Vapor Pressures of the 1-Butyl-3-methylimidazolium Bromide + Water, 1-Butyl-3-methylimidazolium Tetrafluoroborate + Water, and 1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate + Water Systems

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This work presents the vapor pressures of the following binary imidazolium-based ionic liquid (IL) + water solutions: 1-butyl-3-methylimidazolium bromide ([bmim][Br]) + water, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) + water, and 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([hydemim][BF_4]) + water. Vapor pressures were measured by using the boiling-point method in the temperature range of (304.8 to 475.2) K and in the concentration range of (20.0 to 80.0) mol % of ILs and were correlated with an Antoine-type equation. The resulting average absolute deviations (AAD) between the experimental and calculated values were found to be (0.419, 1.16, and 0.682) % for the [bmim][Br] + water, [bmim][BF_4] + water, and [hydemim][BF_4] + water solutions, respectively.

Introduction

Room-temperature ionic liquids (RTILs) have received considerable interest as potential environmentally benign solvents that can be adapted in various types of industrial processes and have also been demonstrated to be powerful green media used in versatile reactions and extractions.[1−4] A major reason for the interest in ILs as green solvents is their negligible vapor pressure, which decreases the risk of technological exposure and the loss of solvent to the atmosphere.[5,6] RTILs are generally salts based on a substituted heterocyclic cation and an inorganic anion such as a halide, $[AlCl_4]^-$, $[BF_4]^-$, or $[PF_6]^-$ existing as a liquid at room temperature. In particular, ILs might be synthesized in an endless number of ways according to the proper combination of ions. Accordingly, their physical and thermal properties strongly depend on the species of cation and anion as well as the length of the alkyl groups on the cation. The target ILs with specially designed molecular structures can be easily synthesized in most cases, but a careful purification process is required to obtain the high-purity ILs that might be useful for special purposes. However, among numerous types of ILs, the imidazolium-based ILs have been widely and favorably used in many applications because of their air and water stability and a wide liquid-state range.[3,4]

To secure the basic physical properties of ILs, we first measured the vapor pressures of aqueous solutions containing three different ILs: 1-butyl-3-methylimidazolium bromide ([bmim][Br]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), and 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([hydemim][BF_4]). These three ILs have good solubility in water. In particular, the measured vapor-pressure data are necessary for calculations on liquid−liquid extractions and absorption heat pump systems[7] and might suggest a reasonable basis for evaluating the affinity between IL and water. Further experimental measurements become necessary for the potential ILs to be applied to industrially important processes.

Experimental Section

Materials. 1-Methylimidazole (99%), 1-chlorobutane (99.5%), 1-bromobutane (99%), 1,1,1-trichloroethane (99.5%), ethyl acetate, and sodium tetrafluoroborate (98%) were supplied by Aldrich. Dichloromethane, 2-chloroethanol, and acetonitrile were supplied by Kauto, Acros, and Merck, respectively. All materials were used without any further purification.

Synthesis of Ionic Liquids. [bmim][BF_4], [bmim][Br], and [hydemim][BF_4] were prepared according to literature procedures[2,4,8−10] The ^1H NMR spectra were recorded on a Bruker DMX 600-MHz NMR spectrometer. Water contents were determined by a 756 Karl Fisher coulometer. Chloride contents were determined by a Metrohm 716 DMS Titrino.

[bmim][BF_4]. A 1000-mL three-necked round-bottom flask fitted with a water condenser and a gas inlet and provided with a Teflon-coated magnetic spin bar was charged under N_2 with 1-methylimidazole (246.3 g, 3 mol). Butyl chloride (390 mL) was added to the reaction vessel with continuous magnetic stirring. The reaction mixture was heated under N_2 at 80 °C for 72 h with stirring until two phases formed. The top phase, containing the unreacted starting material, was decanted, and ethyl acetate (300 mL) was added through mixing. The ethyl acetate was decanted followed by the addition of fresh ethyl acetate, and this step was repeated twice. After the third decanting of ethyl acetate, any remaining ethyl acetate was removed by heating the bottom phase to 60 °C and stirring while under vacuum. The product is slightly yellow and may be crystalline at room temperature, depending on the amount

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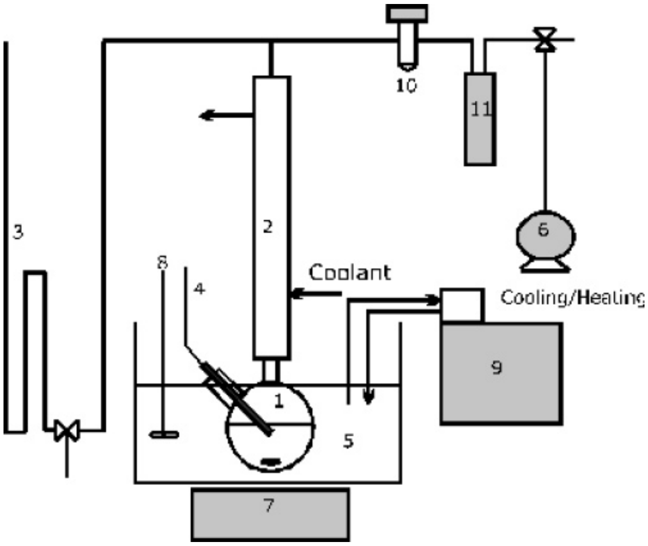

Figure 1. Experimental apparatus for vapor-pressure measurements: 1, sample vessel; 2, condenser; 3, mercury manometer; 4, thermocouple; 5, bath; 6, vacuum pump; 7, 8, stirrer; 9, circulator; 10, needle valve; 11, trap.

of water present. The product was recrystallized from dry acetonitrile and dried under vacuum at 70 °C for 12 h to yield pure crystalline [bmim][[Cl]. A solution of [bmim][Cl] (93 g, 0.531mol) in acetone (500 cm^3) at room temperature was added to sodium tetrafluoroborate (58.3 g, 0.531 mol). After 24 h of stirring, the resulting NaCl precipitate was then filtered through a plug of Celite, and the volatiles were removed by rotary evaporation to leave a yellowish, clear liquid. The product was dried for 3 more days under a high vacuum of 0.03 mmHg. The chemical shifts for the ^1H NMR spectrum (ppm, D_2O) appear as follows: δ 8.71[s, 1H, H(2)], 7.49[s, 1H, H(4)], 7.44[s, 1H, H(5)], 4.21[t, 2H, NCH_2], 3.91[s, 3H, NCH_3], 1.87[m, 2H, NCH_2CH_2], 1.35[m, 2H, $NCH_2CH_2CH_2$] and 0.94[t, 3H, CH_3]. Water and chloride contents were 100 ppm and 1.10%, respectively.

[bmim][Br]. In a three-necked, 1000-mL round-bottomed flask equipped with a reflux condenser, dropping funnel, and magnetic stirrer, under vigorous stirring, 305.64 g (390 mL, 2.85 mol) of freshly distilled bromobutane was added dropwise over 1 h to a solution 225.43 mL (232.2 g, 2.83 mol) of 1-methylimidazole in 200 mL of 1,1,1-trichloroethane at ambient temperature. The mixture was then heated under reflux for 2 h and decanted from the hot solution in a separatory funnel, washed twice with 300 mL of trichloroethane at 50 °C, and then dried under reduced pressure at 40 °C for 3 days. The ^1H NMR spectrum (ppm, D_2O) contains the following peaks: δ 8.91[s, 1H, H(2)], 7.64[s, 1H, H(4)], 7.59[s, 1H, H(5)], 4.32[t, 2H, NCH_2], 4.02 [s, 3H, NCH_3], 1.95 [m, 2H, NCH_2CH_2], 1.42 [m, 2H, $NCH_2CH_2CH_2$], 1.00 [t, 3H, CH_3]. The water content was 200 ppm.

[hydemim][BF$_4$]. A 1000-mL three-necked round-bottom flask fitted with a water condenser and a gas inlet and provided with a Teflon-coated magnetic spin bar was charged under N_2 with 1-methylimidazole (246.3 g, 3 mol). 2-Chloroethanol (200 mL) was added to the reaction vessel. The reaction mixture was heated under N_2 at 80 °C for 120 h. Recrystallization from acetonitrile on cooling was performed repeatedly to give [hydemim][Cl]. [hydemim][Cl] (162 g, 1 mol) in dichloromethane at room temperature was added to sodium tetrafluoroborate (110 g, 1mol). After 24 h of stirring, the resulting NaCl precipitate was then filtered through a plug of Celite. The resulting liquid was dried for 5 more days under high vacuum at (70 to 80) °C. The chemical shifts for ^1H NMR spectrum (ppm, DMSO − d_6) appear as follows: δ 9.05[s, 1H, H(2)], 7.70[s, 1H, H(4)], 7.67[s, 1H, H(5)], 5.14[t, 1H, OH], 4.20[m, 2H, NCH_2 CH_2], 3.86 [s, 3H, NCH_3], 3.72 [t, 2H, NCH_2]. Water and chloride contents were 160 ppm and 1.51%, respectively.

Table 1. Measured Vapor Pressures of the X[bmim][Br] + Water System

$X = 20$ mol %		$X = 40$ mol %		$X = 60$ mol %		$X = 80$ mol %	
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
304.8	3.5	320.6	4.1	355.6	8.8	379.4	11.3
320.6	7.9	332.8	7.2	361.0	11.2	387.4	14.5
326.8	10.8	341.0	10.4	369.2	15.3	392.0	17.4
333.4	14.0	353.8	16.5	376.0	19.2	396.8	19.9
338.4	17.7	359.5	21.4	381.6	24.1	402.4	24.1
343.4	21.1	365.0	25.8	386.8	29.4	407.6	27.5
346.6	24.3	370.8	31.2	395.0	36.4	413.0	32.4
351.6	29.5	375.6	37.4	400.6	42.5	418.5	37.3
356.6	36.4	380.2	43.6	406.8	50.6	422.6	41.3
361.0	43.2	384.6	49.3	411.8	58.4	426.4	47.5
365.8	51.9	387.4	56.6	416.2	68.2	430.8	51.8
368.6	58.1	392.2	64.5	420.2	75.7	434.2	58.1
375.4	72.9	395.8	71.5	425.2	87.6	437.4	62.9
379.4	82.6	400.8	84.1	431.2	103.0	441.6	70.1
383.2	95.8	407.2	103.1			446.4	77.3
385.4	103.2					450.8	83.7
						453.6	91.9
						456.2	96.5
						457.4	101.2

Table 2. Measured Vapor Pressures of the X[bmim][BF$_4$] + Water System

$X = 20$ mol %		$X = 40$ mol %		$X = 60$ mol %		$X = 80$ mol %	
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
311.4	3.9	320.4	3.5	342.0	3.9	375.0	4.3
318.0	6.1	332.0	6.5	353.2	7.2	385.0	6.8
327.8	10.5	341.6	10.2	359.8	10.0	401.0	12.2
335.8	16.0	351.4	15.9	367.4	13.7	413.0	17.8
344.0	22.3	360.4	22.6	374.2	17.6	424.2	24.1
350.8	29.7	369.4	32.1	380.6	22.2	431.4	29.6
358.0	40.6	377.0	41.8	389.0	29.4	435.4	35.5
364.4	53.3	385.2	56.0	396.0	37.3	442.6	43.1
368.4	66.9	389.8	68.2	403.6	45.8	448.4	51.8
376.4	82.4	395.0	82.1	409.2	55.0	451.8	59.0
380.6	102.6	398.4	92.0	414.6	63.0	457.6	68.9
				419.4	74.6	464.8	80.7
				425.0	86.6	475.2	101.6
				430.8	102.2		

Apparatus and Procedure. The vapor pressures were measured by the boiling-point method. The apparatus for the vapor-pressure measurement primarily consisted of an equilibrium vessel with an internal volume of 100 cm^3, a constant-temperature bath, a condenser, a U-tube mercury manometer capable of reading to 0.5 mm, a K-type thermocouple with an accuracy of ±0.1 K, and two stirrers. The K-type thermocouple with the digital thermometer was calibrated with a standard thermometer. The schematic diagram is shown in Figure 1. A sample solution of a desired IL concentration was prepared. The sample solution with an approximate volume of 70 cm^3 was placed in the vessel and evacuated to the proper pressure. The sample solution was then heated and stirred well with a magnetic stirrer to prevent superheating. At thermal equilibrium, the pressure in the apparatus and the temperature of the sample solution were measured. A sample solution of a desired absorbent concentration was used in each run. The condenser was worked with a sufficiently cooled temperature (≈ -10°C) to minimize the amount of condensed vapor because this water vapor can vary the initial concentration.[7,11−14]

Table 3. Measured Vapor Pressures of the X[hydemim][BF$_4$] + Water System

$X = 20$ mol %		$X = 40$ mol %		$X = 60$ mol %		$X = 80$ mol %	
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
325.8	9.2	326.2	5.5	337.2	4.6	352.8	3.3
335.6	15.1	346.2	14.5	367.4	16.3	392.6	12.2
343.2	20.9	353.8	20.1	378.0	21.9	402.0	16.5
350.4	28.9	361.6	26.7	388.2	30.3	420.0	27.5
357.8	38.8	368.0	34.2	395.0	38.5	425.8	32.8
364.2	51.2	375.4	43.8	403.0	48.3	432.2	39.2
370.2	63.5	380.0	55.3	409.8	58.5	435.0	44.2
375.2	76.5	391.0	71.9	416.2	69.4	439.6	50.2
380.4	88.9	396.8	84.5	420.2	80.9	443.8	56.3
383.8	98.8	402.2	100.0	427.4	100.8	448.0	62.6
						454.0	69.7
						458.4	75.8
						462.2	81.9
						464.8	87.9

Table 4. Parameters for the Correlation of Equation 1

i	A	B	AAD %
	[bmim][Br] + water		
0	0.713×10^{1}	-0.169×10^{1}	0.419
1	-0.294×10^{-1}	0.773×10^{-2}	
2	0.499×10^{-3}	-0.226×10^{-3}	
3	-0.370×10^{-5}	0.162×10^{-5}	
	[bmim][BF$_4$] + water		
0	0.715×10^{1}	-0.170×10^{1}	1.16
1	0.101×10^{-1}	-0.514×10^{-2}	
2	-0.443×10^{-3}	0.114×10^{-3}	
3	0.263×10^{-5}	-0.107×10^{-5}	
	[hydemim][BF$_4$] + water		
0	0.711×10^{1}	-0.169×10^{1}	0.682
1	0.614×10^{-2}	-0.420×10^{-2}	
2	-0.578×10^{-3}	0.170×10^{-3}	
3	0.399×10^{-5}	-0.147×10^{-5}	

Results and Discussion

The vapor pressures of the IL + water systems were measured by using a boiling-point method in the temperature range from (304.8 to 475.2) K and in the concentration range from (20.0 to 80.0) mol % of ILs. A description of the apparatus, procedure, and verification were carried out in our previous investigation.[7,11−14] The experimental results are listed in Tables 1 to 3. These values were correlated with an Antoine-type equation that expresses vapor pressure as a function of temperature and concentration

$$\log P = \sum_{i=0}^{3}\left[A_i + \frac{1000B_i}{T - 43.15}\right]X^i \tag{1}$$

where P is the vapor pressure in kPa, A_i and B_i are the regression parameters, T is the absolute temperature in K, and X is the mol %of IL. Parameters A_i and B_i were determined by a least-squares method; the results are shown in Table 4. The AADs between the experimental data and the calculated values were found to be (0.419, 1.16, and 0.682)% for the [bmim][Br] + water, [bmim][BF$_4$] + water, and [hydemim][BF$_4$] + water systems, respectively. These experimental and calculated results are plotted in Figures 2 to 4. These Figures show that the log P versus $1000/(T - 43.15)$ relation at a given concentration appears to be linear over the pressure and temperature ranges considered. The vapor pressures decrease with increasing concentration of ILs, which is a normal result in absorption pairs.

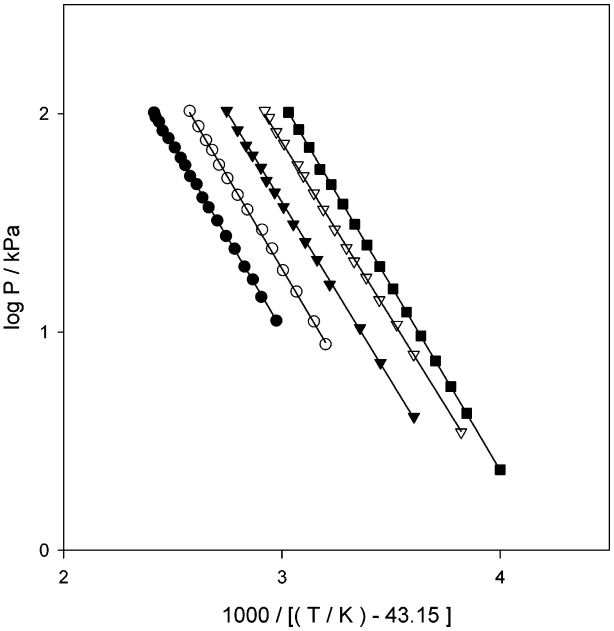

Figure 2. Vapor pressures of the X[bmim][Br] + water system at various temperature and concentration conditions: ■, 0 mol %;[15] ▽, 20 mol %; ▼, 40 mol %; ○, 60 mol %; ●, 80 mol % of [bmim][Br]; −−, calculated.

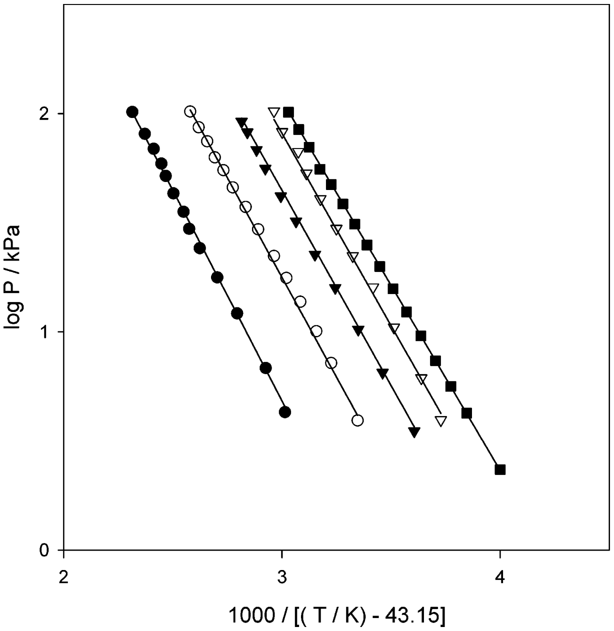

Figure 3. Vapor pressures of the X[bmim][BF$_4$] + water system at various temperature and concentration conditions: ■, 0 mol %;[15] ▽, 20 mol %; ▼, 40 mol %; ○, 60 mol %; ●, 80 mol % of [bmim][BF$_4$]; −−, calculated.

Conclusions

The vapor pressures of [bmim][Br] + water, [bmim][BF$_4$] + water, and [hydemim][BF$_4$] + water systems were measured over wide concentration and temperature ranges. The data set for vapor pressure was fit with an Antoine-type equation, and the results show good agreement between the experimental and calculated values. The suggested pairs will be considered to be potential working fluids or additives to conventional salt + refrigerant systems. These vapor-pressure data will be useful as basic thermodynamic properties for various reactions and liquid−liquid extraction processes. For detailed investigations of

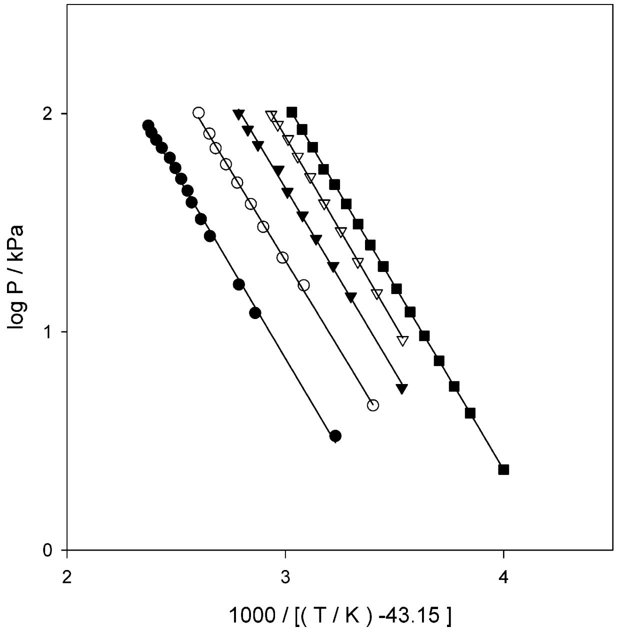

Figure 4. Vapor pressures of the *X*[hydemim][BF$_4$] + water system at various temperature and concentration conditions: ■, 0 mol %;[15] ▽, 20 mol %; ▼, 40 mol %; ○, 60 mol %; ●, 80 mol % of [hydemim][BF$_4$]; −−, calculated.

the suggested IL + water mixtures, more properties such as viscosity, surface tension, and thermal conductivity are required.

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