

Solution Thermodynamics of Imidazolium-Based Ionic Liquids and Water

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This work presents the vapor–liquid equilibrium and the liquid–liquid equilibrium phase behavior and associated thermodynamic properties of water with three ionic liquids: 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([C₈mim][PF₆]), and 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([C₈mim][BF₄]). Although water stable, these compounds are hygroscopic, so the uptake of water vapor is an important issue. Due to the negligible volatility of ionic liquids, we were able to measure vapor–liquid equilibrium using a gravimetric microbalance, which was designed to measure adsorption on solids. The Henry's law constants range from 0.033 to 0.45 bar, with infinite dilution activity coefficients ranging from slight positive deviations from Raoult's law to as high as 8.62. The enthalpies and entropies of absorption are similar to those for the absorption of water into alcohols. In addition, we present water/ionic liquid liquid–liquid equilibria, which is important if water is used as a solvent to extract solutes from ionic liquids. In particular, dissolution of the ionic liquid in the aqueous phase could represent a wastewater treatment challenge. As one possible means for removing ionic liquids from water, we show that activated carbon is effective for this separation.

Introduction

Room-temperature ionic liquids (ILs) are gaining wide recognition as potential environmentally benign solvents, and they have been demonstrated as successful solvents for a variety of reactions.¹ Although the term “ionic liquid” encompasses any solution composed mainly of ions, we will use the term, in the context of this paper, to describe solutions composed entirely of ions and with melting points below room temperature. A major reason for the interest in ILs is their negligible vapor pressure, which decreases the risk of worker exposure and the loss of solvent to the atmosphere.^{2,3} Interest in these compounds has grown since the development of air-stable imidazolium-based ILs.⁴ Although water stable, many ILs are hygroscopic, which has significant practical implications. This is true even for “hydrophobic” ILs—those that are *not* totally miscible with water. In fact, several researchers have reported observations of the uptake of water into various ionic liquids as a function of time.⁵

Qualitative and quantitative liquid–liquid-phase behavior of some ILs with water has been reported. For instance, Dupont and co-workers report that [bmim][BF₄] is miscible with water at room temperature and that [bmim][PF₆] is immiscible based on whether a 50:50 wt % mixture forms one or two phases.⁶ More interestingly, they report that [bmim][BF₄] does phase split at lower temperatures, and they report the composition of both liquid phases at temperatures between –8 and 5 °C. They found that this system showed UCST (upper critical solution temperature) behavior, which is typical of hydrocarbon/water mixtures.⁷ Seddon and co-workers provide some general guidelines on IL/water miscibility.⁵ They indicate that halide, ethanoate, nitrate and trifluoroacetate salts are totally miscible with water, that [PF₆] and [(CF₃SO₂)₂N] salts are immiscible, and that [BF₄] and [CF₃SO₃] salts can be totally miscible or immiscible depending on the substituents on the cation. Moreover, they report the solubility of water in the IL-rich phase

for [C_{*n*}mim][PF₆] and [C_{*n*}mim][BF₄] as a function of chain length between *n* = 4–8 and *n* = 6–10, respectively.

Although two distinct phases can be formed when “hydrophobic” ILs are mixed with water, the mutual solubilities can be quite large. The mutual solubilities are the solubility of the water in the IL-rich phase and the solubility of the IL in the water-rich phase. This partial miscibility can affect properties, as clearly demonstrated for the viscosity,⁵ as well as considerations for potential uses of the ILs. Rogers and co-workers have suggested using water to remove hydrophilic solutes from ILs and have successfully demonstrated this technique for a variety of systems.^{8–10} Fadeev and Meagher showed that [bmim][PF₆] or [C₈mim][PF₆] could be used to extract butanol from an aqueous phase and reported some mutual solubilities for these two systems.¹¹ The cross-contamination of the aqueous and IL-rich phases will be an important issue. The presence of IL in the aqueous stream, in particular, may pose an environmental concern, therefore requiring additional separation steps in the process. Also, as mentioned above, the presence of water in the IL phase can dramatically affect the physical properties.^{5,12,13} Thus, a complete understanding of the phase behavior of ionic liquids with water is very important.

This work presents the vapor–liquid equilibrium and liquid–liquid-phase behavior of water and three ionic liquids: 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([C₈mim][PF₆]), and 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([C₈mim][BF₄]). Data on the selective adsorption of [bmim][PF₆] from aqueous mixtures using activated carbon are also presented.

Experimental Section

Materials. The 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], sample and a 1-octyl-3-methylimidazolium hexafluorophosphate, [C₈mim][PF₆], sample were obtained from Sachem. The [bmim][PF₆] sample had a residual

chloride content of less than 3 ppm and the $[\text{C}_8\text{mim}][\text{PF}_6]$ was approximately 14 ppm chloride. A sample of $[\text{C}_8\text{mim}][\text{PF}_6]$ and 1-octyl-3-methylimidazolium tetrafluoroborate, $[\text{C}_8\text{mim}][\text{BF}_4]$, were obtained from Professor Seddon and co-workers at The Queen's University of Belfast (QUB); the synthesis method is described elsewhere.^{14,15} As received, the two samples from QUB contained significant amounts of chloride. Using a spectrophotometric method,^{16,17} we determined the chloride in the QUB $[\text{C}_8\text{mim}][\text{PF}_6]$ sample to be 1400 ± 100 ppm and 950 ± 100 ppm in the QUB $[\text{C}_8\text{mim}][\text{BF}_4]$ sample. These values were qualitatively confirmed by measurements in Professor Seddon's laboratories. After repeated water washings, the residual chloride in the QUB $[\text{C}_8\text{mim}][\text{BF}_4]$ sample was reduced to less than 300 ppm. All water was deionized using a Milli-Q water filtration system from Millipore. The activated carbon was Norit RO 0.8 pellets from Aldrich.

Vapor-Liquid Equilibrium Apparatus and Measurements. The vapor-liquid equilibrium measurements were made using a gravimetric microbalance (IGA 003, Hiden Analytical). The microbalance consists of a sample pan and counterweight symmetrically configured to minimize buoyancy effects. The balance has a $1 \mu\text{g}$ stable resolution. Approximately 75 mg of ionic liquid sample were added to the sample pan and the chamber was sealed. The sample was dried and degassed by first pulling a coarse vacuum on the sample with a diaphragm pump (MZ 2d, Vacuubrand) and then fully evacuating the chamber to ca. 10^{-9} bar with a turbomolecular pump (TMU 064, Pfeiffer). The sample was heated to about 75°C during this process with an external furnace (SFL TF 1042, Fisher Scientific). As described later, slightly lower temperatures were used on one sample to avoid decomposition. This activation period typically took between 4 and 8 h, during which time the sample mass slowly decreased as residual water and gases were driven off. Once the mass had stabilized for 30 min, the sample was considered pure, and the absorption measurements were initiated.

The furnace was removed and replaced by a water jacket connected to a constant-temperature bath (RTE-111, Neslab). The sample temperature was monitored with a type K platinum thermocouple placed inside the sample chamber and automatically maintained to within 0.1°C of the setpoint. Once the desired temperature of the sample was reached, water vapor was introduced into the sample chamber through a leak valve until a predetermined pressure was reached. Pressures from 0 to 100 mbar were measured using a capacitance manometer (Baratron 626, MKS), and above 100 mbar a strain gauge (PDCR 910, Druck) was used. The pressure was maintained within 0.06% of the setpoint through control of the leak valve and exhaust valve. As the vapor entered the chamber, the sample mass increased as water absorbed into the sample. The weight change was monitored until the mass did not change significantly for 15 min, after which the sample was deemed to have reached equilibrium, thus yielding a single point on the absorption isotherm. This process was repeated through a predetermined set of pressures until the maximum pressure was reached (some fraction of the vapor pressure at the prevailing temperature). Following this, the process was reversed; the water pressure above the sample was gradually reduced in a series of small desorption steps, during which the decrease in sample mass was recorded. Upon completion of this process, a complete absorption/desorption isotherm was obtained. The degree of hysteresis between the two isotherm branches gives an indication of the accuracy of each value. After the completion of an absorption/desorption loop, the sample was dried and degassed

and the mass compared with the initial mass to confirm that the ionic liquid did not volatilize or decompose during the run. Even after performing multiple absorption/desorption experiments over several weeks, none of the samples exhibited a detectable loss in mass.

Two factors are critical in performing these experiments. First, great care must be taken to account for buoyancy effects in the system, even when a symmetric balance is used; we followed a procedure developed in previous work with this microbalance.¹⁸ Second, sufficient time must be allowed for the system to reach equilibrium. The ionic liquid samples used in this study are somewhat viscous, so the diffusion of water into the liquids can be quite slow. This equilibrium time ranged from 1 to 3 h per point, depending on the ionic liquid.

A major advantage of using a microbalance for these measurements is that the weight change can be monitored as a function of time, which allows easy determination of the time necessary for equilibrium to be reached. The assurance of attaining equilibrium is important during the run as well as prior to the run to ensure the sample is sufficiently dried.

Liquid-Liquid Equilibrium Measurements. For the liquid-liquid equilibrium measurements, several mL of both the IL and the water were vigorously mixed in a test tube sealed with Parafilm. For all three of the ILs tested, the phases were allowed to separate for 1 to 2 h after cessation of the stirring in order to ensure clean separation of the phases. Ambient conditions were $22 \pm 1^\circ\text{C}$ and 0.98 ± 0.03 bar. For measurements at temperatures higher than ambient, the sample vials were immersed in a water bath that was controlled to $\pm 1^\circ\text{C}$. Samples from each phase were drawn using a syringe. The IL content in the water-rich phase was analyzed using UV-vis spectroscopy (Cary 3, Varian) which has a sensitivity of ± 0.01 for the absorbance and ± 0.2 nm for the wavelength. The maximum absorbance for each of the ILs, due to the imidazolium ring, is at 211 nm. Calibrations were performed for each of the ILs in water; the resulting values of ϵ_{max} are $4.80 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ for $[\text{bmim}][\text{PF}_6]$, $4.19 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ for $[\text{C}_8\text{mim}][\text{PF}_6]$, and $4.17 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ for $[\text{C}_8\text{mim}][\text{BF}_4]$. The water content of the IL-rich phase was determined using an Karl Fischer titrator (AQUASTAR V-200, EM Science). A sample size of 0.5 g was used for each analysis of $[\text{bmim}][\text{PF}_6]$ and 0.3 g for $[\text{C}_8\text{mim}][\text{PF}_6]$ and $[\text{C}_8\text{mim}][\text{BF}_4]$. We found these sample sizes to be large enough to give reproducible results to about ± 0.2 wt %. Both phases were analyzed after 24 h of stirring and again after 48 h. No noticeable difference in the results confirms that equilibrium was achieved. Multiple measurements were made to ensure reproducibility. Care had to be taken with the samples at elevated temperatures. The aqueous phase samples were diluted with additional water for analysis, so they were not a problem. However, the IL-rich phase samples had to be analyzed (by Karl Fischer titration) immediately upon removal from the equilibration vial. Otherwise, cooling would result in a phase split in the syringe and erroneous results.

Adsorption of IL from Aqueous Solutions. A solution of $[\text{bmim}][\text{PF}_6]$ in water was placed in vials with various amounts of activated carbon (AC) ranging from 0.002 to 0.12 g AC/mL solution. As will be discussed in the results and discussion section, above 0.05 g AC/mL solution, the content of $[\text{bmim}][\text{PF}_6]$ remaining in the equilibrated samples was not detectable. Solutions were mixed by rotating the vials in a water bath at ambient conditions ($22 \pm 1^\circ\text{C}$) for 2 days and also for 2 weeks to ensure that equilibrium was achieved. UV-vis spectroscopy was used to detect the cation content of the aqueous solution. To confirm that the anion was also being removed from the

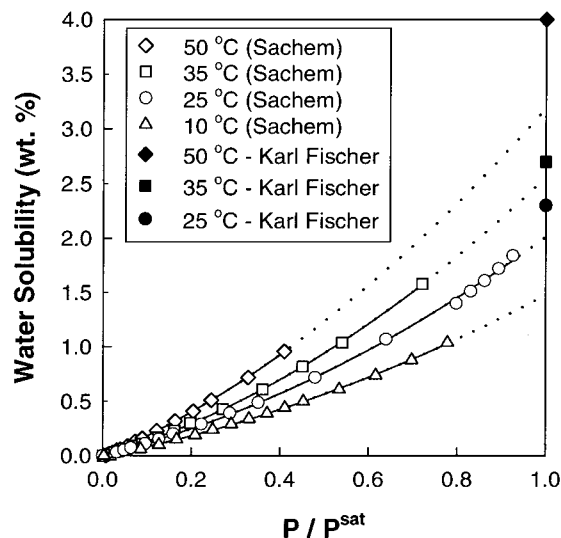


Figure 1. Solubility of Water Vapor in [bmim][PF₆].

solution, a Perkin–Elmer Optima 3300 Axial View Inductively Coupled Plasma Optically Emitting Spectrometer (ICP–OES) was used to detect the phosphorus of the anion remaining in the aqueous solution.

Results and Discussion

Vapor–Liquid Equilibrium Results. The amount of water absorbed by the IL when exposed to various pressures of water vapor was measured for all three ionic liquids (Sachem [bmim][PF₆], QUB [C₈mim][PF₆], and QUB [C₈mim][BF₄]) at three different temperatures: 10 °C, 25 °C, and 35 °C. The low-pressure VLE data for [bmim][PF₆] was also collected at 50 °C. Additional runs were performed at 25 °C with the Sachem [C₈mim][PF₆] and the cleaned QUB [C₈mim][BF₄]. These runs were performed to investigate the effect of chloride contamination on the water vapor solubility. The QUB [C₈mim][PF₆] sample contained approximately 1400 ppm chloride compared to the 14 ppm chloride in the Sachem [C₈mim][PF₆] sample. The cleaned QUB [C₈mim][BF₄] sample contained less than 300 ppm chloride compared to the 950 ppm chloride in the original sample. These results, plotted as the weight percent of water absorbed into the ionic liquids versus the ratio of the pressure of water to the vapor pressure of the water (P/P^{sat}), are shown in Figures 1–3. The Sachem [bmim][PF₆], QUB [C₈mim][PF₆], and original QUB [C₈mim][BF₄] data are shown by the open symbols. The additional runs with the Sachem [C₈mim][PF₆] sample and the cleaned QUB [C₈mim][BF₄] sample are shown as crosses. As can be seen in Figures 2 and 3, chloride impurities at this level do not have any measurable effect on the water vapor solubility. The corresponding values of P^{sat} at each temperature, which are all less than 0.122 bar, are listed in Table 1. The solid lines are meant to guide the eye and the dotted lines indicate the extrapolation of the data out to the vapor pressure of water ($P/P^{\text{sat}} = 1$).

Most of the isotherms were run from 10^{-9} bar to about 80% of the vapor pressure of water to avoid any possibility of condensation of water on the microbalance internals. However, the isotherms for [bmim][PF₆] at 25 °C and [C₈mim][BF₄] at 25 °C and 35 °C were safely extended up to 93% of the vapor pressure.

To ensure that equilibrium was truly achieved, equilibration times of 1 h for [bmim][PF₆] and 3 h for [C₈mim][PF₆] and [C₈mim][BF₄] were allowed for each pressure. These equilibration times were considered sufficient because (1) a significant

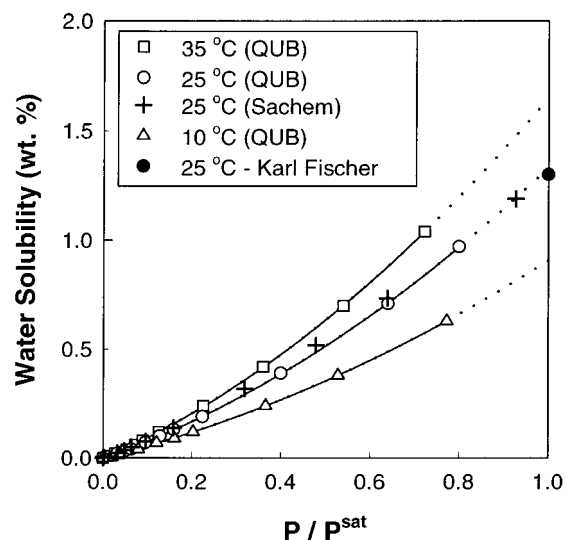


Figure 2. Solubility of Water Vapor in [C₈mim][PF₆].

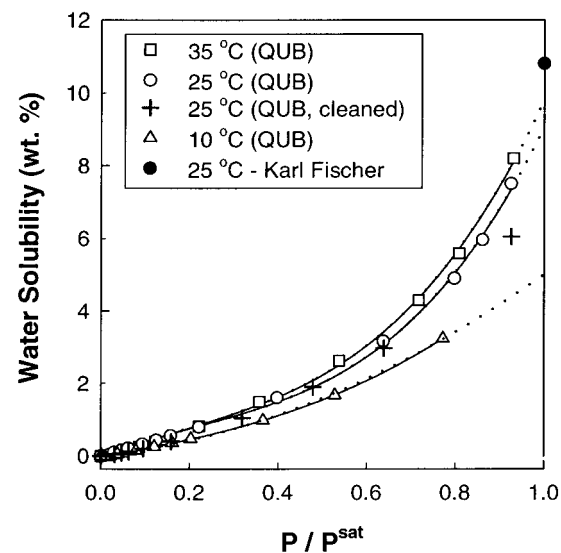


Figure 3. Solubility of Water Vapor in [C₈mim][BF₄].

increase in mass was no longer observed and (2) the hysteresis between the absorption and desorption curves was less than 0.15%. An example of the change in mass as a function of time is shown in Figure 4 for [bmim][PF₆] at 25 °C and a pressure setpoint of 25 mbar. The hysteresis can be seen for a typical isotherm, [bmim][PF₆] at 25 °C, in Figure 5, where the absorption and desorption curves are plotted individually rather than as an average. Because equilibration occurred solely by diffusion, it is not surprising that longer equilibration times would be required for the more viscous samples.¹⁹ Also, several points were collected for [bmim][PF₆] after an equilibration time of 16 h, and these values were consistent with those taken after the shorter equilibration times.

As shown in Figures 1–3, the solubility of water vapor is greatest in [C₈mim][BF₄], which is not surprising because [bmim][BF₄] is totally miscible with water at ambient conditions.⁶ A direct comparison of [C₈mim][PF₆] with [C₈mim][BF₄] (Figures 2 and 3) emphasizes the importance of the anion in determining the amount of water vapor absorbed. The van der Waals volume for the anion [PF₆] has been calculated as 68 Å³, whereas the volume for [BF₄] is only 48 Å³, resulting in a higher charge density for [BF₄] than [PF₆].²⁰ Jureviciute et al. suggested that water is more soluble in systems where the counteranion is tetrafluoroborate rather than hexafluorophos-

TABLE 1: Henry's Law Constants, H_1 , and Infinite Dilution Activity Coefficients, γ^∞ , for Water in [C₈mim][BF₄], [bmim][PF₆], and [C₈mim][PF₆] (the error in γ^∞ Is Consistent with that Given for H_1)

T (°C)	P^{sat} (bar)	[C ₈ mim][BF ₄]		[bmim][PF ₆]		[C ₈ mim][PF ₆]	
		H_1 (bar)	γ^∞	H_1 (bar)	γ^∞	H_1 (bar)	γ^∞
10	0.012	0.033 ± 0.014	2.65	0.09 ± 0.02	6.94	0.11 ± 0.03	8.62
25	0.031	0.055 ± 0.006	1.76	0.17 ± 0.02	5.36	0.20 ± 0.03	6.51
35	0.055	0.118 ± 0.014	2.13	0.25 ± 0.04	4.45	0.30 ± 0.02	5.87
50	0.122			0.45 ± 0.05	3.73		

phate since the [BF₄] is smaller, allowing more room for the water.²¹ Comparing [bmim][PF₆] and [C₈mim][PF₆] in Figures 1 and 2, it is clear that increasing the length of the alkyl chain decreases the solubility of water, as would be expected.

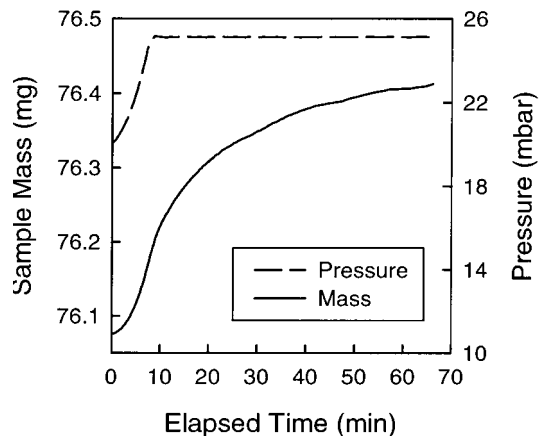
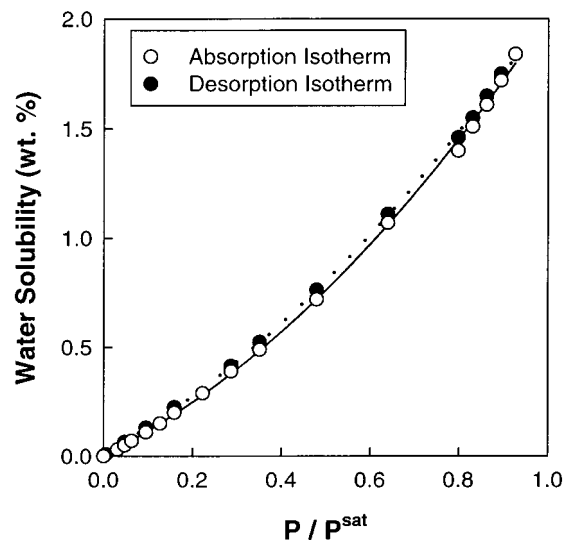
Isotherms for all three compounds exhibit nonlinear increases as the amount of water absorbed in the sample increases at higher pressures. This phenomenon suggests that water is sufficiently soluble in the ILs that water–water interactions are important, as well as water-ion interactions; i.e., the concentrations are well above what could be considered infinite dilution. The IL [C₈mim][BF₄], which has the highest solubility of water, also shows the sharpest increase in the amount of water absorbed as the pressure rises.

It should be emphasized that the values shown in Figures 1–3 are equilibrium solubilities of water vapor in the ILs. The time required to reach these equilibrium values (if, for instance, a vial of IL was left open to wet air) depends on the percent humidity and the mass transfer resistances (i.e., how vigorously the solution was stirred, the velocity of the wet air above the sample, the height of the stagnant air film above the sample, etc.) If these physical conditions were known, along with the diffusivity of water in the IL and the equilibrium solubilities given here, then one could, in principle, calculate the time for water uptake by one of these ILs in any given physical situation. However, the equilibrium solubilities reported here cannot be compared with the values for the amount of water absorbed as a function of time reported by Seddon and co-workers because the relative humidity and physical conditions for mass transfer were not reported.⁵

It should also be noted that the IL samples were dried (and degassed) scrupulously before the introduction of water vapor by heating the IL sample at 75 °C under vacuum at about 8×10^{-9} bar until the mass of the sample remained constant. Constant mass was readily achieved for [C₈mim][BF₄] and [bmim][PF₆]. However, when drying the [C₈mim][PF₆] prior to the run, the mass continued to decrease for over 30 h. When the temperature was lowered to 58 °C, the mass stopped decreasing, suggesting that either the [C₈mim][PF₆] decomposes slightly at 75 °C or that 8×10^{-9} bar is on the order of magnitude of the vapor pressure of the IL itself at 75 °C. We can say with confidence that the vapor pressures of all three of the ILs studied is not significantly greater than 8×10^{-9} bar at 75 °C.

There are several sources of uncertainty in these experiments. The uncertainties in measuring both the pressure and the mass are extremely small, about 0.06% and 0.0013%, respectively. The bulk of the error results from the uncertainty in achieving equilibrium. During absorption, equilibrium is approached from a lower value, whereas equilibrium is approached from a higher value during desorption. Therefore, the two branches provide an upper and lower bound for the uncertainty in the true equilibrium value. As illustrated in Figure 5, this uncertainty is relatively small, less than 0.15%.

Henry's Constants and Infinite-Dilution Activity Coefficients. The Henry's Law constant and activity coefficient are defined in the appendix. Both eqs (A-3) and (A-4) imply that

**Figure 4.** Solubility of Water Vapor in [bmim][PF₆] as a Function of Time at 25 °C and 25 mbar.**Figure 5.** Typical Example of Hysteresis between Absorption and Desorption Isotherms: [bmim][PF₆] at 25 °C.

the solubility is linearly related to the pressure, so they are applicable only for the lowest pressures shown in Figures 1–3. Thus, the low-pressure solubilities of water in ILs can be reported as Henry's constants or infinite-dilution activity coefficients and both of these values are shown for each IL at each temperature in Table 1. These values were found by fitting a polynomial to the data (2nd order for [bmim][PF₆] and [C₈mim][PF₆], 3rd order for [C₈mim][BF₄]) and calculating the limiting slope as the pressure approaches zero. Deviations from the polynomial fits were less than 0.5%. The uncertainties were determined by using the Henry's constant or infinite-dilution activity coefficient calculated for absorption and desorption as the upper and lower bounds.

The Henry's law constants range from 0.033 bar at 10 °C for [C₈mim][BF₄] to 0.45 bar for [bmim][PF₆] at 50 °C, all small values that indicate high solubility of water vapor in the ILs. The infinite dilution activity coefficients are all greater than

TABLE 2: Literature Values for Henry's Law Constants, H_1 , and Infinite Dilution Activity Coefficients, γ^∞ , for Water in Various Organic Solvents

T (°C)	P^{sat} (bar)	Methanol ²³		Ethanol ²³		2-Propanol ²³		Acetone ²³	
		H_1 (bar)	γ^∞	H_1 (bar)	γ^∞	H_1 (bar)	γ^∞	H_1 (bar)	γ^∞
10	0.012								
15	0.017								
25	0.031	0.13	4.19	0.10	3.23	0.10	5.88		
35	0.055	0.09	1.64					0.34	6.18
45	0.096	0.17	1.77			0.34	3.54	0.54	5.63
50	0.122	0.40	3.28						
55	0.157	0.27	1.72			0.53	3.38	0.83	5.29

T (°C)	P^{sat} (bar)	Benzene ²²		Carbon Tetrachloride ²²		Cyclohexane ²²	
		H_1 (bar)	γ^∞	H_1 (bar)	γ^∞	H_1 (bar)	γ^∞
10	0.012	6	500	25	2083	78	6500
15	0.017						
25	0.031	10	323	37	1194	97	3129
35	0.055	13	236	46	836	105	1909
45	0.096						
50	0.122						
55	0.157						

TABLE 3: Enthalpy and Entropy Changes for Water Absorbing in [C₈mim][BF₄], [bmim][PF₆], and [C₈mim][PF₆]

ionic liquid	$-\Delta h_1$ (kJ/mol)	$-\Delta s_1$ (J/mol K)
[C ₈ mim][BF ₄]	34 ± 5	117 ± 18
[bmim][PF ₆]	30 ± 4	104 ± 14
[C ₈ mim][PF ₆]	30 ± 5	102 ± 17

unity, but none are excessively large. For comparison, Table 2 lists H_1 and γ^∞ for water dissolved in several different organic solvents.^{22,23} The H_1 values for water in all three ILs are much smaller than values for water in nonpolar hydrocarbons, indicating a significantly higher solubility of water in the ILs than in nonpolar organics. Likewise, the infinite dilution activity coefficients for water in nonpolar hydrocarbons are extremely large, indicating that water has a high activity in these solutions, much preferring the vapor phase to dissolution in the hydrocarbon. Conversely, the Henry's law constants and infinite dilution activity coefficients of water in various polar organics (alcohols and an aldehyde) are quite similar to the values measured for the three ILs. In fact, the values for the water Henry's constants in the ILs are closest to those in polar solvents such as ethanol and 2-propanol. This similarity is consistent with recent measurements with both absorption and fluorescence spectroscopic probes that indicate these particular ILs have an effective polarity roughly similar to short chain alcohols.^{12,24}

Enthalpy and Entropy of Solution. The Δh_1 and Δs_1 for the three ILs, calculated using eqs (A-9) and (A-10) in the appendix, are listed in Table 3. The uncertainties reported were obtained by comparing the enthalpies and entropies determined for the absorption and desorption branches of the isotherm. Enthalpies and entropies calculated from eqs (A-11) and (A-12) are equivalent for the three different ILs within the range of error. Because the uncertainties in the enthalpies and entropies are greater than the differences in the values between the three different ILs, it is not possible to make any conclusions about the relative strength of interaction of the different ILs with water. Nonetheless, comparison of the enthalpies and entropies for the absorption of water vapor into the three ILs with water absorption into various other liquids is quite instructive.

The Δh_1 and Δs_1 for the absorption of water into various organics solvents are listed in Table 4, along with the enthalpy and entropy of vaporization of water, which is essentially Δh_1 and Δs_1 for water absorbing in water.^{22,23,25} The enthalpies for absorption of water vapor into polar and protic solvents is much

TABLE 4: Literature Values for the Enthalpy and Entropy Changes for Water Absorbing in Various Organic Liquids

liquid	$-\Delta h_1$ (kJ/mol)	$-\Delta s_1$ (J/mol K)
Water ²⁵	44	147
Methanol ²³	40	124
Acetone ²³	38	114
2-Propanol ²³	33	101
Benzene ²²	21.6	92
Toluene ³⁰	18.4	89
Carbon Tetrachloride ²²	18.0	90
Cyclohexane ²²	9.6	70

TABLE 5: Liquid-Liquid Equilibrium Results for Water with [C₈mim][BF₄], [bmim][PF₆], or [C₈mim][PF₆] at Ambient Conditions

ionic liquid	IL in aqueous phase		water in IL phase	
	wt. %	mol fraction	wt. %	mol fraction
[C ₈ mim][PF ₆]	0.7 ± 0.1	3.50 × 10 ⁻⁴	1.3 ± 0.5	0.20
[bmim][PF ₆]	2.0 ± 0.3	1.29 × 10 ⁻³	2.3 ± 0.2	0.26
[C ₈ mim][BF ₄]	1.8 ± 0.5	1.17 × 10 ⁻³	10.8 ± 0.5	0.63

greater than for its absorption into nonpolar solvents, indicating much stronger molecular interactions between water and the polar solvents (including opportunities for hydrogen-bonding). In addition, the entropy decrease upon absorption of water vapor into polar solvents indicates a much greater ordering in the liquid phase than when water dissolves in nonpolar solvents. The enthalpies and entropies of water absorption in the three ILs are most similar to water absorption into polar compounds such as 2-propanol. Once again, this is consistent with solvatochromic studies that suggest the solvent strength of these ILs to be similar to short chain alcohols.^{12,24}

Liquid-Liquid Equilibrium Results. LLE measurements were conducted at ambient conditions (22 ± 1 °C and 0.98 ± 0.03 bar) for all three ILs (Sachem [bmim][PF₆], QUB [C₈mim][PF₆], and QUB [C₈mim][BF₄]) and the results for the compositions of both the IL-rich phases and the water-rich phases are shown in Table 5. The mutual solubilities of water and [C₈mim][PF₆] are lower than those seen for the equivalent IL with a shorter alkyl chain, [bmim][PF₆]. As observed in the vapor-liquid equilibrium measurements, changing the anion from [PF₆] to [BF₄] increases the mutual solubilities substantially, as over 10 wt % water dissolves in [C₈mim][BF₄]. These liquid-liquid equilibrium measurements of the amount of water dissolved in the IL-rich liquid phase are plotted as solid points in Figures 1 through 3. These solubilities are roughly consistent

TABLE 6: Liquid-Liquid Equilibrium Results for Water and Various Organics at Ambient Conditions

organic	org. in aqueous phase		water in org. phase	
	wt. %	mol fraction	wt. %	mol fraction
Benzene	0.176 ³¹	3.9×10^{-4}	0.066 ²²	2.20×10^{-3}
Toluene	0.052 ³²	1.0×10^{-4}	0.045 ³⁰	2.80×10^{-3}
Carbon Tetrachloride	0.08 ³²	9.4×10^{-5}	0.010 ²²	8.60×10^{-4}
Cyclohexane	0.006 ³³	1.3×10^{-5}	0.007 ²²	3.40×10^{-4}
<i>n</i> -Butanol ³⁴	7.38	1.9×10^{-2}	20.3	0.51
Cyclohexanol ³⁴	3.77	7.1×10^{-3}	12.1	0.43
<i>n</i> -Pentanol ³⁴	1.92	3.8×10^{-3}	9.0	0.34
<i>n</i> -Hexanol ³⁴	0.56	1.0×10^{-3}	6.7	0.29
<i>n</i> -Octanol ³⁴	0.051	7.0×10^{-4}	3.5	0.21
<i>n</i> -Decanol ³⁴	3.7×10^{-3}	4.2×10^{-6}	4.0	0.27
<i>n</i> -Dodecanol ³⁴	2.3×10^{-4}	2.3×10^{-7}	1.4	0.13

with what would be predicted by extrapolating the absorption isotherms (dotted lines in Figures 1 through 3) to the point when the pressure of the water above the sample is equal to the water vapor pressure ($P/P^{\text{sat}} = 1$). The LLE measurements were repeated for the low chloride Sachem [C₈mim][PF₆] sample and the cleaned QUB [C₈mim][BF₄] sample. The results were the same as shown in Table 5, within experimental uncertainty. Thus, we conclude that chloride impurities at these levels (<1400 ppm) are not sufficient to affect the LLE with water.

These measurements are also reasonably consistent with measurements by other groups. Fadeev and Meagher reported the mutual solubilities for [bmim][PF₆] and [C₈mim][PF₆] with water, although without any indication of the method of analysis or of the uncertainty in their measurements.¹¹ Their analysis of both phases of the [bmim][PF₆] system and the IL-rich phase of the [C₈mim][PF₆] system match our results within our experimental uncertainty. They reported a solubility of 0.35 wt % [C₈mim][PF₆] in water, which is about half the value we obtained. Seddon and co-workers reported, in graphical form, the solubility of water in the IL, for all three of the ILs studied here.⁵ Their values for [C₈mim][PF₆] and [C₈mim][BF₄] appear to be consistent with our measurements. However, their measurement of the solubility of water in [bmim][PF₆] appears to be slightly lower than ours (about 1.5 wt % instead of 2.3 wt %). Overall, it appears that our measurements of the complete mutual solubilities of all three of these compounds are consistent with the partial data that has appeared elsewhere.^{5,11} On the other hand, the solubilities of water in the ILs reported here are larger than those previously reported by Rogers and co-workers.⁹ Due to the relatively short contact times (on the order of minutes), their solutions may not have reached equilibrium at the time of the measurements. Our experience has shown that several hours of vigorous agitation between the two phases is required for equilibrium to be achieved; even just stirring the phases without breaking the interface between the phases for a period of 24 h was not sufficient for equilibrium to be reached.

For comparison, Table 6 gives LLE data for various organic solvents with water. The mutual solubilities of all three ILs and water are significantly higher than for any of the nonpolar hydrocarbons listed. By contrast, water is totally miscible with acetone, methanol, ethanol, and 2-propanol at room temperature.²⁶ Mutual solubilities of longer chain alcohols with water can be quite high (see Table 6) and are similar to what is observed for the three ILs studied.

Liquid-liquid equilibrium measurements were also taken in our laboratory at temperatures of 35 °C and 50 °C for [bmim][PF₆] and these results are shown in Table 7. They are also plotted as the solid symbols in Figure 1. The liquid-liquid equilibrium values are larger than those predicted by the extrapolation of the VLE data, especially for the higher temperature points. This difference indicates that there is

TABLE 7: Liquid-Liquid Equilibrium Results for Water and [bmim][PF₆] at Various Temperatures

<i>T</i> (°C)	IL in aqueous phase		water in IL phase	
	wt. %	mol fraction	wt. %	mol fraction
25	2.0 ± 0.3	1.29×10^{-3}	2.3 ± 0.2	0.26
35	2.2 ± 0.2	1.40×10^{-3}	2.7 ± 0.3	0.30
50	2.7 ± 1.3	1.74×10^{-3}	4.0 ± 0.3	0.40

significant curvature in the VLE curves that is not fully predicted when the VLE measurements are limited to pressures much below the saturation pressure (i.e., we were only able to obtain VLE data at 50 °C up to about 40% of P^{sat} due to equipment limitations). Although the temperature range is somewhat limited, it is clear that the [bmim][PF₆] – water system exhibits upper critical solution temperature behavior, as was previously reported for [bmim][BF₄] at lower temperatures.⁶ In other words, the mutual solubilities increase as the temperature is increased. This information is important because it indicates that the magnitude of the cross-contamination of water-IL systems will be greater at higher temperatures.

It is clear that the ionic liquids are capable of absorbing significant amounts of water, whether in contact with water vapor or liquid water. Previous articles have illustrated the dramatic effect the presence of water can have on IL physical properties.^{5,12,13} Therefore, it is imperative that the water content of the ILs be considered when investigating physical properties and phase behavior. As practiced by many groups, ionic liquids can be dried under vacuum. After drying under vacuum for 6 days at ambient temperature, we found that the water content of [bmim][PF₆] was reduced to about 0.15 wt %. Heating a water-saturated sample of [bmim][PF₆] to 75 °C under vacuum for 24 h decreased the water content to 0.02 wt %. Longer drying times to achieve lower water contents were not feasible due to the lower detection limits of the titrator used for water analysis.

The substantial solubility of these ionic liquids in the water phase poses additional separation concerns if water were used to extract solutes from the IL phase. These concerns are due to possible impacts ILs may have on aquatic ecosystems and potentially high costs of the ILs compared to other common organic solvents. Ideally, the entire aqueous phase would be recycled, thus eliminating the loss of IL to the environment. If the entire aqueous phase could not be recycled, an additional separation step would be needed to remove the IL from the wastewater stream. One obvious technique for separating ILs from water would be to vaporize the water, but the high energy costs associated with evaporating the water from a dilute aqueous solution makes this method impractical.

Adsorption of IL from Aqueous Solutions Results. One common method for removing organics from water is adsorption onto activated carbon (AC). Table 8 shows that AC does remove [bmim][PF₆] from an aqueous solution. The results from the

TABLE 8: Percent of [bmim][PF₆] Remaining in Water Using Activated Carbon ($\pm 3\%$)

mass of AC/ initial mass of contaminant	[bmim][PF ₆] 2 day eq. time UV-vis	2 day eq. time ICP-OES	2 week eq. time	Toluene ²⁷
0.060				25.4
0.061				28.9
0.076				33.1
0.078				20.9
0.182				18.2
0.294	99			
1.31	82	80		
2.17			88	
3.37	56	46		
4.29			64	
5.31	21	15		
5.75	6			
7.21	2			
9.99			0.15	

ICP-OES are consistent with those from the UV-vis analysis, ensuring that both the cation and the anion are removed from the solution. Also included in the table for comparison are the results from Chatzopoulos et al., who used activated carbon to remove toluene from water.^{27,28} It takes about 50 times less activated carbon to remove toluene from water than to remove [bmim][PF₆]. This result is expected because activated carbon is generally most efficient at removing small, nonpolar compounds such as toluene, rather than polar or ionic species such as ILs. Although this work shows that AC could be used to purify the wastewater stream, it does not allow for the recovery of the IL. Therefore, there would still be a net loss of IL from a process, as well as the concern for the disposal of the AC/IL waste. We are currently investigating alternative separation and regeneration methods. We postulate that a combined anionic and cationic ion-exchange resin would perform better than activated carbon.

Conclusions

The vapor-liquid and liquid-liquid equilibria of [bmim]-[PF₆], [C₈mim][PF₆], and [C₈mim][BF₄] with water indicate that affinity for water is greater for ILs with [BF₄] as the anion than [PF₆], and that water affinity decreases with increasing alkyl chain length. Enthalpy and entropy of absorption measurements show that the strength of the interactions and the ordering experienced when water is absorbed into the ILs is similar to the dissolution of water into short chain alcohols. Also, ionic liquid/water liquid-liquid equilibria exhibit UCST behavior; i.e., the mutual solubilities increase with increasing temperature.

The relatively high solubilities of water in the IL-rich phase and of the IL in the water-rich phase have important implications for the design of processes that use ILs. The presence of water in the IL affects its physical properties, therefore requiring a sound understanding of the properties of the IL/water solution. The contamination of the aqueous phase with the IL may require an additional downstream separation step. As one option, we have shown that activated carbon can be used successfully to remove [bmim][PF₆] from water, but this method is relatively inefficient and does not provide for recovery of the IL. Removal of ILs from water will be especially important when dealing with wastewater streams, as the environmental impact of ILs is still unknown.

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Appendix

The equilibrium condition for water (1) and ionic liquid (2) can be expressed as⁷

$$\phi_1 \cdot y_1 \cdot P = \gamma_1 \cdot x_1 \cdot f_1^o \quad (\text{A-1})$$

Assuming an ideal vapor phase ($\phi_1 = 1$), the IL is nonvolatile ($y_1 = 1$), and taking $f_1^o = P_1^{\text{sat}}$, where P_1^{sat} is the vapor pressure of pure water at temperature T , eq (A-1) may be rewritten as

$$P = \gamma_1 \cdot x_1 \cdot P_1^{\text{sat}} \quad (\text{A-2})$$

The activity coefficient of water in the IL phase, γ_1 , may therefore be determined directly by measuring the mole fraction of water in the IL as a function of the pressure of water above the IL solution.

The Henry's law constant is defined as

$$H_1(T, P) \equiv \lim_{x_1 \rightarrow 0} \frac{f_1^L}{x_1} \quad (\text{A-3})$$

where f_1^L is the fugacity of water in the liquid phase. The Henry's law constant depends on temperature, but is relatively insensitive to pressure, especially over the pressure ranges examined in the present work. Given the assumptions used for eq (A-2), we see that

$$H_1(T) = \lim_{x_1 \rightarrow 0} \gamma_1 \cdot P_1^{\text{sat}} \quad (\text{A-4})$$

or that

$$\gamma_1^\infty = \frac{H_1(T)}{P_1^{\text{sat}}} \quad (\text{A-5})$$

where γ_1^∞ is the infinite-dilution activity coefficient of water in the IL.

The enthalpy and entropy of absorption may be determined from the following thermodynamic relations²⁹

$$\Delta h_1 = \bar{h}_1 - h_1^{\text{ig}} = RT \left(\frac{\partial \ln x_1}{\partial \ln T} \right)_P \left(\frac{\partial \ln a_1}{\partial \ln x_1} \right)_{P,T} \quad (\text{A-6})$$

$$\Delta s_1 = \bar{s}_1 - s_1^{\text{ig}} = R \left(\frac{\partial \ln x_1}{\partial \ln T} \right)_P \left(\frac{\partial \ln a_1}{\partial \ln x_1} \right)_{P,T} \quad (\text{A-7})$$

where \bar{h}_1 and \bar{s}_1 are the partial molar enthalpy and entropy of water in solution, h_1^{ig} and s_1^{ig} are the enthalpy and entropy of pure water in the ideal gas phase, and a_1 is the activity of water in the solution

$$a_1 = \gamma_1 \cdot x_1 \quad (\text{A-8})$$

eqs (A-6) and (A-7) are equivalent to

$$\Delta h_1 = R \left(\frac{\partial \ln P}{\partial (1/T)} \right)_{x_1} \quad (\text{A-9})$$

$$\Delta s_1 = -R \left(\frac{\partial \ln P}{\partial \ln T} \right)_{x_1} \quad (\text{A-10})$$

In the Henry's law regime (i.e., when γ_1 is independent of x_1), the last term in eqs (A-6) and (A-7) is unity. Therefore, those equations can be reduced to their familiar van't Hoff forms⁷

$$\Delta h_1 = -R \left(\frac{\partial \ln x_1}{\partial (1/T)} \right)_P = R \left(\frac{\partial \ln H_1}{\partial (1/T)} \right)_P \quad (\text{A-11})$$

$$\Delta s_1 = R \left(\frac{\partial \ln x_1}{\partial \ln T} \right)_P = -R \left(\frac{\partial \ln H_1}{\partial \ln T} \right)_P \quad (\text{A-12})$$

yielding Δh_1 and Δs_1 , valid at infinite dilution.

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