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Isobaric Vapor−Liquid Equilibria for Water + 2-Propanol + 1-Butyl-3-methylimidazolium Tetrafluoroborate

Lian-Zhong Zhang, Dong-Shun Deng, Jian-Zhi Han, Deng-Xiang Ji, and Jian-Bing Ji*

College of Chemical Engineering and Material Science, Zhejiang University of Technology, Hangzhou 310014,
People's Republic of China

An ebulliometer has been designed for vapor−liquid equilibrium measurement of systems containing an ionic liquid (IL). The new design allows vapor phase sampling and analysis, while the liquid composition is calculated on the basis of synthetic quantities and with regard to vapor phase composition, quantity of vapor material, and vapor-to-liquid circulation ratio. T, x, y data are reported for the system water + 2-propanol + 1-butyl-3-methylimidazolium tetrafluoroborate at 100 kPa and ionic liquid mass fractions of 0.300, 0.500, and 0.700. The quasi-binary system water + 2-propanol presents a temperature minimum when IL mass fraction is kept constant at these three concentrations. Addition of the IL with mass fraction of 0.500 and 0.700 breaks the azeotrope. Activity coefficients are calculated from the experimental data for the volatile components in the IL-containing mixture. The activity coefficients are directly related to the relative volatility of the quasi-binary mixture and show rather complicated composition dependence.

Introduction

Ionic liquids (ILs) are nonvolatile solvents composed of organic cations with organic or inorganic anions. An important feature of ILs is the potential to adjust the physical and chemical properties by the choice of cation (including the substitution group on the cation) and anion. This characteristic makes it possible to develop "designer" ILs for specific application in chemical engineering process (e.g., extractive distillation).[1−3] The performance of ILs as an entrainer depends largely on the vapor−liquid phase behavior, especially the relative volatility enhanced by the addition of ILs to the azeotropic or close boiling mixtures. Due to the great diversity of structure and property, screening of ILs is of crucial importance for their application. The screening can be performed theoretically, experimentally, or in a combined manner.

For the theoretical screening, predictive methods like COSMO-RS[4−6] and UNIFAC[5] are helpful. The UNIFAC method requires experimental data for parameter correlation. Experimental screening requires measurement of vapor−liquid equilibrium (VLE) of IL-containing systems. The measuring technique can be classified into mainly three types:[7] (i) headspace measurement,[4,6,8] providing x, y data at constant temperature; (ii) static measurement,[9] providing P, x data at constant temperature; and (iii) dynamic circulation measurement,[10] providing complete T, x, y data at constant pressure. For detailed thermodynamic investigation, it is favorable to have experimental activity coefficients of the volatile components, which can be obtained from T, x, y measurements at constant pressure. However, due to the tedious analytical procedure required for the IL-containing liquid phase, such experimental data are presently very few for ternary systems in the literature.

In a VLE measurement with double circulation of vapor and liquid phases, the most simple way to avoid liquid phase analysis is to use an ebulliometer and the synthetic technique.[11,12] When both vapor hold-up and vapor circulation are sufficiently small, the liquid phase composition is very close to the overall synthetic composition. The difference may be further corrected by estimated values of vapor and liquid hold-up and vapor-to-liquid circulation ratio on the basis of material balance.[11] However in the design of ebulliometer of previous authors,[11,12] vapor phase sampling was not done when using a synthetic liquid composition. This is because the composition of the vapor condensate is not necessarily the same as the equilibrium vapor phase. When the vapor circulation is sufficiently small, the vapor condensate is actually in equilibrium with the vapor itself. To meet the need of convenient measurement of T, x, y data for IL-containing systems at constant pressure, this work presents a new design of a double circulation ebulliometer, which allows vapor sampling when vapor hold-up and vapor circulation ratios are small. The new design makes it possible for the vapor phase to be sampled and analyzed, and at the same time the liquid phase composition being close to the composition of the synthetic mixture. Furthermore the liquid phase composition can be calculated precisely from known quantities. Using the new apparatus, VLE data were measured for a system composed of water + 2-propanol + 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]). The aqueous mixture is important for the production and recovery of 2-propanol. The IL chosen is commercially available and commonly used.

Experimental Section

Calculation of the Synthetic Liquid Composition. We use the term *synthetic liquid composition* because it is essentially based on known masses of the components and calculated with regard to vapor phase composition, quantity of vapor material, and vapor-to-liquid circulation ratio. The calculation is based on material balance in the ebulliometer. For simplicity, we consider a ternary system in which components 1 and 2 are volatile and component 3 is a nonvolatile IL.

In an ebulliometer (Figure 1), materials are distributed in different forms with three typical compositions: bulk, vapor, and liquid. Bulk materials are mainly in the boiler. Vapor

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* Corresponding author. Phone: +86 571 88320053. E-mail: jjb@zjut.edu.cn.

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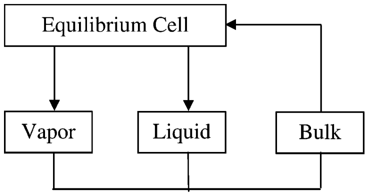

Figure 1. Simplified schematic diagram of an ebulliometer with double circulation of vapor and liquid phases. Vapor−liquid equilibrium is attained at the equilibrium cell. The terms bulk, liquid, and vapor stand for the three typical compositions.

materials may exist in three forms: gaseous state, condensate on the wall of flow path, and vapor condensate in the vapor phase sampling chamber. Liquid materials exist in the flow path before mixing of the vapor and liquid circulation or on the wall of the equilibrium cell.

When the ebulliometer does not have a liquid phase sampling chamber, the amount of liquid materials is small. The liquid composition is also very close to the bulk composition. In this case, we neglect the term of liquid material and the mass balance has the following form:

$$m_{b,1} = m_{s,1} - m_{v,1} \tag{1a}$$

$$m_{b,2} = m_{s,2} - m_{v,2} \tag{1b}$$

$$m_{b,3} = m_{s,3} \tag{1c}$$

where m is the mass of material; subscripts b, s, and v denote bulk, overall synthetic, and vapor, respectively. The overall mass of each component is determined by weighing of every sample added in or taken out of the ebulliometer. The mass of each volatile component in 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 composition y_2, and the molecular weight M_1 and M_2:

$$m_{v,1} = V\rho \frac{y_1 M_1}{(y_1 M_1 + y_2 M_2)} \tag{2a}$$

$$m_{v,2} = V\rho \frac{y_2 M_2}{(y_1 M_1 + y_2 M_2)} \tag{2b}$$

where $y_1 = 1 - y_2$. Therefore, we can calculate the mass fraction of ionic liquid $w_{b,3}$ and mole fraction of component 2 on IL-free basis $x'_{b,2}$:

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

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

These are compositions of the bulk material.

The difference between bulk composition and liquid composition depends on the vapor-to-liquid circulation ratio. The calculation is based on the following material balance for the flow system composed of bulk, liquid, and vapor material:

$$x'_{l,2}(\Delta n'_b - \Delta n_v) + y_2 \Delta n_v = x'_{b,2} \Delta n'_b \tag{4a}$$

$$w_{l,3}(\Delta m_b - \Delta m_v) = w_{b,3} \Delta m_b \tag{4b}$$

where Δn and Δm are respectively the molar and the mass flow rates; subscript l denotes liquid material. A prime symbol indicates the quantity is on IL-free basis.

The vapor-to-liquid circulation ratio *b* can be expressed in molar or mass quantities and on IL-free or IL-containing basis. The liquid flow rate is normally very close to the bulk flow rate, and we can have the following relations:

$$\beta_m = \frac{\Delta m_v}{\Delta m_l} \approx \frac{\Delta m_v}{\Delta m_b} \tag{5a}$$

$$\beta'_m = \frac{\Delta m_v}{\Delta m'_l} \approx \frac{\Delta m_v}{\Delta m'_b} = \frac{\beta_m}{1 - w_{b,3}} \tag{5b}$$

$$\beta'_n = \frac{\Delta n_v}{\Delta n'_l} \approx \frac{\Delta n_v}{\Delta n'_b} = \beta'_m \frac{x'_{b,1} M_1 + x'_{b,2} M_2}{y_1 M_1 + y_2 M_2} \tag{5c}$$

where $x'_{b,1} = 1 - x'_{b,2}$. Equations 4 can now be rewritten as

$$x'_{l,2} = \frac{x'_{b,2} - \beta'_n y_2}{1 - \beta'_n} \tag{6a}$$

$$w_{l,3} = \frac{w_{b,3}}{1 - \beta_m} \tag{6b}$$

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

$$x_{l,1} = \frac{x'_{l,1}}{x'_{l,1} + x'_{l,2} + \dfrac{w_{l,3}}{1 - w_{l,3}} \dfrac{x'_{l,1} M_1 + x'_{l,2} M_2}{M_3}} \tag{6c}$$

$$x_{l,2} = \frac{x'_{l,2}}{x'_{l,1} + x'_{l,2} + \dfrac{w_{l,3}}{1 - w_{l,3}} \dfrac{x'_{l,1} M_1 + x'_{l,2} M_2}{M_3}} \tag{6d}$$

where $x'_{l,1} = 1 - x'_{l,2}$.

Description of the Ebulliometer. The ebulliometer (Figure 2) is made of quartz glass and designed to ensure the accuracy of synthetic liquid composition while vapor phase sampling is allowed. It is based on the design of an inclined measuring cell (A) with a pump-like stirrer (E) to enhance liquid phase circulation.[11,12] The boiler (B) is specially designed with an additional jacket outside the heating tube to stabilize boiling at high IL concentration. Heating is by an electrical heating rod inside the heating tube and a heating belt on the outer wall of the boiler. Vaporization inside the jacket produces bubbles that are released through the holes (C) on top of the jacket to prevent bumping of the main bulk material outside the jacket. To minimize the volume of vapor space and to ensure the accuracy of vapor sampling, the vapor coming out of the equilibrium cell is directly cooled in the vapor condenser (H), while cooling water in the jacket is refrigerated to 278 K. Vapor space in the condenser (H) is less than 10 cm^3. The volume of condensate in the vapor sampling chamber (F) is 0.6 cm^3. Taking into account gaseous state vapor material and vapor condensate adhered on the wall of flowing path, the volume of vapor material in eq 2 is estimated to be 0.8 cm^3, very small as compared to the total sample volume of 270 cm^3 of the ebulliometer. Vapor circulation through the drop counter (M) is normally 0.5 $\text{cm}^3 \cdot \text{min}^{-1}$ while the liquid circulation is around 500 $\text{cm}^3 \cdot \text{min}^{-1}$. During stable operation, there is no gaseous-state flow through the drop counter (M). On the basis of material balance of steady-state flow, the composition of vapor condensate in the vapor sampling chamber should be identical with

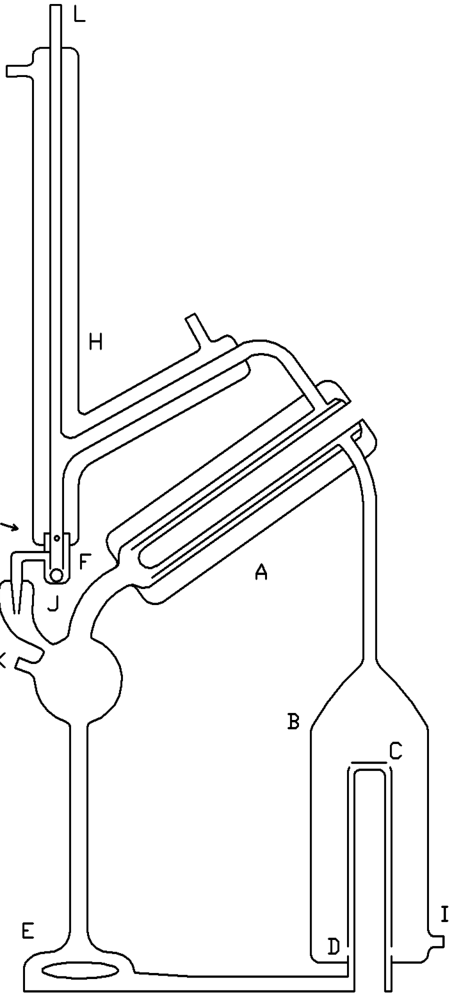

Figure 2. Ebulliometer made of quartz glass featuring vapor phase sampling and synthetic liquid composition. Sample volume is 270 cm^3. The actual location of the vapor condenser (H) is in front of the equilibrium cell and is “stretched” in the drawing to avoid overlapping. Therefore the tube connecting the equilibrium cell (A) and the vapor condenser (H) is kept downward in the actual design. A, equilibrium cell with an outer insulation jacket and a central thermometer well; B, boiler with a heating tube in the central part and a jacket outside the heating tube; C, holes (ϕ 0.5 mm × 4) on top of the jacket; D, holes (ϕ 5 mm × 4) on the lower part of the jacket inside the boiler; E, magnetic stirrer functioned as a centrifugal pump; F, vapor phase sampling chamber (volume of condensate is 0.6 cm^3); G, holes (ϕ 1 mm × 4) in the central tube for pressure balance; H, vapor condenser with a cooling water jacket; I, bulk material sampling port; J, vapor phase sampling port; K, sample injection port; L, pressure measuring port; M, drop counter. Ports I to K are sealed by use of silicon rubber plugs.

the composition of vapor leaving the equilibrium cell. To avoid loss of volatile components by diffusion, connection of pressure measuring port (L) to a pressure buffer is by ϕ 1.6 mm stainless steel tubing of 1.5 m long. During the measurement, the equilibrium cell and the boiler are further insulated by rock wool to ensure best temperature stability and vapor composition consistency.

Experimental Procedure. VLE was determined at a constant pressure of 100 kPa. A 20 dm^3 glass container was used as pressure buffer connected to port L of the ebulliometer. Pressure measurement was by a U-tube filled with water, one end connected to the pressure buffer and another to the atmosphere. The pressure buffer was filled with some 5 Å molecular sieve to avoid interference of water vapor. Atmospheric pressure was measured using a standard barometer. The buffer pressure was adjusted frequently by adding in or taking out small amounts of air with a 50 cm^3 syringe. Stability of pressure is better than ± 0.02 kPa. Uncertainty of the pressure measurement is ± 0.05 kPa.

Temperature measurement was by a standard platinum thermometer (Taihe Instrument Co.) calibrated according to ITS-90 and a 6-1/2-digit multimeter (Kethley model 2000). Uncertainty of the resistance measurement is ± 8 mΩ, which is equivalent to ± 0.08 K for temperature measurement. To simplify the comparison with literature data, most of which conform to IPTS-68, the temperature of ITS-90 was subtracted by 0.02 K. This is the difference of IPTS-68 and ITS-90 at temperatures around (350 to 375) K.

The IL-containing system measured in this work is composed of water, 2-propanol, and [bmim][BF_4]. Water was double distilled. 2-Propanol was analytical grade reagent and was used without further purification. Purity of 2-propanol was checked by GC, and the result was 99.9 %, while Karl Fischer analysis indicated 230 ppm water content. The boiling point of water and 2-propanol measured at 100 kPa was respectively 372.78 K and 355.01 K, which is in good agreement with literature value of 372.79 K[13] and 355.09 K.[14] The ionic liquid was prepared using previously published methods.[15] 1-Methylimidazole was reacted with 1-bromobutane under a nitrogen atmosphere to produce 1-butyl-3-methylimidazolium bromide ([bmim][Br]), which was purified by recrystallization in ethyl acetate/acetonitrile solvent. The ionic liquid [bmim][BF_4] was then produced by anion metathesis between [bmim][Br] and $NaBF_4$ in aqueous solution. The [bmim][BF_4] product was then extracted by 1,2-dichloroethane and washed with water repeatedly until no Cl^- was detected in the aqueous phase. After distillation of the solvent, [bmim][BF_4] was dried for 6 h under vacuum at 390 K. Karl Fischer analysis showed 290 ppm water content in the IL.

For analysis of vapor composition with water mole fraction less than 0.1, the Karl Fischer method was applied. Uncertainty of water composition in mole fraction is ± 0.0001 or relatively 0.5 %, whichever is the greater. When water mole fraction is greater than 0.1, samples were analyzed by gas chromatograph (Fuli 9790J), equipped with a 3 m column of Porapak-Q (80/100). Oven temperature was at 433.2 K. Carrier gas was hydrogen, and detection was by TCD at 453.2 K. A calibration curve was prepared for the GC analysis. Uncertainty of the GC analysis is ± 0.002 in mole fraction.

Verification of the synthetic composition was by sampling of the bulk material and analysis of water and IL content. The IL mass fraction was determined gravimetrically by complete vaporization of a 10 cm^3 sample under vacuum and 390 K to determine the weight of the volatile components and the weight of the residual ionic liquid. The analytical error was less than ± 0.0005 in mass fraction of IL. The amount of water in the sample was analyzed by the Karl Fischer method, which had a relative analytical error less than ± 0.5 %.

Measurement of VLE was carried out in a way of continuous synthesis. At the beginning of the measurement, certain amounts of 2-propanol and [bmim][BF_4] were introduced into the ebulliometer to form the first synthesis. The water content of 2-propanol and [bmim][BF_4] was 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. Liquid circulation was enhanced by the pump-like stirrer and was kept at approximately 500 $cm^3 \cdot min^{-1}$. Vapor circulation was maintained at 0.5 $cm^3 \cdot min^{-1}$ by adjustment of heating power. For the simplicity of calculation, we neglected the influence of density and the vapor-to-liquid circulation ratio was set at $\beta_m = 0.001$. When

Table 1. Vapor−Liquid Equilibrium Data for the System Water (1) + 2-Propanol (2) + [bmim][BF$_4$] (3) at 100 kPa

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
						$w_3 = 0.300$							
0.99803	0.99753	355.70	0.00177	0.8960	2.68	1.08	0.5511	0.6812	354.22	0.4164	0.5111	1.54	1.37
0.9535	0.9495	355.38	0.0418	0.8588	2.35	1.09	0.4529	0.6379	354.48	0.5111	0.4231	1.41	1.54
0.9172	0.9146	355.14	0.0748	0.8282	2.24	1.10	0.3579	0.6224	354.89	0.6042	0.3367	1.22	1.86
0.8864	0.8899	354.95	0.1028	0.8022	2.11	1.11	0.2652	0.6094	355.55	0.6963	0.2513	1.07	2.38
0.8212	0.8334	354.62	0.1626	0.7467	2.04	1.13	0.1827	0.5929	356.63	0.7793	0.1742	0.95	3.20
0.7373	0.7796	354.34	0.2403	0.6745	1.84	1.18	0.1108	0.5561	358.49	0.8525	0.1063	0.88	4.59
0.6492	0.7262	354.23	0.3230	0.5978	1.71	1.25							
						$w_3 = 0.500$							
0.99708	0.99748	356.29	0.00231	0.7878	2.05	1.20	0.5323	0.6916	355.38	0.3966	0.4515	1.50	1.51
0.9770	0.9799	356.23	0.0183	0.7742	2.07	1.20	0.4287	0.6511	355.82	0.4926	0.3697	1.34	1.71
0.9173	0.9305	355.92	0.0661	0.7334	2.00	1.22	0.3329	0.6278	356.39	0.5842	0.2915	1.18	2.04
0.8496	0.8720	355.62	0.1215	0.6862	2.02	1.24	0.2345	0.6077	357.46	0.6813	0.2087	1.02	2.65
0.7372	0.7864	355.29	0.2159	0.6056	1.92	1.28	0.1395	0.5606	360.27	0.7782	0.1261	0.90	3.65
0.6405	0.7339	355.18	0.2998	0.5341	1.72	1.36							
						$w_3 = 0.700$							
0.99488	0.99703	358.72	0.00316	0.6144	1.61	1.40	0.4457	0.6822	358.74	0.4015	0.3229	1.34	1.83
0.9596	0.9761	358.65	0.0252	0.5983	1.63	1.42	0.3538	0.6282	359.85	0.4821	0.2639	1.25	1.98
0.9320	0.9602	358.62	0.0427	0.5854	1.60	1.42	0.2821	0.5957	360.43	0.5483	0.2155	1.16	2.25
0.8663	0.9205	358.53	0.0855	0.5541	1.60	1.45	0.2010	0.5447	361.97	0.6271	0.1578	1.08	2.66
0.7569	0.8574	358.35	0.1604	0.4993	1.53	1.51	0.1256	0.4897	364.57	0.7046	0.1012	0.98	3.40
0.6527	0.8016	358.31	0.2362	0.4439	1.45	1.59	0.0850	0.4231	366.60	0.7479	0.0695	0.96	3.98
0.5488	0.7385	358.42	0.3165	0.3850	1.41	1.68							

[a] Compositions reported are of equilibrium liquid. For simplicity subscript l is omitted. [b] Mole fraction on IL-free basis. [c] Mole fraction on IL-containing basis.

Table 2. Influence of the Vapor-to-Liquid Circulation Ratio β_m and the Volume of Vapor Material V on the Result of Bulk and Liquid Compositions

β_m	V/cm^3	$w_{b,3}$	$w_{l,3}$	$x'_{b,2}$	$x'_{l,2}$	β_m	V/cm^3	$w_{b,3}$	$w_{l,3}$	$x'_{b,2}$	$x'_{l,2}$
					Reported Value: $w_3 = 0.300$; $x'_2 = 0.99803$						
0.001	0.8	0.2998	0.3001	0.99803	0.99803	0.0005	0.8	0.2998	0.3000	0.99803	0.99803
0.001	1.2	0.3004	0.3007	0.99803	0.99803	0	0.8	0.2998	0.2998	0.99803	0.99803
0.001	0.4	0.2993	0.2996	0.99803	0.99803	max deviation[a]		0.0006	0.0006	0.00000	0.00000
0.002	0.8	0.2998	0.3004	0.99803	0.99803						
					Reported Value: $w_3 = 0.300$; $x'_2 = 0.1108$						
0.001	0.8	0.2999	0.3002	0.11111	0.11083	0.0005	0.8	0.2999	0.3001	0.11111	0.11097
0.001	1.2	0.3001	0.3004	0.11080	0.11053	0	0.8	0.2999	0.2999	0.11111	0.11111
0.001	0.4	0.2997	0.3000	0.11142	0.11114	max deviation [a]		0.0002	0.0002	0.00031	0.00031
0.002	0.8	0.2997	0.3003	0.11142	0.11087						
					Reported Value: $w_3 = 0.500$; $x'_2 = 0.99708$						
0.001	0.8	0.4997	0.5002	0.99708	0.99708	0.0005	0.8	0.4997	0.5000	0.99708	0.99708
0.001	1.2	0.5005	0.5010	0.99708	0.99708	0	0.8	0.4997	0.4997	0.99708	0.99708
0.001	0.4	0.4989	0.4994	0.99708	0.99708	max deviation [a]		0.0008	0.0008	0.00000	0.00000
0.002	0.8	0.4997	0.5007	0.99708	0.99708						
					Reported Value: $w_3 = 0.500$; $x'_2 = 0.1395$						
0.001	0.8	0.4998	0.5003	0.13986	0.13950	0.0005	0.8	0.4998	0.5000	0.13986	0.13986
0.001	1.2	0.5001	0.5006	0.13947	0.13910	0	0.8	0.4998	0.4998	0.13986	0.13986
0.001	0.4	0.4995	0.5000	0.14025	0.13989	max deviation [a]		0.0003	0.0005	0.00039	0.00037
0.002	0.8	0.4998	0.5008	0.13986	0.13913						
					Reported Value: $w_3 = 0.700$; $x'_2 = 0.99488$						
0.001	0.8	0.6997	0.7004	0.99488	0.99488	0.0005	0.8	0.6997	0.7000	0.99488	0.99488
0.001	1.2	0.7007	0.7014	0.99487	0.99487	0	0.8	0.6997	0.6997	0.99488	0.99488
0.001	0.4	0.6986	0.6993	0.99489	0.99489	max deviation [a]		0.0011	0.0011	0.00001	0.00001
0.002	0.8	0.6997	0.7011	0.99488	0.99488						
					Reported Value: $w_3 = 0.700$; $x'_2 = 0.0850$						
0.001	0.8	0.6998	0.7005	0.08559	0.08503	0.0005	0.8	0.6998	0.7002	0.08559	0.08531
0.001	1.2	0.7001	0.7008	0.08535	0.08478	0	0.8	0.6998	0.6998	0.08559	0.08559
0.001	0.4	0.6995	0.7002	0.08584	0.08527	max deviation [a]		0.0003	0.0007	0.00025	0.00058
0.002	0.8	0.6998	0.7012	0.08559	0.08445						

[a] Maximum absolute deviation compared with the result of $\beta_m = 0.001$ and $V = 0.8$ cm^3.

equilibrium was established, vapor condensate was sampled and analyzed. The density of the vapor condensate was calculated based on correlation of literature data at 275.15 K:[16]

$$\rho/(\text{g}\cdot\text{cm}^{-3}) = 0.99979 - 0.37002y_2 + 0.17323y_2^2 \qquad (7)$$

As described previously, the volume of vapor material in eq 2 was set at 0.8 cm^3. Therefore the equilibrium liquid composition was calculated by eq 6, and 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 certain amount of bulk material with 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. The measurement was repeated until $x'_{l,2}$ is smaller than 0.2.

Table 3. Comparison of Synthetic and Analytical Bulk Compositions

$w_{b,3}$			$x'_{b,2}$		
synthetic	analytical	Δ^a	synthetic	analytical	Δ^a
0.2998	0.3005	−0.0007	0.95354	0.95361	−0.00007
0.2999	0.3001	−0.0002	0.1111		
0.4997	0.4988	0.0009	0.97695	0.97714	−0.00019
0.4998	0.4992	0.0006	0.1399		
0.6997	0.6993	0.0004	0.95963	0.95934	0.00029
0.6998	0.7005	−0.0007	0.0856		

[a] Δ = synthetic − analytical.

Results and Discussion

VLE of the system water (1) + 2-propanol (2) + [bmim][BF$_4$] (3) have been measured at three constant IL mass fractions: $w_3 = 0.300$, 0.500, and 0.700. For the simplicity of denotation, the subscript l is omitted in expression of the liquid phase compositions. Results are shown in Table 1. Complete *T*, *x*, *y* data are reported at constant pressure of 100 kPa. Activity coefficients are calculated directly from the experimental data for the volatile components in the saturated IL-containing mixture. In the calculation of activity coefficients, fugacity coefficients of the vapor mixture and the pure vapor at reference state are calculated by correlations[17] and parameters[18] available in the literature.

Temperature stability in the measurement was better than 0.01 K. For the system investigated, equilibrium temperature measured is insensitive to the rate of liquid circulation. By decreasing the liquid circulation to approximately half of the normal amount, the resulting change in temperature was less than 0.02 K. Taking into account the uncertainty of resistance measurement of the platinum thermometer, the uncertainty of the reported equilibrium temperature is ± 0.11 K.

The reported liquid composition is based on the calculation of eqs 1 to 7 with $\beta_m = 0.001$ and $V = 0.8$ cm^3. Influence of these parameters on the result of bulk and liquid compositions was demonstrated in Table 2, with β_m ranging from 0 to 0.002 and *V* ranging from (0.4 to 1.2) cm^3. Comparison was made for six representative points of measurement with different IL and water content. It can be observed that the results of bulk and liquid compositions are insensitive to the value of β_m and *V*. For the β_m and *V* values investigated, IL mass fraction $w_{b,3}$ or $w_{l,3}$ deviates no more than ± 0.0011, as compared with the result of $\beta_m = 0.001$ and $V = 0.8$ cm^3. The deviation of $x'_{b,2}$ or $x'_{l,2}$ is no more than ± 0.00001 at low water concentrations and increases slightly when water content becomes significantly large. For all the points of measurement considered, the maximum deviation of $x'_{b,2}$ or $x'_{l,2}$ is ± 0.00058.

As there is not a liquid phase sampling chamber in our design of the ebulliometer; sample taken from port I (Figure 2) is a part of the bulk material. The synthetic bulk composition was verified by analysis of IL and water contents; the results are listed in Table 3. The deviation of IL mass fraction is less than ± 0.001 for all of the points of measurement investigated. Water composition was verified by Karl Fischer analysis for samples with low water concentrations. The consistency of synthetic and analytical results of $x'_{b,2}$ is better than ± 0.0003.

The *T*, x'_2 and *T*, y_2 relations obtained from the experimental measurement are shown in Figure 3. The quasi-binary system of water + 2-propanol presents a minimum temperature when the IL mass fraction is kept constant. The temperature minima are not related to azeotropes because x'_2 and y_2 are not the same. Similar behavior has been reported for the system 2-propanol + water + calcium nitrate.[19] For systems with IL mass fractions of 0.500 and 0.700, y_2 is always greater than x'_2, indicating the breaking of azeotrope.

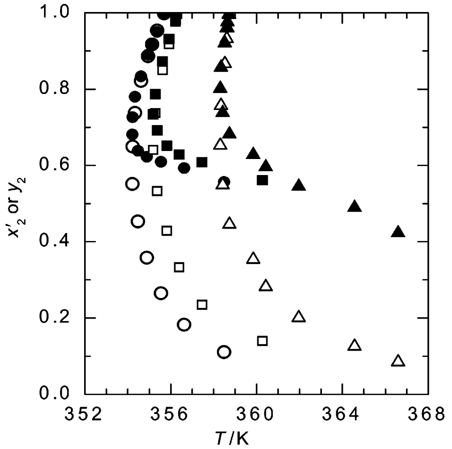

Figure 3. *T*, x'_2, y_2 diagram for the system water (1) + 2-propanol (2) + [bmim][BF$_4$] (3) at 100 kPa and constant IL mass fractions: ○, ●, $w_3 = 0.300$; □, ■, $w_3 = 0.500$; △, ▲, $w_3 = 0.700$. Solid points represent *T*, x'_2 relation; hollow points represent *T*, y_2 relation.

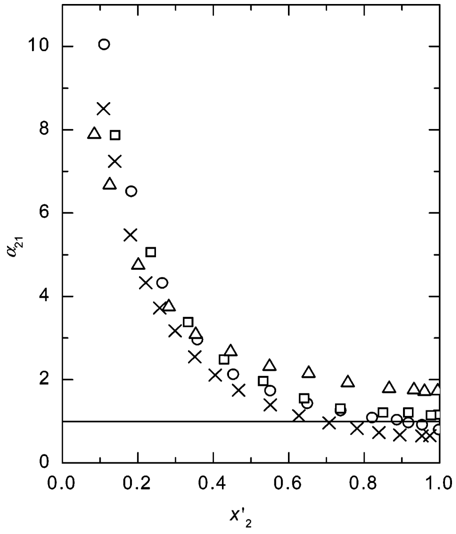

Figure 4. Relative volatility α_{21} for the quasi-binary system water (1) + 2-propanol (2) at 100 kPa with addition of ionic liquid [bmim][BF$_4$] (3): ○, $w_3 = 0.300$; □, $w_3 = 0.500$; △, $w_3 = 0.700$; ×, calculated from literature data for IL-free system.[20]

The effect of the ionic liquid on the phase behavior of the quasi-binary system of water (1) + 2-propanol (2) was also demonstrated in Figure 4, in which the relative volatility is calculated by $\alpha_{21} = (y_2/x'_2)/(y_1/x'_1)$. When the IL mass fraction is 0.300, an azeotrope still exists, and the azeotropic composition shifts significantly to the alcohol end. In the alcohol-rich region, α_{21} is insensitive to water content and increases with the rise of the IL content. When IL mass fraction increases to 0.700, the relative volatility is 1.7, indicating large amount of ionic liquid [bmim][BF$_4$] is required if it is used as the entrainer for distillation of 2-propanol.

According to the modified Raoult's law:

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \tag{8}$$

in which $i = 1$, 2 and P_i^{sat} is the vapor pressure of component *i*. The vapor phase is treated as an ideal gas in this case, and the resulting error is normally less than 2 % for the system

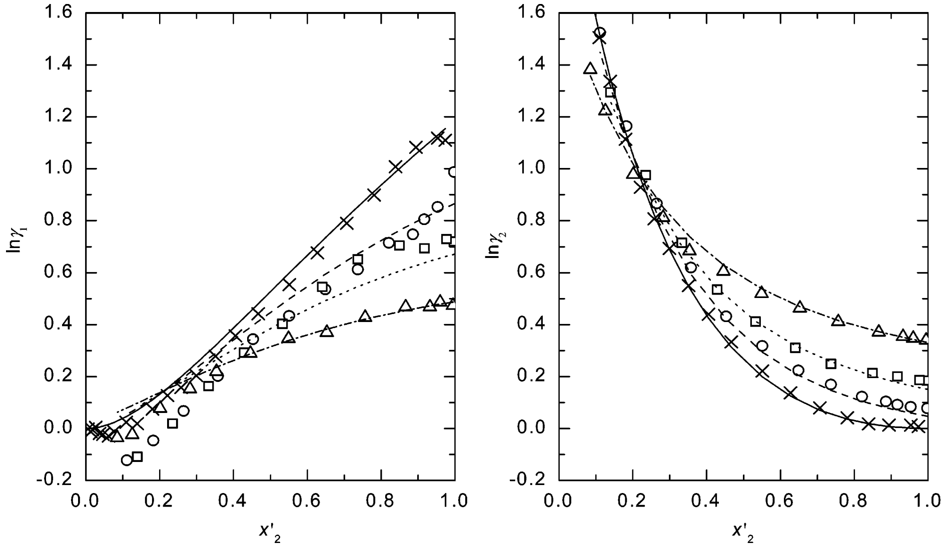

Figure 5. Logarithms of the activity coefficients of water ln γ_1 and 2-propanol ln γ_2 in the saturated liquid mixture water (1) + 2-propanol (2) + [bmim][BF$_4$] (3) at 100 kPa: ○, $w_3 = 0.300$; □, $w_3 = 0.500$; △, $w_3 = 0.700$; ×, literature data for the IL-free system.[20] Lines are correlations by NRTL equation.

investigated. Applying the relation $x'_2/x'_1 = x_2/x_1$, we have

$$\alpha_{21} = \frac{\gamma_2}{\gamma_1}\frac{P_2^{\mathrm{sat}}}{P_1^{\mathrm{sat}}} \tag{9}$$

The ratio $P_2^{\mathrm{sat}}/P_1^{\mathrm{sat}}$ is an important contribution in the formulation of α_{21}, and it is insensitive to temperature and keeps effectively unchanged at 1.96 in the present measurement. Therefore eq 9 presents the direct relation of relative volatility with the activity coefficients. The effect of ionic liquid on α_{21} can be illustrated by its effect on the activity coefficients.

The activity coefficients of water (1) and 2-propanol (2) in the saturated liquid mixtures containing [bmim][BF$_4$] (3) are shown in Figure 5. In the alcohol-rich region, the addition of IL has a significant effect on γ_1 and γ_2, with the decrease of γ_1 and the increase of γ_2. This accounts for the increase of relative volatility α_{21}. If the IL mass fraction is kept constant and x'_2 is decreased, further increase of γ_2 and decrease of γ_1 is observed. Moreover the change of γ_1 and γ_2 with respect to x'_2 depends on the IL concentration. The change is more significant if IL concentration is low. As a result, γ_1 has almost the same value at $x'_2 = 0.4$ to 0.5 for all the three IL concentrations and γ_2 presents the same behavior at $x'_2 = 0.3$ to 0.4.

The activity coefficients were correlated with the NRTL equation.[21] In the correlation, the binary parameters for water and 2-propanol were fixed as $g_{12} - g_{22} = 6900.81$ J·mol^{-1}, $g_{21} - g_{11} = 77.49$ J·mol^{-1}, and $\alpha_{12} = 0.3$, which were taken from the literature.[20] The value for α_{13} and α_{23} were also set as 0.3. The remaining four binary parameters were fitted by optimization of the following objective function:

$$F = 100\sqrt{\frac{1}{N}\sum_{n=1}^{N}\left(\frac{\gamma_{1,\mathrm{exp}} - \gamma_{1,\mathrm{cal}}}{\gamma_{1,\mathrm{exp}}}\right)_n^2} + 100\sqrt{\frac{1}{N}\sum_{n=1}^{N}\left(\frac{\gamma_{2,\mathrm{exp}} - \gamma_{2,\mathrm{cal}}}{\gamma_{2,\mathrm{exp}}}\right)_n^2} \tag{10}$$

where $N = 37$, which is the number of data points listed in Table 1. The objective function is composed of the relative root-mean-square deviations of the activity coefficients of water (the first term) and 2-propanol (the second term). Results for the optimized parameters are $g_{13} - g_{33} = 4981.7$ J·mol^{-1}, $g_{31} - g_{11} = -2901.3$ J·mol^{-1}, $g_{23} - g_{33} = 8525.5$ J·mol^{-1}, and $g_{32} - g_{22} = -1621.1$ J·mol^{-1}. The calculated activity coefficients were shown in Figure 5. The NRTL model provides good correlation for the activity coefficient of 2-propanol, with a relative root-mean-square deviation of 2.7 %. However there is a relatively large deviation of 8.6 % for the activity coefficient of water.

Conclusions

An ebulliometer is presented for T, x, y measurement of IL-containing systems at constant pressure. The vapor composition is obtained by sampling and analysis, while the liquid composition is based on synthetic quantities and is calculated with regard to vapor phase composition, quantity of vapor material, and vapor-to-liquid circulation ratio. The ebulliometer is successfully applied in the determination of the system water (1) + 2-propanol (2) + [bmim][BF$_4$] (3) at 100 kPa and IL mass fractions of 0.300, 0.500, and 0.700. T, x'_2, y_2 diagram presents temperature minimum when IL mass fraction is kept constant. Breaking of azeotrope has been observed at IL mass fraction $w_3 = 0.500$ and 0.700. The relative volatility of the quasi-binary mixture of water + 2-propanol is directly related to the activity coefficients, which show rather complicated composition dependence.

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