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Solubility of Alcohols and Aromatic Compounds in Imidazolium-Based Ionic Liquids

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Liquid−liquid equilibria for 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) or 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) + 1-propanol, + 1-butanol, and + 1-pentanol in the temperature range of (293.92 to 364.88) K and the solubility of benzene, toluene, and thiophene in [BMIM][PF_6] and [BMIM][BF_4] in the temperature range of (298.15 to 343.15) K have been measured using the cloud point method. The liquid−liquid equilibrium data were correlated by the nonrandom two-liquid (NRTL) equation, and the root-mean-square deviations of the mole fractions for [BMIM][PF_6] or [BMIM][BF_4] + 1-propanol, 1-butanol, and 1-pentanol are shown as follow: 0.0041, 0.0065, 0.0043, 0.0065, 0.0053, and 0.0019, respectively. In addition, it is found that the solubility of benzene, toluene, and thiophene in the ionic liquids was independent of temperature.

Introduction

Primary research on properties of mixtures containing ionic liquids has focused on developing and understanding the relationship between structures of the cation and anion and physical properties. The thermodynamic properties and behaviors of mixtures containing ionic liquids are required for the development of new processes. An accepted thermodynamic model requires some basic thermophysical data, such as melting point, boiling point, critical properties, and reliable experimental phase equilibrium data such as vapor−liquid equilibrium (VLE), liquid−liquid equilibrium (LLE), and solid−liquid equilibrium (SLE).[1−16,24,25] The measurement of the LLE of mixtures containing ionic liquid (IL) has been increasingly popular for applications in liquid−liquid extraction.[17]

Wagner et al.[1] have systematically studied liquid−liquid phase transitions in mixtures of ILs with nonionic solvents and have reported phase diagrams and the location of critical points in the binary systems (1-hexyl-3-methylimidazolium tetrafluoroborate + water or + alcohols). Shiflett et al.[2] determined the liquid−liquid miscibility temperatures for the binary system of [BMIM][PF_6] + 1-butanol. Brennecke et al.[4−6] presented a systematic study of the impact of different factors on the phase behavior of imidazolium-based and pyridinium-based ILs with alcohols. Ortega et al.[7] studied the behavior of 1-butyl-3-methylpyridinium tetrafluoroborate in mixtures of water and alcohols. Lynden-Bell et al.[8] presented a simulation study to illustrate the observed solubility differences of benzene in 1-methyl-3-methylimidazolium hexafluorophosphate and 1-methyl-3-methylimidazolium chloride. Rogers et al.[15] demonstrated that 1-butyl-3-methylimidazolium chloride could be induced to form aqueous biphasic systems (ABS) when contacted with concentrated solutions of the water-structuring salt, K_3PO_4.

Table 1. Comparison of Experimental and Literature Values of Densities ρ for Pure Compounds

		ρ/g·cm^{-3}				ρ/g·cm^{-3}	
ionic liquid	*T*/K	exptl	ref 22[a]	ionic liquid	*T*/K	exptl	ref 23[b]
[BMIM][PF_6]	298.15	1.36657	1.36600	[BMIM][BF_4]	298.15	1.19203	1.2069
	303.15	1.36223	1.36186		303.15	1.18838	1.1986
	308.15	1.35792	1.35772		313.15	1.18125	1.1908
	313.15	1.35363	1.35359		323.15	1.17418	1.1830
	323.15	1.34533	1.34533		333.15	1.16709	1.1758
					343.15	1.16017	1.1684
					353.15	1.15263	1.1613

[a] Water content of ionic liquid in ref 22 < $75\cdot10^{-6}$. [b] Water content of ionic liquid in ref 23 < $485\cdot10^{-6}$.

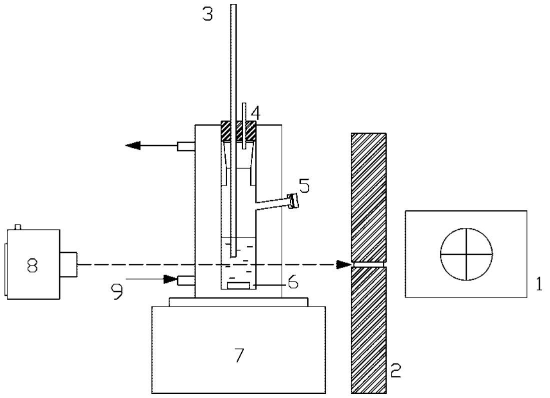

Figure 1. Setup of the phase equilibrium measurement: 1, light source; 2, pore plate; 3, platinum resistance thermometer; 4, N_2 flush; 5, septum for addition; 6, magnetic stirring rod; 7, magnetic stirrer; 8, DDC camera; 9, circulating thermostat.

Review of Approaches for Measuring Solubility. Different methods have been utilized for measuring the LLE. Pletnev et al.[18] proposed a polyvinyl-chloride-plasticized membrane ion-selective electrode (ISE) based on conventional ion-exchangers as a cheap universal tool to detect ILs in water. The method is applicable for ILs with a wide range of solubility in water. They tested ISEs for widely used alkylimidazolium ILs. Additionally, UV spectroscopy, thermogravimetry, and electrospray ionization mass spectrometry have been reported to measure the solubility of ILs in water.[19,20]

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Table 2. Experimental Data of Liquid−Liquid Equilibrium of [BMIM][PF$_6$] + Alcohols at p = 0.1 MPa

1-propanol		1-butanol		1-pentanol	
x_{IL}	T/K	x_{IL}	T/K	x_{IL}	T/K
0.0013	305.92	0.0105	353.22	0.0020	337.87
0.0026	310.94	0.0121	358.47	0.0030	347.16
0.0039	319.87	0.0153	364.88	0.0041	354.53
0.0051	324.86	0.3866	364.54	0.0051	359.14
0.0064	329.26	0.4058	362.20	0.6191	363.44
0.0090	335.96	0.4270	360.03	0.6606	356.97
0.0146	338.82	0.4505	357.76	0.6975	349.26
0.0209	345.38	0.4666	354.73	0.7433	340.71
0.0343	351.40	0.4826	353.03	0.7972	329.10
0.0674	357.30	0.4999	350.88	0.8429	317.17
0.1487	359.27	0.5184	348.43	0.8895	301.36
0.2019	357.83	0.5397	344.83		
0.2620	354.44	0.5778	340.29		
0.3113	350.24	0.5989	337.26		
0.3653	345.29	0.6170	334.58		
0.4190	338.04	0.6463	330.74		
0.4762	331.68	0.6729	325.04		
0.5342	323.36	0.7017	318.90		
0.5878	315.35	0.7332	311.87		
0.6326	308.17	0.7576	304.30		
0.6840	297.32	0.7777	296.98		

Table 3. Experimental Data of Liquid−Liquid Equilibrium of [BMIM][BF$_4$] + Alcohols at p = 0.1 MPa

1-propanol		1-butanol		1-pentanol	
x_{IL}	T/K	x_{IL}	T/K	x_{IL}	T/K
0.0095	299.16	0.0043	301.57	0.0026	310.74
0.0181	306.72	0.0058	303.19	0.0056	324.92
0.0213	308.61	0.0069	307.04	0.0073	330.38
0.0276	310.28	0.0085	309.53	0.0109	334.52
0.0348	311.44	0.0106	312.10	0.0195	340.85
0.0476	312.16	0.0126	314.87	0.0363	344.86
0.0583	312.33	0.0168	317.95	0.0603	346.03
0.1311	311.00	0.0199	320.34	0.0971	345.76
0.1445	310.62	0.0260	323.22	0.1515	345.76
0.1615	309.89	0.0345	325.75	0.2074	344.60
0.1780	309.38	0.0526	328.74	0.2632	343.60
0.1996	308.57	0.1339	329.92	0.3240	341.65
0.2396	306.63	0.2217	327.84	0.3896	338.43
0.2722	304.77	0.2965	325.63	0.4436	334.80
0.3017	302.85	0.3494	323.25	0.4918	331.03
0.3403	299.83	0.3877	321.00	0.5403	327.02
0.3607	297.86	0.4277	318.77	0.5646	323.92
0.3855	295.73	0.4574	316.85	0.6011	319.36
0.4019	293.92	0.4866	314.83	0.7037	303.92
		0.5142	312.74		
		0.5451	310.57		
		0.5686	307.76		
		0.5918	305.30		
		0.6170	302.59		
		0.6444	298.54		

The so-called cloud point method has been extensively used in literature.[1,2,4−17,24,25] The binodal curves were determined by the addition of a known amount of substance (IL or organic solvent) to a known composition mixture with the second component at a known temperature. The end point is affirmed by the disappearance of turbidity in the mixtures. The constant water-bath temperature is maintained by means of a built-in temperature controller, and it is monitored with a thermometer. Until now, there were two ways to determine the cloud point. One way is to measure the intensity of laser light. Heintz et al.[9,10] proposed an apparatus to measure the LLE of a small amount of liquid mixtures with relatively high differences in density and viscosity. The optical system consists of a laser emitter as the light source and a photodiode as the light sensor. In this apparatus, the cloud point was determined by detecting the laser signal intensity accompanied by the turbidity degree.

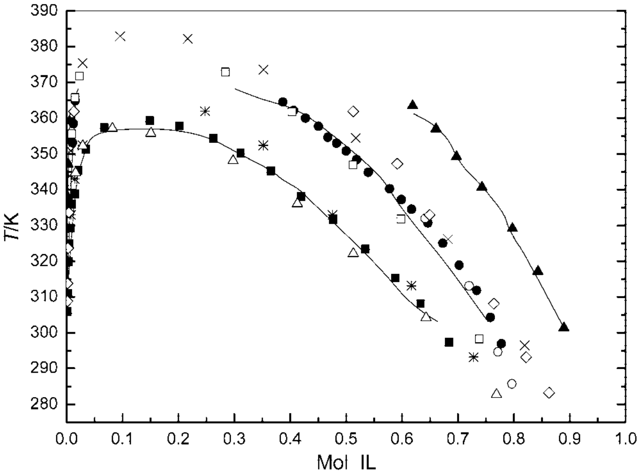

Figure 2. Experimental liquid−liquid equilibrium diagrams for [BMIM][PF$_6$] + 1-propanol: ■, this work; □, data shown in the Supporting Information; *, ref 24. [BMIM][PF$_6$] + 1-butanol: ●, this work; ○, ref 2; □, ref 16; ◇ ref 24; ×, ref 25. [BMIM][PF$_6$] + 1-pentanol: ▲, this work. Solid line for LLE is calculated by means of the NRTL equation.

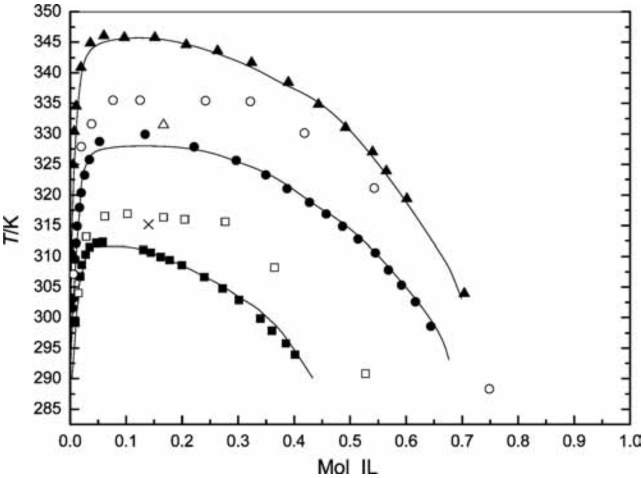

Figure 3. Experimental liquid−liquid equilibrium diagrams for [BMIM][BF$_4$] + 1-propanol: ■, this work; □, ref 5; ×, ref 1. [BMIM][BF$_4$] + 1-butanol: ●, this work; ○, ref 5; □, ref 1. [BMIM][BF$_4$] + 1-pentanol: ▲, this work. Solid line for LLE is calculated by means of the NRTL equation.

Table 4. Experimental Data of Solubility of Benzene, Toluene, and Thiophene in the Ionic Liquids at p = 0.1 MPa

	[BMIM][PF$_6$]				[BMIM][BF$_4$]	
			ref 26			
	T/K	x_{IL}	T/K	x_{IL}	T/K	x_{IL}
benzene	298.15 to 343.15	0.3114	293.1 353.2	0.3471 0.3411	298.15 to 343.15	0.4831
toluene	298.15 to 353.15	0.5164	293.1 383.7	0.5680 0.5639	298.15 to 353.15	0.6889
thiophene	298.15 to 343.15	0.2348			298.15 to 343.15	0.3801

The other way to determine the cloud point is the direct observation of the turbidity, which is more simple but makes it difficult to gain a convincing result. Domańska et al.[11−14,26] measured the solubility of 1-dodecyl-3-methylimidazolium chloride ([C$_{12}$MIM][Cl]) and 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF$_6$]) in alcohols and [EMIM][PF$_6$] and [BMIM]-[PF$_6$] in aromatic hydrocarbons as well as the phase equilibrium of binary mixtures containing ILs. They determined the cloud point by increasing the temperature through the cloud point because they found the procedure of controlling the decrement temperature to be very difficult.

Table 5. Correlation of the LLE Data by Means of the NRTL Equation: Parameters ($g_{12} - g_{22}$) and ($g_{21} - g_{11}$) and Calculation of Deviations σ_x[a]

		$g_{12} - g_{22}$			$g_{21} - g_{11}$			
		$\mathrm{J \cdot mol^{-1}}$			$\mathrm{J \cdot mol^{-1}}$			
ionic liquids	solvent	a_{12}	b_{12}	$c_{12} \cdot 10^{-6}$	a_{21}	b_{21}	$c_{21} \cdot 10^{-6}$	σ_x
[BMIM][PF$_6$]	1-propanol	3.8473	−2560.3	0.4415	−1.2333	731.3	−0.1101	0.0041
	1-butanol	2.6908	−1824.8	0.3252	−0.5310	283.9	−0.0377	0.0065
	1-pentanol	0.7272	−527.8	0.1128	−0.3171	150.3	−0.0150	0.0043
[BMIM][BF$_4$]	1-propanol	13.8700	−8351.0	1.2705	−8.7743	5140.1	−0.7552	0.0065
	1-butanol	9.2385	−5756.6	0.9106	−4.0728	2404.9	−0.3563	0.0053
	1-pentanol	2.5342	−1646.5	0.2831	−3.3318	2046.1	−0.3155	0.0019

[a] See eq 2.

Experimental Section

Materials. [BMIM][PF$_6$] and [BMIM][BF$_4$] were obtained from Henan Lihua Pharmaceutical with a mass fraction of > 0.98 and a water mass fraction < $2 \cdot 10^{-3}$, and they were used after being vacuum desiccated for at least 48 h to remove trace amounts of water. The analysis utilizing the Karl Fisher technique indicated that the water contents of [BMIM][PF$_6$] and [BMIM][BF$_4$] were < $280 \cdot 10^{-6}$ and $920 \cdot 10^{-6}$, respectively. Other chemicals used in this study were supplied by Tianjin Guangfu Research Institute. Organic solvents were dried over 0.4 nm molecular sieves and were particularly degassed by ultrasound prior to their use. The mass fraction purities tested by gas chromatography were as follows: 1-propanol (> 0.998), 1-butanol (> 0.998), 1-pentanol (> 0.998), benzene (> 0.998), toluene (> 0.998), and thiophene (> 0.998). During the course of the experiments, the purity of the ILs was monitored by density measurements.

Density Measurements. The densities of the pure ILs were measured with a high-precision vibrating-tube digital density meter (density/specific gravity meter DA 505, KEM, Japan) whose uncertainty in temperature measurement was ± 0.01 K. The uncertainty in density measurement was $\pm 5 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$. Density measurements were reproducible to $\pm 3 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$. The data compared with refs 22 and 23 are shown in Table 1.

Apparatus and Procedure. The cloud point method was applied to determine the binodal coexisting curves of the LLE and the solubility of aromatic compounds in imidazolium-based ILs. The apparatus illustrated in Figure 1 mostly includes a jacketed glass vessel, which has a working volume of 15 mL and is enclosed by a circulating water bath with a thermostat (type 501A, Shanghai Laboratory Instrument Works) controlling the water bath within 0.01 K. The vessel was sealed to prevent the evaporation of solvent or solute, and the procedure was monitored by a digital camera to determine the cloud point during the measurement. As shown in Figure 1, the light emitted through the pore plate makes the soluble phenomenon clear. In the meantime, the camera can take pictures, which indicate the degree of solubility.

Solubility of Alcohols. The accuracy of the measurement of the temperature was improved by the calibrated thermometer inside the cell. (See Figure 1.) The dry nitrogen flush entered the sealed vessel. The measurements were started with a known mass of IL added to vessel. After a known mass of organic solvent was added to the IL, the temperature was increased at a rate of $0.05\ \mathrm{K \cdot s^{-1}}$ until the turbid liquid became transparent. Then, the temperature was decreased 0.03 K at one time and was maintained for about 10 min. This step was repeated several times to confirm the cloud point temperature within ± 0.03 K. The mixture was adequately stirred during the procedure, which was monitored by a photographic camera. Then, another known mass organic solute was added, and the cloud point temperature was measured. The addition of organic solute was continued until $x_{\mathrm{IL}} > x_{\mathrm{IL(UCST)}}$, where $x_{\mathrm{IL(UCST)}}$ stands for the mole fraction of the IL at the upper critical solution temperature (UCST). The components were interchanged, and the IL was added to the organic solvent until $x_{\mathrm{IL}} < x_{\mathrm{IL(UCST)}}$. The results were proved to be reliable by the comparison of the consistency of values of the UCST to within ± 0.1 K when the measurement started from $x_{\mathrm{IL}} = 0$ and $x_{\mathrm{IL}} = 1$.

Solubility of Aromatic Compounds. The beginning of measurement was analogous to the procedure mentioned above. A known mass of IL was added to the cell at constant temperature and stirred continuously. Then the aromatic compound was added until the mixture became slightly turbid, and this procedure was also monitored by the photographic camera. All of the measurements were repeated twice, and the average value was taken.

The overall uncertainty in the measurement depends on the purity of the solvent and solute and the precision of the calibrated thermometer and electronic digital balance. The temperature was measured by a calibrated platinum resistance thermometer (R-009-312, China) with an uncertainty of ± 0.01 K. The liquids added to the vessel were prepared by mass using a BP210s balance whose accuracy was within ± 0.01 mg. The average uncertainty in the mole fraction of the mixtures was estimated to be less than ± 0.0001.

Results and Discussion

In this work, the LLE for a number of binary ILs + alcohol systems and the solubility of aromatic compounds in the ILs were measured.

Solubility of Alcohols. The alcohols investigated for each IL are listed as follow: [BMIM][PF$_6$] +1-propanol, 1-butanol, or 1-pentanol; [BMIM][BF$_4$] + 1-propanol, 1-butanol, or 1-pentanol. The solubility for the mixtures is given in Tables 2 and 3. Phase diagrams for the above systems, most of which exhibit a UCST, are shown in Figures 2 and 3. A comparison of measured data with the same systems ([BMIM][PF$_6$] + alcohols) in literature[2,16,24,25] confirms the accuracy of our LLE data. The experimental data for systems composed of [BMIM][BF$_4$] with alcohols are also compared with values in the literature.[1,5] Although the same behaviors of UCST are observed in experiment and literature, the LLE data from Brennecke et al.[5] are always higher than values measured in our work. In the work of Brennecke et al.,[5] water contents of ILs and organic solvents are less than those of our work. Admittedly, a higher water content of materials used here could cause an increase in the mutual solubility. On the contrary, it could also lead to a decrease in UCST, as observed by Brennecke et al.[5] Additionally, alcohols are highly soluble in ILs for their mole fraction being more than 60 % in most cases, whereas ILs tend to be less miscible in organic solvents. The ways in which different alcohols and ILs influence the solubility are demonstrated in the following sections.

Alcohols' Chain Lengths. The liquid−liquid phase behavior of the IL [BMIM][PF_6] with alcohols shown in Figure 2 indicates that the UCST moves to a higher temperature with an increasing chain length of alcohols, and systems of [BMIM][BF_4] with alcohols have similar behavior, as shown in Figure 3. The behaviors of UCST demonstrated in ref 26 are similar. The solubility of alcohols in the same IL is in the order 1-propanol > 1-butanol > 1-pentanol.

Ionic Liquids' Anion. As shown in Tables 2 and 3, the saturated mole fraction of 1-propanol with [BMIM][BF_4] at 308.57 K is 0.8004, whereas the value of 1-propanol with [BMIM][PF_6] at 308.17 K is 0.3764. This indicates that the solubility of 1-propanol in [BMIM][BF_4] is much higher than that in [BMIM][PF_6] at the same temperature. Therefore, by similar results derived from other comparisons, it can be established that the alcoholic affinity for the different ILs was [BMIM][BF_4] > [BMIM][PF_6].

Solubility of Aromatic Compounds. The solubilities of benzene, toluene, and thiophene in ILs [BMIM][PF_6] and [BMIM][BF_4] are listed in Table 4. Experimental data are compared with data from Domańska et al.,[26] and the difference between them may result from the different ranges of temperature and water content. In the work of Domańska et al.,[26] no water contents for the ILs were mentioned, except that they were used without further purification. The relative ionic affinity for the same IL is in the order thiophene > benzene > toluene, whereas the aromatic affinity for the different ILs is [BMIM]-[PF_6] > [BMIM][BF_4].

In addition to our experimental work, all of the IL + alcohol systems were modeled by the general nonrandom two-liquid (NRTL) equation.[14]

The temperature-dependent model adjustable parameters, $g_{12} - g_{22} = a_{12} \cdot T^2 + b_{12} \cdot T + c_{12}$ and $g_{21} - g_{11} = a_{21} \cdot T^2 + b_{21} \cdot T + c_{21}$, were found by the minimization of the objective function F

$$F = \sum_i \left[\left(\ln x_1 \gamma_1 - \ln x_1^* \gamma_1^* \right)^2 + \left(\ln x_2 \gamma_2 - \ln x_2^* \gamma_2^* \right)^2 \right] \quad (1)$$

The root-mean-square deviation of the mole fraction was defined as follows

$$\sigma_x = \left(\frac{\sum_{i=1}^{n} (\Delta x_1)_i^2 + \sum_{i=1}^{n} (\Delta x_1^*)_i^2}{2n - 2} \right)^{\frac{1}{2}} \quad (2)$$

where n is the number of experimental LLE points and Δx is defined as

$$\Delta x = x_{\text{calcd}} - x_{\text{exptl}} \quad (3)$$

Utilized in the correlation of different binary systems, the value of parameter α (α = 0.2 or 0.3) was determined for the calculation of the NRTL equation. Values of model parameters obtained by fitting phase curves and the corresponding deviations are given in Table 5. It is found that both positive and negative deviations from experimental data were obtained and were not significant in most systems in Figures 2 and 3.

Conclusions

LLE data for 1-propanol, 1-butanol, and 1-pentanol and the solubility of benzene, toluene, and thiophene in ILs [BMIM]-[PF_6] and [BMIM][BF_4] have been measured. Most systems composed of alcohols and ILs show UCST behavior, and their mutual solubility increases with the increasing length of the alkyl chain of the alcohols. Calculated values derived from the NRTL equation are in good agreement with experimental data. The solubility of aromatic compounds in ILs is in the order benzene > toluene > thiophene, and it has less to do with the temperature.

Supporting Information Available:

List of imidazolium-based ionic liquids investigated and liquid−liquid equilibrium data. This material is available free of charge via the Internet at http://pubs.acs.org.

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