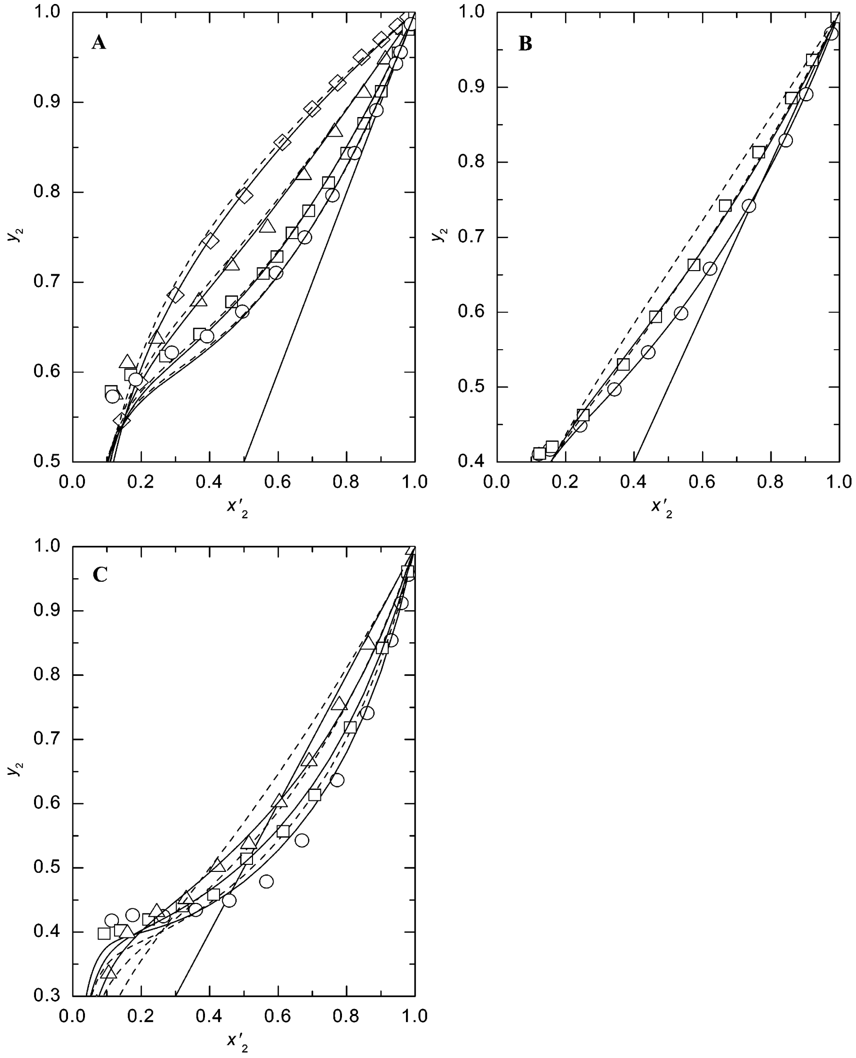

Figure 1. Experimental and calculated y_2, x'_2 diagram for three ternary systems containing ILs at 100 kPa. (A) Water (1) + 2-propanol (2) + [emim][BF$_4$] (3): ○, $w_3 = 0.300$; □, $w_3 = 0.400$; △, $w_3 = 0.600$; ◇, $w_3 = 0.800$. (B) Water (1) + 1-propanol (2) + [emim][BF$_4$] (3): ○, $w_3 = 0.600$; □, $w_3 = 0.700$. (C) Water (1) + 1-propanol (2) + [bmim][BF$_4$] (3): ○, $w_3 = 0.300$; □, $w_3 = 0.500$; △, $w_3 = 0.700$. Lines were calculated by the NRTL binary parameters in Table 5: solid line, parameters from correlation of ternary VLE data; dashed line, parameters from correlation of binary boiling temperature data.

on the VLE data collected. As all the VLE measurements were completed in 8 h, we measured the stabilities of equilibrium temperature and vapor-phase composition in such a period of time. For the ternary systems of water (1) + 2-propanol (2) + [emim][BF$_4$] (3) and water (1) + 2-propanol (2) + [bmim][BF$_4$] (3), the measurements were performed at $w_3 = 0.500$ and $x'_2 = 0.7$. Here x'_2 is the liquid-phase mole fraction of component 2, namely, 2-propanol, calculated on IL-free basis. We did not observe a measurable drift of temperature and vapor-phase composition. Temperature stability was better than 0.02 K. Deviation of vapor-phase composition was less than 0.002 in mole fraction.

The effect of the ionic liquids on the phase behavior of the volatile components can be observed in Figure 1. At a given value of x'_2, the vapor-phase mole fraction of 1- or 2-propanol, y_2, increases with the increase of IL mass fraction. This indicates the enhancement of the relative volatilities of 1- or 2-propanol to water. For the enhancement of the relative volatilities, [emim][BF$_4$] has a more significant effect than [bmim][BF$_4$]. For the mixture of water + 1-propanol, the azeotrope is broken with addition of [emim][BF$_4$] at $w_3 = 0.700$, whereas a larger amount of [bmim][BF$_4$] would be required to achieve this effect. For the mixture of water + 2-propanol, a smaller amount of the ILs is required to break the azeotrope. The azeotrope is broken with the addition of [emim][BF$_4$] at $w_3 = 0.400$ or with the addition of [bmim][BF$_4$] at $w_3 = 0.500$.[8]

The T, x'_2 and T, y_2 relations of the quasibinary systems of water + 1-propanol and water + 2-propanol are shown in Figure 2. Demonstrated are results at the highest mass fraction of the ILs. At a constant IL mass fraction of $w_3 = 0.700$, the quasibinary system of water + 1-propanol presents a minimum temperature with the addition of [bmim][BF$_4$]. The temperature minimum is not related to an azeotrope because x'_2 and y_2 are not the same. The azeotrope of the quasibinary system exists at approximately $x'_2 = 0.6$; however, the azeotrope has nothing to do with the temperature minimum. When [emim][BF$_4$] is added to water + 1-propanol at $w_3 = 0.700$, y_2 is always greater than x'_2, indicating the breaking of the azeotrope. Although the azeotrope is broken, a temperature minimum still exists in the T, x'_2 and T, y_2 curves. For the quasibinary system of water + 2-propanol, the temperature minimum disappears with the addition of [emim][BF$_4$] at $w_3 = 0.800$. As a summary, the diagrams demonstrated belong to three typical types of diagrams for systems

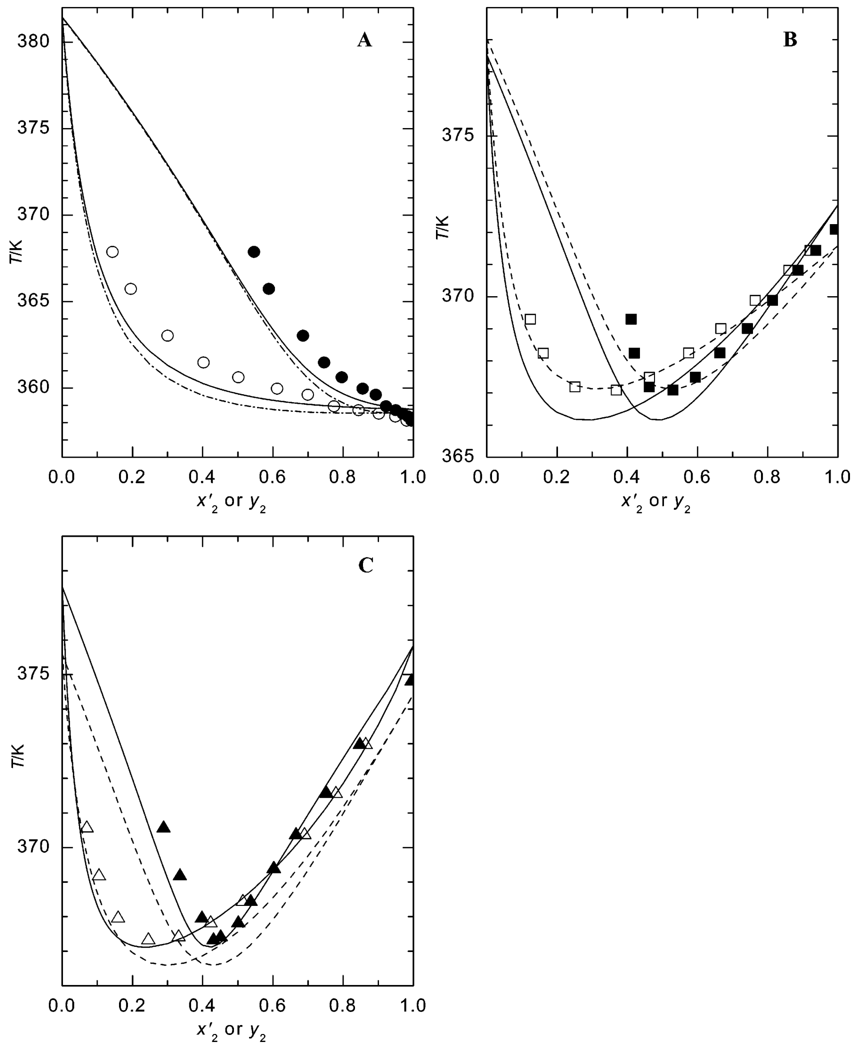

Figure 2. Experimental and calculated T, x'_2, y_2 diagram for three ternary systems containing ILs at 100 kPa. (A) Water (1) + 2-propanol (2) + [emim][BF$_4$] (3): ○, ●, $w_3 = 0.800$. (B) Water (1) + 1-propanol (2) + [emim][BF$_4$] (3): □, ■, $w_3 = 0.700$. (C) Water (1) + 1-propanol (2) + [bmim][BF$_4$] (3): △, ▲, $w_3 = 0.700$. Lines were calculated by the NRTL binary parameters in Table 5: solid line, parameters from correlation of ternary VLE data; dashed line, parameters from correlation of binary boiling temperature data.

Table 5. NRTL Parameters Δg Obtained from Correlations of Ternary VLE Data or Binary Boiling Temperature Data at 100 kPa and Mean Absolute Deviations, δT and δy, for Calculation of Ternary VLE

	binary parameters[c]				deviations	
mixture	Δg_{13} J·mol^{-1}	Δg_{31} J·mol^{-1}	Δg_{23} J·mol^{-1}	Δg_{32} J·mol^{-1}	δT [a] K	δy [b]
Binary Parameters Obtained from Correlation of Ternary VLE Data in Tables 1−3						
water (1) + 2-propanol (2) + [emim][BF$_4$] (3)	4807.0	−3403.9	9772.2	−683.03	0.54	0.0107
water (1) + 1-propanol (2) + [emim][BF$_4$] (3)	4664.7	−2428.4	7248.2	388.76	0.62	0.0087
water (1) + 1-propanol (2) + [bmim][BF$_4$] (3)	−1816.1	9542.1	4332.4	1243.4	0.50	0.0123
Binary Parameters Obtained from Correlation of Binary Boiling Temperature Data in Table 4						
water (1) + 2-propanol (2) + [emim][BF$_4$] (3)	5935.5	−4030.0	9661.9	−588	0.72	0.0105
water (1) + 1-propanol (2) + [emim][BF$_4$] (3)	5935.5	−4030.0	10413	−1048.4	0.29	0.0268
water (1) + 2-propanol (2) + [bmim][BF$_4$] (3)[d]	10368	−4326.5	9659.7	−1994	1.05	0.0163
water (1) + 1-propanol (2) + [bmim][BF$_4$] (3)	10368	−4326.5	9881.5	−2475.9	0.55	0.0349

[a] $\delta T = \sum|T_{\text{calcd}} - T_{\text{exptl}}|/N$. [b] $\delta y = \sum|y_{2,\text{calcd}} - y_{2,\text{exptl}}|/N$. [c] Binary parameters for water and 2-propanol were fixed as $\Delta g_{12} = 6900.81$ J·mol^{-1}, $\Delta g_{21} = 77.49$ J·mol^{-1}, and $\alpha_{12} = 0.3$, which were taken from ref 14. Binary parameters for water and 1-propanol were fixed as $\Delta g_{12} = 7896.7$ J·mol^{-1}, $\Delta g_{21} = 1648.8$ J·mol^{-1}, and $\alpha_{12} = 0.477$, which were taken from ref 15. The values for α_{13} and α_{23} were set as 0.3. [d] Experimental ternary VLE data from ref 8.

containing ILs at constant IL mass fraction: (1) the azeotrope is broken and T, x'_2 and T, y_2 curves do not have a temperature minimum (Figure 2A); (2) the azeotrope is broken but T, x'_2 and T, y_2 curves have a temperature minimum (Figure 2B); (3) the azeotrope remains, and T, x'_2 and T, y_2 curves have a temperature minimum; however, the azeotrope has nothing to do with the temperature minimum (Figure 2C).

The experimental ternary VLE data were correlated with the NRTL equation.[13] In the correlations, the binary parameters for water and 1- or 2-propanol were taken from the literature.[14,15] For the simplicity of application, the binary

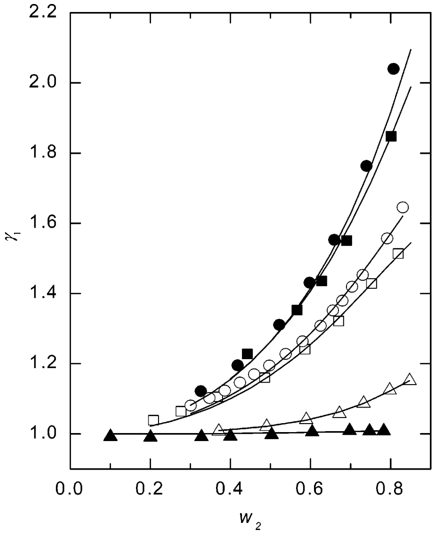

Figure 3. Experimental and calculated activity coefficients of the volatile component γ_1 in relation to IL mass fractions w_2 for six binary mixtures containing ILs: △, water (1) + [bmim][BF$_4$] (2); ○, 2-propanol (1) + [bmim][BF$_4$] (2); □, 1-propanol (1) + [bmim][BF$_4$] (2); ▲, water (1) + [emim][BF$_4$] (2); ●, 2-propanol (1) + [emim][BF$_4$] (2); ■, 1-propanol (1) + [emim][BF$_4$] (2). Lines were calculated by NRTL parameters (Table 5) obtained from correlation of the binary boiling temperature data.

parameters were regarded as temperature independent and the values of α_{13} and α_{23} were set as 0.3. The remaining four binary parameters were fitted by optimization of the following objective function

$$F = \sum_{n=1}^{N} \left| T_{\text{calcd}} - T_{\text{exptl}} \right| / N + 100 \sum_{n=1}^{N} \left| y_{2,\text{calcd}} - y_{2,\text{exptl}} \right| / N \quad (1)$$

where N is the number of data points. Results for the optimized parameters and deviations in the correlations are summarized in Table 5. The VLE results calculated by the binary parameters are also shown in Figures 1 to 2. The correlations provide correct trends of the T, x'_2 and T, y_2 curves. The correlations of the y_2, x'_2 curves are good at low water concentrations. However, when the water mole fraction is large, the calculated vapor compositions of 1- or 2-propanol are significantly smaller than the experimental value. This might be related to dissociation of the ionic liquids into ions at high water concentrations.

The boiling temperature data of the binary systems were also correlated by the NRTL equation. The binary parameters were fitted by optimization of the following objective function

$$F = \sum_{n=1}^{N} \left| T_{\text{calcd}} - T_{\text{exptl}} \right| / N \qquad (2)$$

where N is the number of data points. Results of the optimized parameters are shown in Table 5. Experimental and calculated activity coefficients of the volatile components are shown in Figure 3. The optimized parameters were used to calculate the ternary VLE data, and the deviations with the experimental values are also given in Table 5. Results of the calculated VLE are also shown in Figures 1 to 2. It can be observed that the parameters from the binary boiling temperature data provide correct trends of the T, x'_2 and T, y_2 curves. For the system water + 2-propanol + [emim][BF$_4$], the vapor compositions calculated by these parameters are in good agreement with the experimental values, at least when the water mole fraction is low. However, for the systems water + 1-propanol + [emim]-[BF$_4$] and water + 1-propanol + [bmim][BF$_4$], the calculated values of y_2 are apparently larger than the experimental values. As shown in the correlation of the ternary system water + 2-propanol + [bmim][BF$_4$],[8] the NRTL model provided good correlation for the activity coefficient of 2-propanol, whereas there were relatively large deviations for the activity coefficient of water. For the three ternary systems in this work, we have also observed that correlation by the NRTL equation is good for the activity coefficient of 1- or 2-propanol. The positive deviation of y_2 is related to the negative deviation of the activity coefficient of water, γ_1. For the ternary systems containing 1-propanol, the water mole fraction in the vapor phase, y_1, has a relatively larger value as compared with that for the ternary systems containing 2-propanol. Consequently, a deviation in γ_1 causes a more significant deviation in y_1 for the ternary systems containing 1-propanol. The deviation in y_1 is identical with the deviation in y_2. These might be the reasons why we

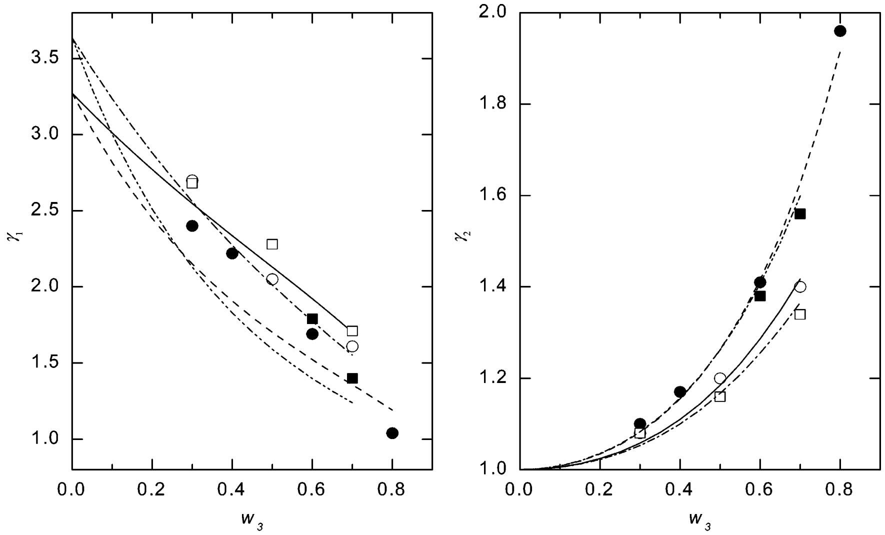

Figure 4. Activity coefficients of the volatile components, γ_1 and γ_2, in relation to IL mass fraction w_3 for ternary mixtures containing ILs at $P = 100$ kPa and $x'_1 = 0$. Points were obtained from trends of experimental data: ○, water (1) + 2-propanol (2) + [bmim][BF$_4$] (3) from ref 8; □, water (1) + 1-propanol (2) + [bmim][BF$_4$] (3) from Table 3; ●, water (1) + 2-propanol (2) + [emim][BF$_4$] (3) from Table 1; ■, water (1) + 1-propanol (2) + [emim][BF$_4$] (3) from Table 2. Lines were calculated by NRTL parameters (Table 5) obtained from correlation of binary boiling temperature data: solid line, water (1) + 2-propanol (2) + [bmim][BF$_4$] (3); dashed line, water (1) + 2-propanol (2) + [emim][BF$_4$] (3); dashed dot line, water (1) + 1-propanol (2) + [bmim][BF$_4$] (3); dashed dot dot line, water (1) + 1-propanol (2) + [emim][BF$_4$] (3).

observe apparently large deviations in y_2 for the ternary systems of water + 1-propanol + [emim][BF_4] and water + 1-propanol + [bmim][BF_4].

It should be noted that the optimized parameters are dependent on the initial values used. Starting from different initial values, the optimization would provide different results. In the correlation of binary systems containing an IL, the boiling temperature is only dependent on the activity coefficient of the volatile component. Because of a lack of information about the activity coefficient of the IL, the optimization becomes more uncertain. The parameters listed in Table 5 were chosen from a few optimized parameters to give reasonable results of calculation of the ternary VLE. Therefore, the calculated results cannot be regarded as predictions.

The effect of [emim][BF_4] and [bmim][BF_4] on the phase behavior of the volatile components is also illustrated in Figure 4, in which the experimental and calculated activity coefficients of the volatile components in the ternary mixtures containing ILs are given. The activity coefficients are related to the conditions of $P = 100$ kPa and $x'_1 = 0$. For the activity coefficients of 1- or 2-propanol, γ_2, it is clear that this condition is the same as that in the binary mixtures with the ILs. In Figure 4, the values of γ_2 calculated by the binary parameters from correlation of the boiling temperature data, are in good agreement with the values obtained from the trends of the ternary VLE data. The binary parameters also provided reasonable results for the activity coefficient of water, γ_1. For systems containing [emim][BF_4], the calculated γ_1 had negative deviation, especially for the aqueous mixtures of 1-propanol at high IL contents.

The activity coefficients are related to the relative volatility α_{21} by the formulation

$$\alpha_{21} = \frac{\gamma_2}{\gamma_1} \cdot \frac{P_2^{\text{sat}}}{P_1^{\text{sat}}} \tag{3}$$

It is clear that the significant difference of 1-propanol and 2-propanol in the phase behavior of their aqueous mixtures results from the ratio $P_2^{\text{sat}}/P_1^{\text{sat}}$, which is a natural contribution to α_{21}. The effect of ILs on α_{21} can be separately depicted by their effect on γ_1 and γ_2. Because the ILs under investigation are composed of the same anion and different cations, the effect of the ILs also reflects the effect of the cations. It can be observed that addition of [emim][BF_4] has a slightly stronger effect on the decrease of γ_1, indicating the interactions of the cations with water are in the order $[\text{emim}]^+ > [\text{bmim}]^+$. This is consistent with the results in Figure 3, in which the activity coefficient of water in $[\text{emim}]^+$ is smaller than in $[\text{bmim}]^+$. Although the addition of the ILs results in the decrease of γ_1, it results in the increase of γ_2. The addition of $[\text{emim}]^+$ causes a more rapid increase of γ_2, indicating the interactions of the cations with 1- or 2-propanol are in the order $[\text{emim}]^+ < [\text{bmim}]^+$. In the IL-containing mixtures, results in Figures 3 and 4 also show that 1-propanol has relatively smaller activity coefficients than 2-propanol. This should be related to the fact that 1-propanol has relatively stronger interactions with the ILs than 2-propanol.

Conclusions

Isobaric T, x, y data were measured for three ternary systems containing ILs. Activity coefficients of the volatile components were obtained without the need of a thermodynamic model of the liquid phase. The effect of the ILs on the relative volatility of the volatile components was depicted separately by their effect on the activity coefficients. The ILs under investigation had the same anion and different cations. Results of the activity coefficients showed that $[\text{emim}]^+$ has a stronger interaction with water than $[\text{bmim}]^+$; however, it has a weaker interaction with 1-propanol or 2-propanol. The ternary VLE were also calculated from binary parameters of the NRTL equation, which were obtained from correlations of experimental boiling temperature data of binary systems containing the ILs.

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Received for review February 19, 2007. Accepted May 1, 2007. The authors gratefully appreciate the financial support by the Science Foundation of Zhejiang Province (Z405507).

JE700092D