Liquid Phase Behavior of Ionic Liquids with Water and 1-Octanol and Modeling of 1-Octanol/Water Partition Coefficients

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This study examines the effect of structural components of an ionic liquid (IL), including the choice of the anion, alkyl chain length on the cation, and substitution on the cation, on the mutual solubility with water and with 1-octanol. This is important because ionic liquids have been shown to be good replacements for organic extraction solvents in some liquid separations. In addition, we use the measured data to predict 1-octanol/water partition coefficients for the ionic liquids using the nonrandom two liquid (NRTL) and electrolyte nonrandom two liquid (eNRTL) excess Gibbs energy models. Specifically, the mutual solubilities of 15 different imidazolium, pyridinium, and quaternary ammonium ionic liquids with water were measured at (23.5 ± 1) °C. An increase in the alkyl chain length or the substitution decreases the mutual solubility with water. The $[BF_4]^-$ and $[B(CN)_4]^-$ anions are significantly more hydrophilic than $[PF_6]^-$, $[(CF_3SO_2)_2N]^-$, and $[(CF_3SO_2)_3C]^-$. The mutual solubilities of 10 ILs with 1-octanol were measured at (23.5 ± 1) °C. For these systems, the longer the alkyl chain, the more soluble the IL was in the alcohol, while ring substitution has little effect. From this data, 1-octanol/water partition coefficients of 10 ionic liquids were predicted using the NRTL and eNRTL models.

Introduction

Ionic liquids (ILs) are pure salts that are liquid below 100 °C, usually at room temperature. Generally, they are composed of a large organic cation and an inorganic or organic polyatomic anion. Two properties of ILs give them an advantage over traditional organic solvents: their wide liquidus range and their negligible vapor pressure.[1−3] Fadeev and Meagher have shown that ILs would be apt replacements in separations.[4] Previous research has shown that the anion and, to a lesser degree, the cation influence the thermodynamic and thermophysical properties of the ILs, such as viscosities or melting points.[5,6] This principle extends to the binary liquid−liquid equilibrium behavior of ILs with both water and 1-octanol.[7−18] The goals of this study are (1) to determine the effect of the anion, the alkyl chain length, and the substitution of the cation on the mutual solubility with water and with 1-octanol and (2) to use the measured data to model the 1-octanol/water partition coefficients (K_{ow}). K_{ow} indicates the partitioning of an infinitely dilute solute between equilibrated 1-octanol-rich and water-rich phases at room temperature. It is a measure of a compound's tendency to bioaccumulate in the environment and has even been used as an estimate of a compound's toxicity.[19] Calculating a K_{ow} is really a ternary liquid−liquid-phase equilibrium problem, where one is concerned with the tie-line on the ternary diagram that is dilute in the solute (the IL). Therefore, phase equilibrium calculations for IL/1-octanol/water ternary systems can provide K_{ow} predictions. Techniques for calculating ternary phase behavior involving ILs from the NRTL and eNRTL models using only binary data have been addressed elsewhere.[20,21]

Experimental Section

Materials. 1-Octanol was purchased from Sigma-Aldrich (111-87-5, 99.9+ % purity, HPLC grade, $w_{H_2O} = 5 \cdot 10^{-4}$ by a Karl Fischer coulometer) and used as received. The water was deionized by a Millipore purification system (> 18 MΩ·cm resistivity). The ILs used in this study are listed in Table 1, with the full names, abbreviations, and drawn structures. All the ILs used in this work, except [HOemim][Tf_2N], [bmpy][Tf_2N], [emim][$B(CN)_4$], and [bmim][Tf_3C], were made according to previously described methods.[8,10,11,22] [bmpy][Tf_2N] was purchased from Strem Chemicals; [bmim][Tf_3C] was obtained from Covalent Associates; and [emim] [$B(CN)_4$] was received from Merck KGaA. All three were used as received.

[HOemim][Br] was made by mixing 2-bromoethanol (540-51-2, Aldrich, 95 %) and 1-methylimidazole (616-47-7, Aldrich, 99 %, redistilled over KOH) at 70 °C under nitrogen until the reaction had come to completion. Mixing [HOemim][Br] and [Li][Tf_2N] in water gave [HOemim][Tf_2N].

Standard purification methods were followed for all the ILs made in our laboratory and have been described elsewhere.[6,10,11] The bromide content for all ILs was measured using a Cole-Parmer Bromide Specific probe (27502-05, accurate within $w_{Br^-} = 1 \cdot 10^{-5}$). The bromide contents for all ILs are reported in Table 1. All the ILs used in the 1-octanol/IL study were dried under a vacuum (~1.3 Pa) for 24 h at 70 °C. Water contents were measured by a Karl Fischer coulometer (Metrohm 831 KF coulometer, accurate within $w_{H_2O} = 5 \cdot 10^{-6}$) and are reported in Table 1.

Solubility in Water. As previously described,[7,10] mixtures of IL and water were placed in airtight vials with a stir bar. They were mixed for about 12 h, such that the stir bar breaks the interface and good mixing occurs. The phases in the samples were then allowed to separate for an additional 12 h. The composition of IL in the water-rich phase and the composition of the water in the IL-rich phase were then analyzed. The concentration of imidazolium or pyridinium cations was determined with a UV−visible spectrophotometer (Varian Cary 1). Table 2 shows the absorption wavelengths for the various cations

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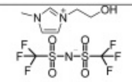
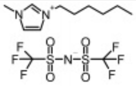
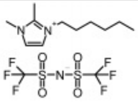
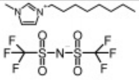
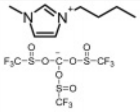
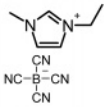
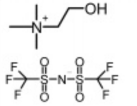
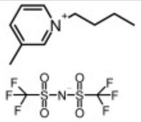
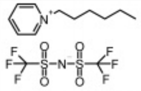
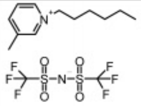
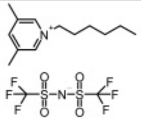
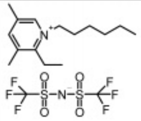
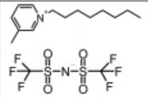
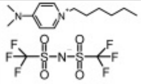
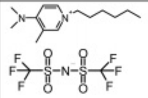
10.1021/je7003935 CCC: $37.00

Table 1. General IL Structure and Impurity Data

Name	Abbreviation	Structure	Bromide Content $10^6 \times w_{Br^-}$	Water Content $10^6 \times w_{H_2O}$
1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[HOemim][Tf$_2$N]		< 10	
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[hmim][Tf$_2$N]		< 15	
1-hexyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide	[hmmim][Tf$_2$N]		< 18	
1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[omim][Tf$_2$N]		< 14	
1-butyl-3-methylimidazolium tris(trifluoromethylsulfonyl)methide	[bmim][Tf$_3$C]		< 18 (Chloride)	
1-ethyl-3-methylimidazolium tetracyanoborate	[emim][B(CN)$_4$]		< 10 (Chloride)	45
2-hydroxyethyl-N,N,N-trimethylammonium bis(trifluoromethylsulfonyl)imide	[choline][Tf$_2$N]		< 20 (Chloride)	30
1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[bmpy][Tf$_2$N]		< 10	15
1-hexylpyridinium bis(trifluoromethylsulfonyl)imide	[hpy][Tf$_2$N]		< 10	120
1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[hmpy][Tf$_2$N]		< 10	30
1-hexyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide	[hmmpy][Tf$_2$N]		< 10	150
1-hexyl-2-ethyl-3,5-dimethylpyridinium bis(trifluoromethylsulfonyl)imide	[hemmpy][Tf$_2$N]		< 10	70
1-octyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide	[ompy][Tf$_2$N]		< 10	20
1-hexyl-4-(dimethylamino)pyridinium bis(trifluoromethylsulfonyl)imide	[hDMApy][Tf$_2$N]		< 10	90
1-hexyl-3-methyl-4-(dimethylamino)pyridinium bis(trifluoromethylsulfonyl)imide	[hmDMApy] [Tf$_2$N]		< 15	15

used in this study. The water content was measured with a Karl Fischer coulometer. For [choline][Tf$_2$N], the concentration of IL in the water-rich phase was measured gravimetrically because the IL does not absorb in the UV−visible range. Three samples were made for each ionic liquid, and for a sample, each phase was analyzed three times.

Table 2. UV Absorbance Wavelength of ILs

ionic liquid	absorbance wavelength (nm ± 1 nm)
[HOemim][Tf_2N]	210
[hmim][Tf_2N]	211
[hmmim][Tf_2N]	211
[omim][Tf_2N]	211
[bmim][Tf_3C]	211
[emim][$B(CN)_4$]	210
[choline][Tf_2N]	no absorbance
[bmpy][Tf_2N]	265
[hpy][Tf_2N]	262
[hmpy][Tf_2N]	266
[hmmpy][Tf_2N]	270
[hemmpy][Tf_2N]	277
[ompy][Tf_2N]	266
[hDMApy][Tf_2N]	289
[hmDMApy][Tf_2N]	299

Table 3. IL/Water Mutual Solubility for Imidazolium-Based ILs at 23.5 ± 1 °C and Atmospheric Pressure

ionic liquid	$100 \cdot w_{IL}$ in H_2O-rich phase	$100 \cdot w_{H_2O}$ in IL-rich phase
[emim][Tf_2N][10]	1.71 ± 0.3	2.02 ± 0.3
[emim][$B(CN)_4$]	4.2 ± 0.2	11.7 ± 0.15
[HOemim][Tf_2N]	9.4 ± 0.3	8.7 ± 0.2
[bmim][Tf_2N][10]	0.73 ± 0.3	1.6 ± 0.3
[bmim][Tf_3C]	0.11 ± 0.01	0.53 ± 0.01
[bmim][PF_6][10]	1.96 ± 0.3	2.30 ± 0.3
[bmim][BF_4][28]	miscible	miscible
[hmim][Tf_2N]	0.23 ± 0.01	1.07 ± 0.01
[omim][Tf_2N]	0.19 ± 0.02	0.91 ± 0.01
[hmmim][Tf_2N]	0.18 ± 0.01	0.80 ± 0.01

Table 4. IL/Water Mutual Solubility for Pyridinium-Based ILs at (23.5 ± 1) °C and Atmospheric Pressure

ionic liquid	$100 \cdot w_{IL}$ in H_2O-rich phase	$100 \cdot w_{H_2O}$ in IL-rich phase
[bmpy][Tf_2N]	0.47 ± 0.01	1.11 ± 0.01
[hpy][Tf_2N]	0.28 ± 0.01	1.10 ± 0.01
[hmpy][Tf_2N]	0.17 ± 0.01	0.88 ± 0.01
[hmmpy][Tf_2N]	0.08 ± 0.01	0.69 ± 0.03
[ompy][Tf_2N]	0.15 ± 0.01	0.74 ± 0.02
[hDMApy][Tf_2N]	0.08 ± 0.01	0.94 ± 0.02
[hemmpy][Tf_2N]	0.16 ± 0.05	0.56 ± 0.04
[hmDMApy][Tf_2N]	0.05 ± 0.01	0.70 ± 0.02

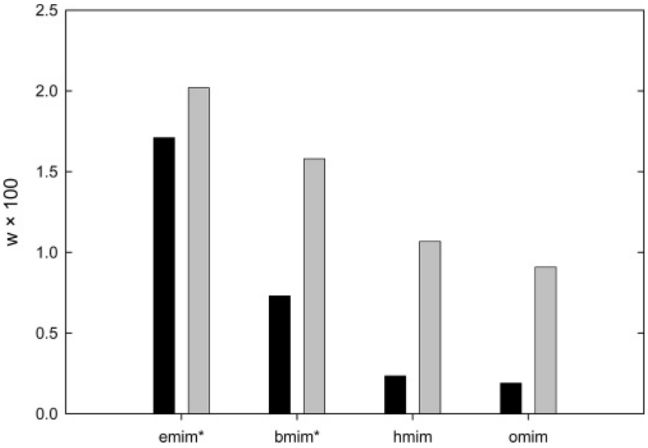


Figure 1. Effect of the alkyl chain length on the mutual solubility with water for [Tf_2N] ILs: black bar, mass fraction of IL in the water-rich phase·100; gray bar, mass fraction of water in the IL-rich phase·100 (*Crosthwaite et al.[10]).

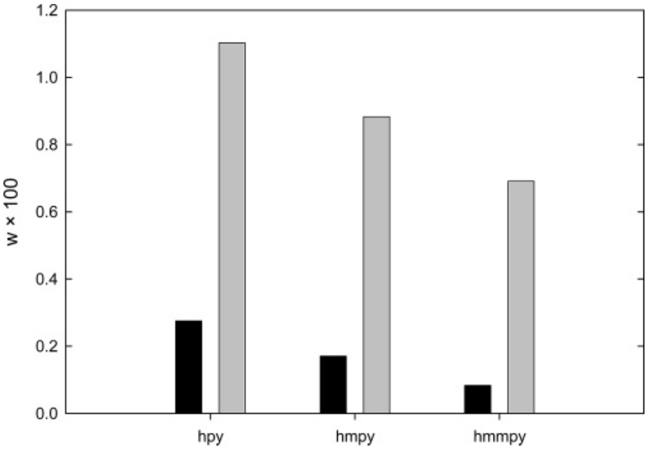


Figure 2. Effect of the substitution on the mutual solubility with water for [Tf_2N] ILs. black bar, mass fraction of IL in the water-rich phase·100, gray bar, mass fraction of water in the IL-rich phase·100.

Solubility in 1-Octanol. Similarly to the IL/water systems, samples of IL and 1-octanol were made and mixed for more than 12 h, and the phases were allowed to separate for 12 additional hours. The compositions of both phases were analyzed. The concentration of imidazolium or pyridinium cations was again determined using UV−visible spectrophotometry. The 1-octanol content was measured with a high-pressure liquid chromatograph equipped with refractive index detection (Perkin-Elmer system: ISS 200 Autosampler, LC 410 Quaternary Pump, series 200a RI detector, series 200 Column Oven, Bio-Rad Aminex HPX-87C column).

Results and Discussion

IL/Water Mutual Solubility. Table 3 shows the mutual solubility of water and imidazolium-based ILs, along with the uncertainty in the measurements. All concentrations are in mass fraction (multiplied by 100 in the table). The data for the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]), and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) were published by Crosthwaite et al.[10] and are used as a comparison. The solubilities of [hmim][Tf_2N] in water ($w = 0.0023$) and of water in [hmim][Tf_2N] ($w = 0.0107$) agree with values published by McFarlane et al. ($w = 0.0028$ IL in water, and $w = 0.011$ water in IL).[15] Table 4 shows the water and the pyridinium-based IL mutual solubilities with uncertainties. The mutual solubility of [choline][Tf_2N], the only quaternary ammonium IL studied, with water is $w = (0.103 \pm 0.006)$ IL in the water-rich phase and $w = (0.092 \pm 0.003)$ water in the IL-rich phase.

Three trends are readily apparent from the data listed in Tables 3 and 4. First, it is evident that as the alkyl chain length increases the ILs become more hydrophobic. This is emphasized in Figure 1, which shows the effect of increasing the length of the alkyl chain on the cation on the mutual solubility values. Both the IL solubility in the water-rich phase and the water solubility in the IL-rich phase decrease with an increase in the alkyl chain from ethyl to octyl. Increasing the size of the hydrophobic part of the cation decreases the IL's polarity[23] and, therefore, its ability to interact with water.

The addition of more alkyl groups to the cation ring also makes the ILs more hydrophobic, as shown in Figure 2 for [hpy][Tf_2N], [hmpy][Tf_2N], and [hmmpy][Tf_2N]. Replacing one or more hydrogens, which have been shown to be acidic,[24] with more stable and hydrophobic alkyl groups reduces the ability of ILs to hydrogen bond with hydrogen bond acceptors like water, in addition to making them more generally more hydrophobic.

Table 5 compares the mutual solubility of ILs and water for [emim]$^+$ and [bmim]$^+$ ILs with various anions keeping the

Table 5. Effect of the Anion on the Water Solubility at (23.5 ± 1) °C and Atmospheric Pressure

ionic liquid	$100 \cdot w_{IL}$ in H_2O-rich phase	$100 \cdot w_{H_2O}$ in IL-rich phase
[emim][Tf_2N][10]	1.71 ± 0.3	2.02 ± 0.3
[emim][$B(CN)_4$]	4.2 ± 0.2	11.7 ± 0.15
[bmim][Tf_2N][10]	0.73 ± 0.3	1.6 ± 0.3
[bmim][Tf_3C]	0.11 ± 0.01	0.53 ± 0.01
[bmim][PF_6][10]	1.96 ± 0.3	2.30 ± 0.3
[bmim][BF_4][28]	miscible	miscible

Table 6. IL/1-Octanol Mutual Solubility at (23.5 ± 1) °C and Atmospheric Pressure

ionic liquid	$100 \cdot w_{IL}$ in 1-octanol-rich phase	$100 \cdot w_{1-\mathrm{octanol}}$ in IL-rich phase
[emim][$B(CN)_4$]	0.98 ± 0.05	6.0 ± 0.5
[bmpy][Tf_2N]	0.74 ± 0.05	6.5 ± 1
[hpy][Tf_2N]	1.7 ± 0.1	10.6 ± 0.5
[hmpy][Tf_2N]	1.88 ± 0.1	10.0 ± 0.5
[hmmpy][Tf_2N]	1.5 ± 0.2	11.5 ± 2
[hemmpy][Tf_2N]	1.1 ± 0.1	10.5 ± 0.5
[ompy][Tf_2N]	5.0 ± 0.1	21.1 ± 0.5
[hDMApy][Tf_2N]	1.90 ± 0.05	13.5 ± 0.5
[hmDMApy][Tf_2N]	1.37 ± 0.05	12.0 ± 1
[choline][Tf_2N]	5.5 ± 1	0.80 ± 0.5

cation constant. $[BF_4]^-$ is very hydrophilic; [bmim][BF_4] and water are completely miscible at room temperature. The ILs with other anions form two-phase systems with water at room temperature. $[B(CN)_4]^-$ and $[PF_6]^-$ ILs are significantly less hydrophobic than $[Tf_2N]^-$ ILs. The solubility of [emim][$B(CN)_4$] in water is nearly three times greater than [emim][Tf_2N]. Likewise, the solubility of [bmim][PF_6] in the water-rich phase is roughly three times greater than [bmim][Tf_2N]. The most hydrophobic anion listed is $[Tf_3C]^-$.

From Tables 3 and 4, it is shown that adding a hydroxyl group to the end of the alkyl chain increases the mutual solubility with water, while adding an amino group strongly decreases the mutual solubility with water.

IL/1-Octanol Mutual Solubility. Table 6 shows the mutual solubility of 1-octanol and eight different pyridinium ILs, as well as one imidazolium and one quaternary ammonium IL. The trends in solubility of IL in the 1-octanol-rich phase and of 1-octanol in the IL-rich phase observed here for pyridinium ILs are consistent with previously published data.[10−12] An increase in the alkyl chain length on the cation leads to a measurable increase in the solubility of both the IL in the 1-octanol and the 1-octanol in the IL. For instance, the IL solubility in 1-octanol increases from 0.74 % to 5 % by replacing a butyl chain in [bmpy][Tf_2N] with an octyl chain in [ompy][Tf_2N]. This trend is different than that observed for mutual solubilities with water and can be attributed to van der Waals interactions between the alkyl chain on the alcohol and the alkyl chain on the cation.

Substituting methyl groups for hydrogen atoms on the pyridinium ring does not have a significant effect on the mutual solubilities with 1-octanol. For instance, [hpy][Tf_2N], [hmpy][Tf_2N], and [hmmpy][Tf_2N] all have similar mutual solubilities with 1-octanol. The increased van der Waals interactions must balance any loss in weak hydrogen bonding. Adding a dimethylamino group to the ring increases the 1-octanol solubility in the IL, while not affecting the IL solubility in 1-octanol. In this case, a polar group is added to the ring, increasing dipolar interactions between the cation and the alcohol.

Changing the cation to a quaternary ammonium increases the IL solubility in 1-octanol, while having no effect on the 1-octanol solubility in the IL. With the quaternary ammonium salt, the charge is more localized than in the imidazolium or pyridinium ILs.

Table 7. eNRTL Solvent/Cosolvent Properties for 1-Octanol and Water

compound	ρ ($g \cdot cm^{-3}$)	ϵ	ref
1-octanol	0.82	10.0	Smyth & Stoops[29]
water	1.00	78.30	Robinson & Stokes[30]

Error Analysis. Error analysis of all the data was accomplished with a simple propagation of error (± 0.01 in absorbance, ± 0.0001 in mass, and ± 1 μg of water by Karl Fischer) and a least-square regression of the UV−visible absorption calibrations. The propagated error was compared to the standard deviation of the composition measurements, and the larger of the two is reported here as they were practically equal.

Modeling of K_{ow}. Previous work has shown that the NRTL and eNRTL models are adequate for predicting K_{ow} values for ILs.[21] The density and dielectric constants of the two solvents (water and 1-octanol) are needed for these calculations and are shown in Table 7. The binary interaction parameters needed for the NRTL and eNRTL models were obtained from fits of the binary IL/1-octanol and IL/water data presented here. The necessary 1-octanol/water data[25] are readily available. The parameter estimation techniques have been described elsewhere.[21] The binary parameters for the NRTL and eNRTL models can be found in Table 8 and Table 9, respectively.

The K_{ow} is defined as

$$K_{ow} = \frac{C_{IL}^{oct}}{C_{IL}^{water}} = \frac{8.37x_{IL}^{oct}}{55.5x_{IL}^{water}} \qquad (1)$$

where C_{IL}^{oct} is the concentration of IL in the 1-octanol-rich phase; C_{IL}^{water} is the concentration of IL in the aqueous phase; x_{IL}^{oct} is the mole fraction of IL in the 1-octanol-rich phase, and x_{IL}^{water} is the mole fraction of IL in the aqueous phase. K_{ow} values predicted by both models (binary parameters were fitted only to binary data) for a variety of ILs are presented in Table 10. Previously published work has shown that the eNRTL model, especially, can give good estimates of the partitioning of ILs between 1-octanol and water.[21] It is more accurate than the NRTL model, which is more sensitive to alkyl chain length on the cation. It should be noted that a value of $\rho = 25$ for the "closest approach" parameter was used for the eNRTL model for all the calculations necessary for determination of K_{ow} values. ρ is a parameter related to the closest approach of ionic centers.

Use of the original value of $\rho = 14.9$ did not result in any parameter solutions for some of the binary parameter estimation problems, as explained elsewhere.[20,21] The original value of $\rho = 14.9$ was estimated by regressing data for small inorganic electrolytes,[26,27] which it can be argued have smaller distances of closest approach than ILs. Thus, it is reasonable to speculate that larger organic electrolytes should have a larger value of ρ. The larger value of $\rho = 25$ was chosen arbitrarily by Simoni et al.[21]

From our calculations, it appears that an increase in the alkyl chain length on the cation or substitution of hydrogen atoms with methyl groups on the cation ring increases the K_{ow}. Because an increase in the alkyl chain length decreases the solubility of the IL in the water-rich phase while increasing the solubility of the IL in the alcohol-rich phase, this is the expected trend. In addition, substitution of methyl groups on the cation ring decreases the solubility of the IL in the water-rich phase, while not affecting the solubility in the alcohol-rich phase, which leads

Table 8. NRTL Binary Interaction Parameters[a] for K_{ow}'s

	NRTL; α = 0.2					
ionic liquid	Δg_{12} / $J \cdot mol^{-1}$	Δg_{21} / $J \cdot mol^{-1}$	Δg_{13} / $J \cdot mol^{-1}$	Δg_{31} / $J \cdot mol^{-1}$	Δg_{23} / $J \cdot mol^{-1}$	Δg_{32} / $J \cdot mol^{-1}$
[emim][B(CN)$_4$]	2090.0	11062.	−4582.5	18173.	861.86	22421
[bmpy][Tf$_2$N]	363.56	14532.	456.22	20211.	861.86	22421
[hpy][Tf$_2$N]	−847.05	13788.	582.77	21491.	861.86	22421
[hmpy][Tf$_2$N]	−794.66	13634.	1187.55	22323.	861.86	22421
[hmmpy][Tf$_2$N]	−1242.3	14423.	1929.6	23689.	861.86	22421
[hemmpy][Tf$_2$N]	−1181.6	15280.	1995.8	22145.	861.86	22421
[ompy][Tf$_2$N]	−2740.1	13400.	1514.5	22588.	861.86	22421
[hDMApy][Tf$_2$N]	−1723.1	14462.	1231.2	24277.	861.86	22421
[hmDMApy][Tf$_2$N]	−1512.5	15070.	1978.1	24862.	861.86	22421
[choline][Tf$_2$N]	5748.5	6594.8	−5408.5	18316.	861.86	22421

[a] System for K_{ow} calculations: IL (1)/1-octanol (2)/water (3).

Table 9. eNRTL Binary Interaction Parameters[a] for K_{ow}'s

	eNRTL; α = 0.2; ρ = 25					
ionic liquid	Δg_{12} / $J \cdot mol^{-1}$	Δg_{21} / $J \cdot mol^{-1}$	Δg_{13} / $J \cdot mol^{-1}$	Δg_{31} / $J \cdot mol^{-1}$	Δg_{23} / $J \cdot mol^{-1}$	Δg_{32} / $J \cdot mol^{-1}$
[bmpy][Tf$_2$N]	11510	−2554.6	−2649.0	20411	861.86	22421
[hpy][Tf$_2$N]	−2424.1	4542.1	−2480.1	21482	861.86	22421
[hmpy][Tf$_2$N]	−2524.7	4682.7	−1930.3	21963	861.86	22421
[hmmpy][Tf$_2$N]	−2029.3	4006.5	−1204.0	22870	861.86	22421
[hemmpy][Tf$_2$N]	−6066.6	11576	−1224.6	21436	861.86	22421
[ompy][Tf$_2$N]	−6944.8	13267	−1632.5	22057	861.86	22421
[hDMApy][Tf$_2$N]	−6379.2	12090	−1791.4	23713	861.86	22421
[hmDMApy][Tf$_2$N]	−6268.3	11950	−1098.2	23925	861.86	22421

[a] System for K_{ow} calculations: IL (1)/1-octanol (2)/water (3).

Table 10. K_{ow}'s

	K_{ow}'s from		
ionic liquid	NRTL[a]	eNRTL[a]	literature
[emim][B(CN)$_4$]	0.169		
[bmpy][Tf$_2$N]	1.62	1.40	
[hpy][Tf$_2$N]	5.88	2.90	
[hmpy][Tf$_2$N]	11.8	4.71	
[hmmpy][Tf$_2$N]	23.8	9.21	
[hemmpy][Tf$_2$N]	7.89	5.09	
[ompy][Tf$_2$N]	23.8	7.22	
[hDMApy][Tf$_2$N]	23.8	11.3	
[hmDMApy][Tf$_2$N]	23.8	15.2	
[choline][Tf$_2$N]	0.268		
acetone[31]			0.575
methanol[31]			0.17
n-hexane[32]			10000

[a] Mole fraction of ionic liquid in the overall system: $z_1 = 0.0001$.

to a further increase in the K_{ow}. This is all captured adequately by both models. Adding a dimethylamino group to the pyridinium ring increases the K_{ow}, which is due to the increase in the IL solubility in the alcohol-rich phase, while decreasing the solubility of the IL in the water-rich phase. Having a quaternary ammonium cation decreases the K_{ow}. Because replacing the cation with a quaternary ammonium increases both the IL solubility in the water-rich phase and the IL solubility in the 1-octanol-rich phase, this indicates that the ammonium salt affects the miscibility with water more than with the alcohol. Because both NRTL and eNRTL are good models for the binary phase behavior, they predict all the anticipated trends in K_{ow}. For [emim][B(CN)$_4$] and [choline][Tf$_2$N], no binary parameter solution exists at $\rho = 25$, so no predictions are provided for K_{ow} with the eNRTL for those two compounds. We are not aware of any experimental data with which to compare these predictions but include them here to show the utility of the binary data when combined with an appropriate thermodynamic model.

Conclusions

Developing an understanding of how changes to the cation and anion affect the phase behavior of ILs with other liquids is important for the development of models and for predicting phase equilibria. In this work, we determined the effect of the chain length and the substitution on the cationic ring and the effect of various hydrophobic anions on the mutual solubility of the ILs with water and with 1-octanol. We found that an increase in the alkyl chain length or in the substitution on the ring decreases the mutual solubility of the IL with water. Of the anions tested, ILs with the $[BF_4]^-$ anion had the largest mutual solubility with water, followed by those with the $[B(CN)_4]^-$, $[PF_6]^-$, and $[Tf_2N]^-$ anions. The IL with the $[Tf_3C]^-$ anion had the smallest mutual solubility with water. For the mutual solubility of ILs with 1-octanol, we found that the trends observed for imidazolium ILs[11,12] also applied to pyridinium ILs. By increasing the alkyl chain length on the cation, the mutual solubilities increased, while replacement of the hydrogen at the C2 position of the ring with a methyl group resulted in a decrease in the mutual solubilities. Using the binary phase equilibrium data obtained in this study, we predicted the K_{ow} of 10 ILs using the NRTL and eNRTL excess Gibbs free energy models. The K_{ow} for the ILs in this study were in the same range or slightly higher than acetone or methanol and much lower than hexane. Increasing the alkyl chain length or adding methyl substitution on the cation increases the K_{ow}. Adding a dimethylamino group to the ring increases the K_{ow}. Having a quaternary ammonium cation decreases the K_{ow}.

Acknowledgment

We thank Merck KGaA for the sample of [emim][B(CN)$_4$] and are grateful to Reilly Industries (now Vertellus Specialties Inc.) for providing the pyridine starting materials used in synthesizing the pyridinium ILs used in this work.

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Received for review July 10, 2007. Accepted August 27, 2007. We acknowledge financial support for the project from the National Oceanic and Atmospheric Administration (NOAA) and the State of Indiana 21st Century Research and Technology Fund (909010455).

JE7003935