

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/50849099>

Hydrogen-Bonding Interactions and Protic Equilibria in Room-Temperature Ionic Liquids Containing Crown Ethers

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · MARCH 2011

Impact Factor: 3.3 · DOI: 10.1021/jp201193f · Source: PubMed

CITATIONS

12

READS

25

3 AUTHORS:



Timothy W Marin

Benedictine University

54 PUBLICATIONS **810** CITATIONS

SEE PROFILE



Ilya Shkrob

Argonne National Laboratory

143 PUBLICATIONS **2,163** CITATIONS

SEE PROFILE



Mark L Dietz

University of Wisconsin - Milwaukee

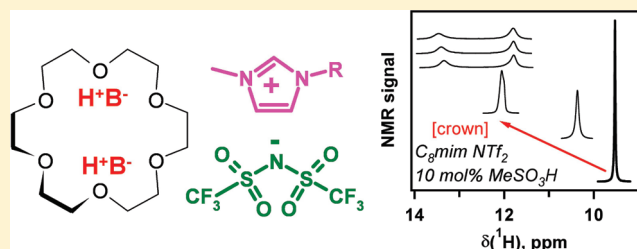
150 PUBLICATIONS **4,424** CITATIONS

SEE PROFILE

Hydrogen-Bonding Interactions and Protic Equilibria in Room-Temperature Ionic Liquids Containing Crown Ethers

Timothy W. Marin,^{†,‡} Ilya A. Shkrob,^{*,†} and Mark L. Dietz^{†,§}[†]Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave, Argonne, Illinois 60439, United States[‡]Chemistry Department, Benedictine University, 5700 College Road, Lisle, Illinois 60532, United States[§]Department of Chemistry and Biochemistry, University of Wisconsin – Milwaukee, Milwaukee, Wisconsin 53211, United States

ABSTRACT: Nuclear magnetic resonance (NMR) spectroscopy has been used to study hydrogen-bonding interactions between water, associated and dissociated acids (i.e., nitric and methanesulfonic acids), and the constituent ions of several water-immiscible room-temperature ionic liquids (ILs). In chloroform solutions also containing a crown ether (CE), water molecules strongly associate with the IL ions, and there is rapid proton exchange between these bound water molecules and hydronium associated with the CE. In neat ILs, the acids form clusters differing in their degree of association and ionization, and their interactions with the CEs are weak. The CE can either promote proton exchange between different clusters in IL solution when their association is weak or inhibit such exchange when the association is strong. Even strongly hydrophobic ILs are shown to readily extract nitric acid from aqueous solution, typically via the formation of a 1:1:1 {H₃O⁺•CE}NO₃[−] complex. In contrast, the extraction of methanesulfonic acid is less extensive and proceeds mainly by IL cation–hydronium ion exchange. The relationship of these protic equilibria to the practical application of hydrophobic ILs (e.g., in spent nuclear fuel reprocessing) is discussed.

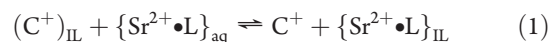


1. INTRODUCTION

Room temperature ionic liquids (ILs) are solvents consisting of irregularly shaped organic cations in combination with any of a variety of anions.^{1–7} Hydrophobic ILs^{1–4} have been suggested as replacements for molecular organic diluents in a number of chemical separations, including the wet processing of spent nuclear fuel via liquid–liquid extraction.^{2–12} Applications such as these involve contact of the ILs with aqueous solutions, many of which are oxidizing and highly acidic (e.g., 1–5 M nitric acid). These high concentrations of aqueous acid are required not only to prevent hydrolysis of the metal ions present, but also to shift the extraction equilibria. That is, because the transfer of a metal ion to an IL phase without the concurrent loss of the constituent ions to the aqueous phase requires the formation of a neutral complex, high anion concentrations, by promoting neutral complex formation, drive the equilibrium toward greater extraction into the IL phase.^{2–4}

As we have noted previously,^{2,9} the partitioning of a metal ion into an IL in the presence of a neutral extractant can be a complicated process, the details of which remain incompletely understood. Among the many unresolved issues are the details of the interactions among the constituent ions, water molecules, acids, and neutral complexing agents (e.g., crown ethers (CEs) and organophosphorus reagents).^{2–12} As a first step toward addressing this deficiency, we have examined several representative ILs containing either of two typical CEs, the latter of which has been extensively applied in studies of the viability of ILs as extraction solvents: 18-crown-6 (18C6) and dicyclohexano-18-crown-6 (DCH18C6).

Both of these compounds readily form 1:1 complexes with hydronium (H₃O⁺), alkali (Alk⁺), and alkaline earth (e.g., Sr²⁺) cations.^{2,9–11} (Note that dicyclohexano groups increase the hydrophobicity of the CE and its solubility in ILs.) DCH18C6 dissolved in various 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (bistriflimide) ILs (C_nmim NTf₂, with the carbon number *n* = 2–10, Scheme 1) has been examined for use in ⁹⁰Sr extraction from nitric acid solutions. For short-chain 1-alkyl-3-methyl-imidazolium cations (*n* ≤ 5), the extraction (typically involving 0.01–0.1 M ionophore, L) has been found to proceed via an ion-exchange reaction (reaction 1)^{2,10,11} in which the constituent cation of the IL (C⁺) enters the aqueous phase, while the {Sr²⁺•L} complex enters the IL phase:^{2,9}

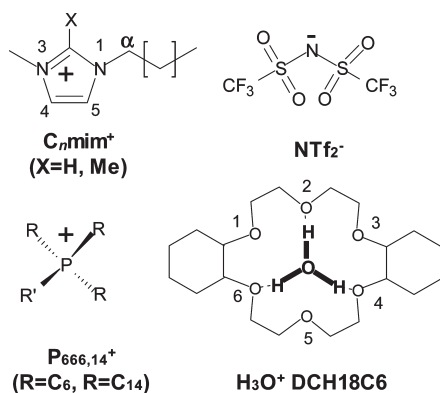


Certain recent evidence suggests that at sufficiently high aqueous acidities, this process can be partially or completely supplanted by a second type of ion-exchange process in which the extracted metal ion is exchanged for a hydronium ion present as part of a hydronium ion-CE complex.⁹ For more hydrophobic (i.e., long-chain) IL cations, however, extraction of the neutral {Sr²⁺•L} (NO₃)₂ complex (reaction 2) prevails at high concentrations of

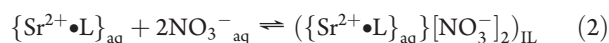
Received: February 4, 2011

Revised: February 23, 2011

Published: March 24, 2011

Scheme 1. The Structure of the Constituent Ions and the $\{H_3O^+ \bullet DCH18C6\}$ Complex

HNO_3 (1–3 M):



While the occurrence of these reactions is presently well-established and their practical ramifications recognized, significant gaps remain in our fundamental understanding of these systems. For example, recent studies^{7,12} indicate that ~ 10 mol % nitric acid can be extracted from 3 M aqueous HNO_3 into C_n mim PF_6 (1:1 v/v), suggesting that the IL diluent is considerably modified in the presence of significant acid concentrations. Little is known, however, concerning the relevant protic equilibria or the state of water in hydrophobic ILs.^{13,14} Similarly, relatively little is known about the effects of the presence of neutral extractants (e.g., ionophores such as CEs) on such equilibria. That such issues warrant investigation is demonstrated by a recent study^{15,16} in which C_n mim⁺ cations were found to form 2:1 complexes with CEs (reaction 3), in which the H(2), methyl, and H_α protons (Scheme 1) form H-bonds with the opposing oxygens in the CE ring (e.g., O(2) and O(5), Scheme 1).



Clearly such binding could interfere with host–guest interactions involving the CE and metal ions. In this study, we attempt to assess the nature and strength of interactions among the various components present in a water/acid-laden IL containing a CE, and consider the implications of the results for the utility of representative imidazolium and phosphonium ILs (e.g., trihexyltetradecylphosphonium bistriflimide, abbreviated as $P_{666,14}$ NTf₂) as extraction solvents.

2. EXPERIMENTAL SECTION

The crystalline compound $\{H_3O^+ \bullet 18C6\}TfO^-$ was synthesized as described previously (Tf = CF_3SO_2).¹⁷ The ILs 1-octyl-3-methylimidazolium bistriflimide and its 1-decyl- analogue (hereafter abbreviated as C_8 mim NTf₂ and C_{10} mim NTf₂, respectively; Scheme 1) were synthesized as described in ref 9. All other chemicals were obtained from Aldrich in their purest form and used as received. $P_{666,14}$ NTf₂ (Scheme 1) was obtained from Cytec and used without further purification. Due to their inherently high water content, in certain cases, some ILs were dried in a vacuum oven at 90° for 24 h before use. The mole fraction of residual water was determined using ¹H nuclear

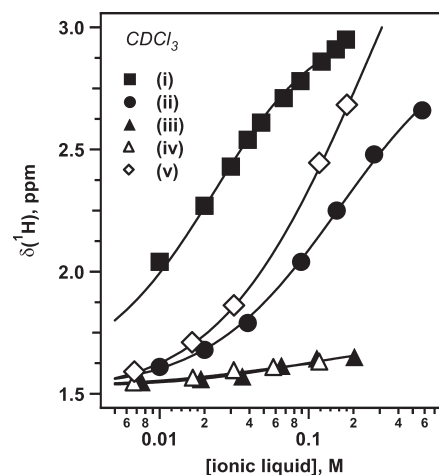


Figure 1. Chemical shift of the NMR signal from water protons in $CDCl_3$ in the presence of (i) C_4 mim $MeSO_3$, (ii) C_4 mim TfO, (iii) C_4 mim NTf₂, (iv) 2-Me- C_3 mim NTf₂, and (v) $P_{666,14}$ NTf₂ (see the caption). The solid lines drawn through the signals are the least-squares fits to the equilibrium reaction 4 with the fit parameters given in Table 1. These ILs contained the following mole fraction of water: (i) 39, (ii) 12, (iii) 9.2, (iv) 9.4, and (v) 7.7 mol %.

Table 1. IL–Water Binding in $CDCl_3$ (Reaction 4)

cation	anion	$\delta(^1H)$ free, ppm	$\delta(^1H)$ bound, ppm	K_w , M ^{−1}
C_4 mim	$MeSO_3$	1.55 ± 0.02	3.05 ± 0.03	108 ± 12
C_4 mim	TfO	1.51 ± 0.01	3.00 ± 0.04	6.8 ± 0.5
C_4 mim	NTf ₂	1.53 ± 0.01	1.71 ± 0.03	12 ± 5
2Me C_3 mim	NTf ₂	1.53 ± 0.01	1.67 ± 0.02	26 ± 11
$P_{666,14}$	NTf ₂	1.49 ± 0.01	4.67 ± 0.14	4.6 ± 0.4

magnetic resonance (NMR) spectroscopy. The proton chemical shifts reported hereafter are given versus a tetramethylsilane standard. Further ¹⁴N and ¹⁹F NMR spectroscopy was conducted (section 3.3) to determine concentrations of species containing these constituent atoms, as these ions distribute between the IL and aqueous phases. Traces of d_6 -benzene (1–5 wt %) in the IL solutions were used to lock the NMR frequency. CD_3NO_3 was used as an internal standard for ¹⁴N nuclei in the IL; for ¹⁹F nuclei, trifluoroacetic acid (TFA) was used as the internal standard in the aqueous phase; for ¹H nuclei, methanol was used. The NMR spectra were obtained using an Avance III 500 MHz spectrometer (Bruker BioSpin, 11.7 T). (For a general discussion of the NMR spectroscopy of ILs, see ref 18. An example of applying ¹H NMR to the study of “proton” species in a thermomorphic, task-specific IL composed of carboxylated cations has been given in ref 19.)

3. RESULTS

3.1. IL–Water Interaction in d_3 -Chloroform. All of the ILs were found to dissolve readily in $CDCl_3$. The presence of water in them (even in those that have been dried) can be discerned from the resonance line of the water protons observed at ~ 1.5 ppm, which progressively increases in $\delta(^1H)$ as more IL is added. Integration of the line allows the estimation of the concentration of water in the ILs (C^+A^-).



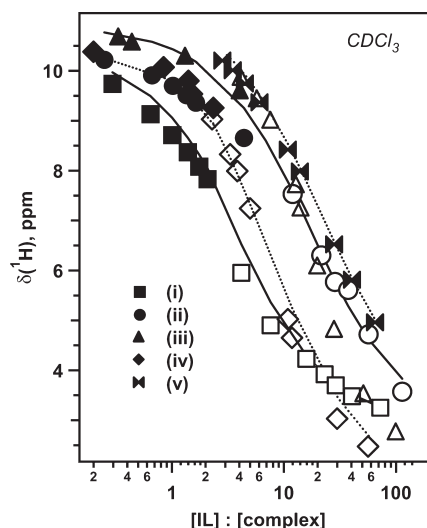


Figure 2. The effect of the addition of $\{\text{H}_3\text{O}^+ \cdot 18\text{C6}\}\text{TfO}^-$ on the “proton” shift (the same numbering as in Figure 1). The filled symbols correspond to (i) 0.12 M, (ii) 0.1 M, (iii) 0.12 M, (iv) 0.054 M, and (v) 0.184 M of the 18C6 complex. The open symbols correspond to (i) 1.3 M, (ii) 0.18 M, (iii) 0.2 M, and (iv) 0.12 M of the IL. The solid lines are the best fit to a model in which the hydronium ion in the complex is in rapid exchange with the free and IL-bound water molecules in the CDCl_3 solution.

As the concentration of the IL is increased, the chemical shift of the water proton changes as shown in Figure 1, suggesting binding between the constituent ions and the water molecules. Assuming that equilibrium (reaction 4) is rapidly established, the plot can be readily fit, yielding the chemical shifts of the free and bound water molecules and the equilibrium constant K_w (Table 1). The latter correlates with the hydrophobicity: water-soluble $\text{C}_4\text{mim TfO}$ exhibits the largest binding constant, whereas hydrophobic $\text{P}_{666,14} \text{NTf}_2$ interacts very weakly. More interesting is the large difference between $\text{C}_4\text{mim CF}_3\text{SO}_3$ and $\text{C}_4\text{mim CH}_3\text{SO}_3$: the fluorination in the anion decreases the K_w value by an order of magnitude. This suggests that water mainly binds to the anion; the same is suggested by the increase in K_w when the cation is methylated at carbon-2 (Scheme 1). Such methylation is expected to decrease H-bonding to water molecules.²⁰ However, it also decreases H-bonding between the IL ions, resulting in *stronger* interactions of the anion with the bound water molecule. This effect is also suggested by the fact that bistriflimide ILs exhibit smaller changes in chemical shift of bound water protons as compared to the ILs involving CH_3SO_3^- and CF_3SO_3^- anions. The increase in this chemical shift for the $\text{P}_{666,14}^+$ cation may be due to solvent screening exerted by the cation.

Because TfOH is poorly soluble in chloroform, it was introduced into d_3 -chloroform solutions as the $\{\text{H}_3\text{O}^+ \cdot 18\text{C6}\}\text{TfO}^-$ complex. In a CDCl_3 solution of this crystalline compound, the hydronium exhibits a chemical shift $\delta(^1\text{H})$ of ~ 11 ppm. As the molar ratio of the IL (relative to the complex) increases, $\delta(^1\text{H})$ decreases, eventually reaching values close to those observed for IL-bound water (Figure 2). The same behavior is witnessed for other ILs that we studied. The simplest way to account for these observations is to assume that (either free or CE-bound) hydronium ions are in rapid H-exchange equilibrium with (either free or IL-bound) water molecules.

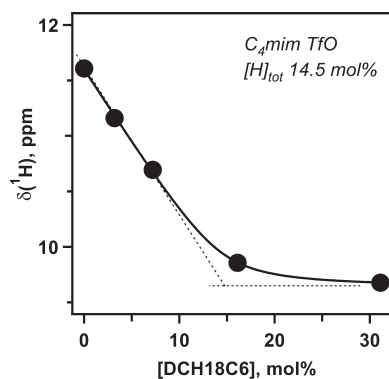
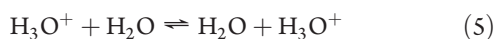
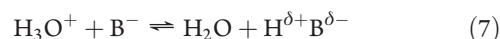


Figure 3. Concentration dependence of the chemical shift $\delta(^1\text{H})$ for the protic impurity in $\text{C}_4\text{mim TfO}$ (ca. 14.5 mol %) as a function of the mole fraction of DCH18C6. The solid line is the best fit to the two-site model discussed in the text. The dashed lines are guides to the eye.

One can envision reactions in which the IL cation(s) bind(s) to the CE, replacing the hydronium via reaction 3 coupled to proton equilibria reactions (B^- is TfO^- anion in the complex or the constituent anion of the IL):



after which the released water molecule undergoes binding reaction 4. While our simulations do not exclude such reactions, it appears that the main effect of IL addition is in the introduction of trace amounts of water: as more IL-bound water is introduced into the solution, this water exchanges protons with H_3O^+ via rapid reactions 5, 6, and 7, and the chemical shift of the “protons” begins to decrease (Figure 2). If there are additional effects from reaction 3, these were too small to recognize.

3.2. Acids in Neat ILs. The $\text{C}_4\text{mim TfO}$ solvent obtained from Aldrich contained an unidentified protic impurity ($\text{H}^{\delta+}\text{B}^{\delta-}$, most likely, TfOH) that was equivalent to 14.5 mol % (the molarity of this IL is 4.5 M). A single resonance line of this species is observed at ~ 11.6 ppm. As the concentration of DCH18C increases to 1.4 M, the observed $\delta(^1\text{H})$ first decreases linearly with the CE concentration and then approaches a value of 9.63 ppm (Figure 3). This behavior is consistent with the formation of the $\text{L} \cdot (\text{H}^{\delta+}\text{B}^{\delta-})_n$ or $\{\text{H}_3\text{O}^+ \cdot \text{L}\}\text{B}^-$ complexes in the IL solution, and we fitted these using the simplest model in which free and CE-bound “protons” undergo rapid site exchange. The resulting equilibrium constant, $24.5 \pm 7 \text{ M}^{-1}$, is several orders of magnitude lower than the constant for $\{\text{H}_3\text{O}^+ \cdot \text{L}\}\text{B}^-$ formation in polar molecular solvents such as chloroform (where this constant is $\sim 10^6 \text{ M}^{-1}$).²¹ This result suggests that either (i) the CE binds $\text{H}^{\delta+}\text{B}^{\delta-}$ in an associated form, resulting in weak proton–CE interactions,^{22–24} or (ii) cation–CE binding reaction 3¹⁵ inhibits the complexation of the H_3O^+ or $\text{H}^{\delta+}\text{B}^{\delta-}$ by the CE. Either possibility is surprising in view of the expected strong complexation of protic species with CEs in ILs, as the latter generally promote ion solvation and hence ionization. Nevertheless, further experiments supported these conclusions.

To achieve greater control over the solution conditions, the polar, water-miscible IL $\text{C}_4\text{mim TfO}$ was replaced with the hydrophobic IL $\text{C}_8\text{mim NTf}_2$ (neat molarity of 2.73 M), which contained only 2.4 mol % water (yields a single resonance line at 2.37 ppm). As the addition of neat TfOH and HNTf₂ to the ILs

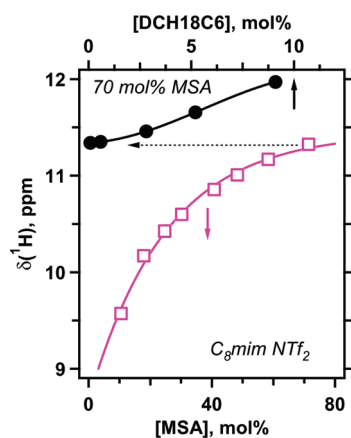


Figure 4. To the bottom: the chemical shift of the “proton” (open squares) as a function of the mole fraction of MSA in $C_8\text{mim NTf}_2$. To the top: the chemical shift of the “proton” (filled circles) as a function of the mole fraction of DCH18C6 for $C_8\text{mim NTf}_2$ containing 70 mol % MSA. The residual concentration of water in this IL was 2.4 mol %.

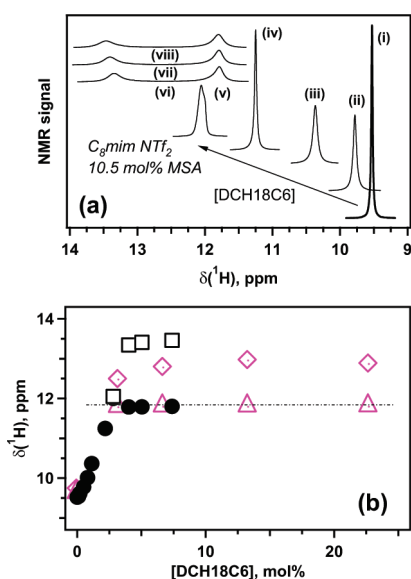


Figure 5. (a) The fragment of the ^1H NMR spectrum from $C_8\text{mim NTf}_2$ containing 10.5 mol % MSA and (i) 0, (ii) 0.5, (iii) 1.1, (iv) 2.2, (v) 2.8, (vi) 4, (vii) 5, and (viii) 7.4 mol % DCH18C6. (b) The chemical shifts of the “protons” corresponding to the NMR peaks shown in panel (a) for 10.5 mol % MSA (filled circles and open squares) and 14 mol % MSA (open diamonds and triangles).

led to their gradual decomposition, we chose less reactive methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$, MSA) as the solute. As shown in Figure 4, addition of MSA gradually increases the $\delta(^1\text{H})$ of the (single) resonance line of the “proton” to ~ 11.4 ppm for 75 mol % MSA. As even for 10 mol % MSA, the mole ratio of MSA to (residual) water is 4:1, and the evolution of the apparent chemical shift can only reflect clustering and partial dissociation of the $\text{H}^{\delta+}\text{B}^{\delta-}$ acid molecules in the hydrophobic IL, suggesting extensive speciation and rapid proton-exchange equilibria, such as the following:

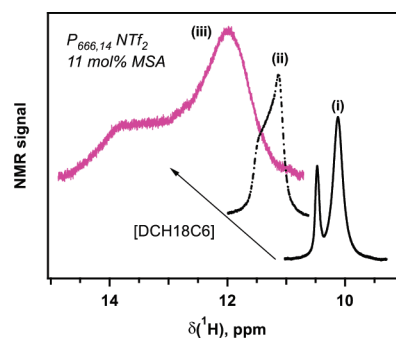
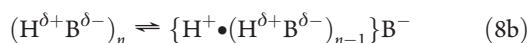
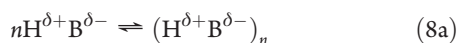


Figure 6. Same as Figure 5a for $P_{666,14} \text{NTf}_2$ containing 11 mol % MSA and (i) 0, (ii) 2, and (iii) 5 mol % DCH18C6. The NMR signals were normalized for the ease of comparison.

When 10 mol % DCH18C6 is added to 70 mol % MSA, $\delta(^1\text{H})$ increases from 11.34 to 11.97 ppm, suggesting additional CE-MSA interactions (Figure 4). The binding constant of the complex formation must be low, as this change occurs in the molar range; however, in this system only a fraction of the CEs can be bound to the MSA (which is in a large molar excess). Therefore, we repeated the same experiment for the IL containing 10.5 mol % MSA (Figure 5a). In the presence of 3 mol % DCH18C6, the single resonance line of the “proton” splits into two lines, with one of the peaks remaining at 11.86 ppm while $\delta(^1\text{H})$ for the other peak gradually increases to 12.86 ppm (Figures 5a and 5b), approaching the same values observed in the solution containing 70 mol % MSA (where this speciation is not apparent, due to the rapid exchange (see Figure 4). This experiment suggests that the MSA can be bound by the CE in (at least) two distinct ways, and the exchange of the protons between these two bound species is slow on the NMR time scale. On the basis of the observed chemical shifts, we tentatively assign these H-bound species to the $\{\text{L} \cdot (\text{H}^{\delta+}\text{B}^{\delta-})\}$ and $\{\text{L} \cdot (\text{H}^{\delta+}\text{B}^{\delta-})_2\}$ complexes.

Similar behavior was observed in hydrophobic IL $P_{666,14} \text{NTf}_2$ (Figure 6), in which the clusters of MSA can be observed even without the CE. For $P_{666,14} \text{NTf}_2$ containing 11 mol % MSA (Figure 6, trace (i)), there are two “proton” peaks at 10.93 and 10.47 ppm that collapse to a single peak at 11.05 ppm when the mole fraction of MSA increases to 45 mol % (not shown). When 2 mol % DCH18C6 is added to a solution containing 11 mol % DCH18C6, there is accelerated H-exchange between the two “proton” sites (as both of the resonances shift by ~ 1 ppm; see Figure 6, trace (ii)). When more DCH18C is added (Figure 6, trace (iii)) the resonance lines undergo further shift and broadening. We conclude that the CE catalyzes H-exchange between (at least) two forms of the MSA that are present in this hydrophobic ILs. Our results hint to the complexity of acid-IL interactions in hydrophobic ILs and extensive “proton” speciation in such liquids.

3.3. ILs in Contact with Aqueous Acids. The distribution of ions and molecules between the ILs and aqueous phase was studied using ^{19}F , ^{14}N , and ^1H NMR spectroscopy. 1:1 v/v solutions of hydrophobic ILs with or without 0.1 M DCH18C6 were vortexed for 5 min with 3 M DNO_3 or 3 M MSA in D_2O (or 3:1 $\text{H}_2\text{O}:\text{D}_2\text{O}$ mixtures). The IL and aqueous phases were then separated by centrifugation. Previous research^{2,9–12} has suggested that in the presence of a neutral extractant, short-chain C_nmim^+ cations ($n = 2–5$) readily exchange with hydronium^{11,12} and metal ions^{2,9,10} present in aqueous solutions, so we chose long-chain IL cations ($n = 8,10$) for which cation exchange was inhibited.

Table 2. Composition of Both Phases for 1:1 v/v Equilibration of $C_n\text{mim NTf}_2$ Containing 0.1 M DCH18C6 with 3 M Methanesulfonic Acid in 99 at% D_2O (All Concentrations Are in mM)

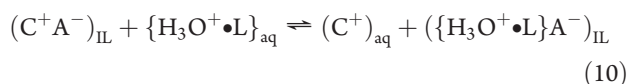
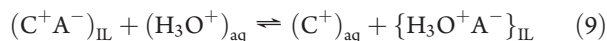
	$C_n\text{mim}^+ \text{NTf}_2^-$	IL		IL + 0.1 M DCH18C6	
		N	8	10	10
IL phase	$[\text{MeSO}_3^-]$	~0	~0	6.5	24.2
	$[\text{H}]_{\text{total}}$	52	55	73	100
	$\delta(^1\text{H})$, ppm	2.44 ^a	2.39	5.54	5.23
aq. phase ^b	$[C_n\text{mim}^+]$	3.3	1.6	17.3	22.2
	$[\text{NTf}_2^-]$	2.5	0.8	0.6	1.4

^a Water impurity in $C_8\text{mim NTf}_2$ has $\delta(^1\text{H}) \approx 2.37$ ppm (2.4 mol %).^b $[\text{CE}]_{\text{aq}} \sim 0.33$ mM.**Table 3.** Composition of Both Phases for 1:1 v/v Equilibration of $C_n\text{mim NTf}_2$ and $P_{666,14} \text{NTf}_2$ with 3 M DNO_3 in 99 at% D_2O and 1:3 v/v $\text{H}_2\text{O}:D_2O$ (All Concentrations Are in mM)^a

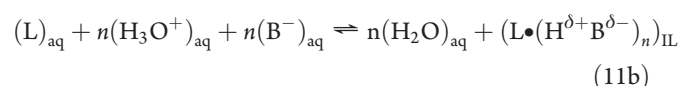
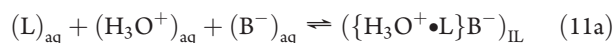
	$C^+ \text{NTf}_2^-$	IL			IL + 0.1 M DCH18C6		
		$C_8\text{mim}$	$C_{10}\text{mim}$	$P_{666,14}$	$C_8\text{mim}$	$C_{10}\text{mim}$	$P_{666,14}$
IL phase	$[\text{NO}_3^-]$	230	156	45	345 (285) ^b	373 (289)	150
	$[\text{H}]_{\text{total}}$	33		24	46 (442)	58 (495)	23
	$\delta(^1\text{H})$, ppm ^c	5.19 ^c	^d	6.41	6.57 (6.459)	6.74 (6.311)	9.30
aq. phase	$[\text{C}^+]$	1.8	0.6		12.2 (14.8)	2.8 (2.5)	1.7
	$[\text{NTf}_2^-]$	19	13	13.5	4.1 (7)	8.2 (3.2)	1.7

^a $[\text{CE}]_{\text{aq}} \sim 2\text{--}3$ mM. ^b In parentheses: for aqueous solution containing 3:1 $D_2O:H_2O$. ^c Chemical shift for water/hydronium proton. For 0.8 M DCH18C6, $\delta(^1\text{H})$ is 9.624 ppm. ^d Not observed.

Tables 2 and 3 summarize the concentrations of the species found in each phase. Hydronium can be extracted via cation-exchange reactions



or neutral extraction of the acid,



For 3 M MSA, the loss of the IL to the aqueous phase is 1–3 mM. The concentration of the CH_3SO_3^- anion in the IL is negligible, and $\delta(^1\text{H})$ for the extrinsic “protons” is close to that observed for traces of water in these ILs (~ 2.4 ppm), suggesting that most of these “protons” are present in the form of extracted water

molecules. When 0.1 M DCH18C6 is added to the ILs, the loss of NTf_2^- is still negligible, but ~ 20 mM of the $C_n\text{mim}^+$ cations are lost to the aqueous phase, whereas 6.5 mM (for $n = 8$) or 24.2 mM (for $n = 10$) CH_3SO_3^- enters the aqueous phase. This charge balance suggests that cation-exchange reaction 9 generally prevails over neutral extraction reaction 10; in both cases the concentration of the extracted acid is quite low.

An entirely different situation was observed for the extraction of nitric acid. The loss of NTf_2^- remained low, as in the MSA system, and the degree of cation exchange was comparable to that for MSA, while the extent of neutral extraction (reactions 11a) of the nitric acid increased more than 10-fold. The results shown in Table 3 suggest that 1.1–1.3 molecules of HNO_3 were extracted per molecule of CE. Note that 1:1:1 complex formation would have prevailed had the extraction occurred via reaction 11a. By dilution of D_2O with H_2O (3:1), the total concentration $[\text{H}]_{\text{tot}}$ of the “protons” in $C_{10}\text{mim NTf}_2$ is $4 \times 0.495 \text{ M} \approx 2 \text{ M}$ (Table 3). In the simplest two-site rapid-exchange model (with mole fractions f_1 and $f_2 = 1 - f_1$ for the two species), the two “proton” species are (CE-bound) H_3O^+ ($\delta_1 \approx 11$ ppm, see Section 3.2) and water ($\delta_2 \approx 2.74$ ppm), and the observed chemical shift $\delta(^1\text{H})$ is given by

$$\delta(^1\text{H}) = (3f_1\delta_1 + 2f_2\delta_2)/(3f_1 + 2f_2) \quad (12)$$

Solving this equation for $\delta(^1\text{H}) \approx 6.31$ ppm gives 1:1.8 mol/mol (water–hydronium–water) speciation, $[\text{H}_2\text{O}] \approx 0.47 \text{ M}$, and $[\text{NO}_3^-] = [\text{H}_3\text{O}^+] \approx 0.263 \text{ M}$ versus the observed $[\text{NO}_3^-] = 0.289 \text{ M}$. Since this good correspondence would not occur had the extraction proceeded via reaction 11b (as the mole fraction of the “proton” would be lower), we conclude that neutral extraction of the protons occurs via reaction 11a. In the absence of the CE, $\delta(^1\text{H}) \approx 5.19$ ppm and the speciation is 1:3.1 mol/mol, with $[\text{H}_2\text{O}] \approx 0.48 \text{ M}$. It is seen that the amount of the extracted water (~ 15 mol %) does not change significantly upon the addition of DCH18C6, the nitric acid was all dissociated (with or without the CE), and most of the extra nitric acid extracted in the presence of the CE was extracted as the 1:1:1 complex.

For comparison with these imidazolium ILs, we also examined a phosphonium IL, $P_{666,14} \text{NTf}_2$ (Table 3). While the loss of the constituent ions was low, the extraction of nitric acid was quite substantial, although it was 2.5 times less than for $C_{10}\text{mim NTf}_2$. The chemical shift of the extracted “protons” is significantly greater in $P_{666,14} \text{NTf}_2$ as compared to $C_{10}\text{mim NTf}_2$ (9.3 vs 6.3 ppm), suggesting that this more hydrophobic IL extracts ~ 2 times less water relative to H_3O^+ than the imidazolium ILs.

4. DISCUSSION

While it is frequently assumed that CE-assisted extraction of strong acids ($\text{H}^{\delta+}\text{B}^{\delta-}$) into molecular liquids involves fully dissociated $\{\text{H}_3\text{O}^+\cdot\text{L}\}\text{B}^{-21,25}$ or incompletely dissociated 1:1:1 $\text{L}\cdot(\text{H}_2\text{O}\cdots\text{H}^{\delta+}\text{B}^{\delta-})$ acid–water–CE formation,^{21–25} 2:2:1 acid–water–CE complexes, $\text{L}\cdot(\text{H}_2\text{O}\cdots\text{H}^{\delta+}\text{B}^{\delta-})_2$, involving incompletely dissociated acids (such as nitric acid) have been reported previously.^{21–24} Hydronium complexes have been observed for ClO_4^- , PF_6^- , I^- , Br_3^- , TfO^- , SbF_6^- , and PtCl_6^{2-} ,²⁵ while the 1:1:1 acid–water–CE complexes have been observed for carboxylates (formic, acetic, and cyanoacetic acids) and some other organic anions.²¹ The X-ray crystallographic structure of the 2:2:1 HBF_4 –water–CE complexes for 18C6 was given by Atwood et al.,²³ and Raman spectra of such 2:2:1 complexes for dichloropicric acid, HNO_3 , H_3PO_4 and

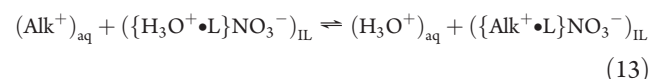
H₂TiF₆ were examined by Chenevert et al.²⁴ Crystalline forms of such complexes can be obtained by crystallization from ethers containing a minimal amount of water, and incomplete dissociation of acids in such solids is strongly suggested by vibrational spectroscopy.²⁴ In these HNO₃ complexes, two water molecules are each bound to O(1) and O(3) oxygens of the CE, and these water molecules are also bound to the oxygens of the nitrate anions by ionic H-bonds.²² The extraction of the 1:1 and 2:1 HNO₃:DCH18C6 complexes by 1-octanol from aqueous solutions of nitric acid was observed by Dietz et al.,²² who found that 0.5 M DCH18C6 can extract ~0.8 M of HNO₃ from 6 M nitric acid solutions. Similar suggestions have also been made by other researchers (see ref 22 for a review).

It has been tacitly assumed that strong acids in hydrophobic ILs would be extracted by CEs as hydronium complexes.^{2,11,12} Our results indicate significant extraction of a neutral species of both water and nitric acid and suggest that the 1:1:1 complex is indeed the prevalent form in the IL. Nevertheless, as the stoichiometry is inexact, some 2:2:1 complexation may also occur as a minor reaction. Cation exchange reactions 9 and 10 are the prevalent modes for extraction of MSA (with or without the CE, respectively), while extraction of a neutral species prevails for HNO₃ (with or without the CE).

Without (or with little) water present in the IL (Section 3.2), the situation is more complex, as the acids are not fully ionized, and, apparently, the molecules are clustered. This is suggested by the unexpectedly low protonation constant for DCH18C6 in C₄mim TfO (implicating the L•(H^{δ+}B^{δ-})_n complex formation) and by multiple resonance lines (and slow site exchange) of the “protons”. The CEs can serve either as catalysts of the “proton” site exchange (in some ILs) or inhibitors of this exchange through stronger binding to the (H^{δ+}B^{δ-})_n clusters (in other ILs). As these CE–acid interactions appear to be weak, the constituent cations (that also form H-bonds with the bridging oxygens in the CEs) compete with these acid clusters, and so the CE–acid interactions are extremely sensitive to the IL structure.

5. CONCLUSIONS

The practical import of our study is recognition of the extent of water and nitric acid extraction by hydrophobic ILs contacting strong nitric acid solutions that are typical of those encountered in spent nuclear fuel reprocessing.^{2–12} This extraction proceeds via extraction of a neutral species, and the degree of the extraction is similar to that observed in molecular solvents of intermediate polarity, such as 1-octanol.²² Our study suggests that the CEs are completely protonated in C_nmim NTf₂ solutions equilibrated with aqueous phases containing high (e.g., 3 M) nitric acid concentrations and that the extraction of metal ions (for example, Alk⁺), in addition to reactions analogous to reactions 1 and 2, can involve metal ion–hydronium exchange (reaction 13), a process proposed previously⁹ on the basis of the nitric acid dependency of sodium ion extraction into C₁₀mim NTf₂:



Such equilibria may partly account for the complicated nitric acid concentration dependences of the distribution coefficients for extraction of mono- and divalent cations observed in such extractions systems.^{2,9,10}

Another direct consequence of the significant extraction of HNO₃ is the difficulty that such extraction presents for electro-deposition of extracted metal ions for the one-pot extraction/electroreduction strategies.^{7,8} Most of the metal ion extraction reactions based on *neutral complex extraction* (which is, typically, much more selective than the cation exchange) involve high acidity to shift the extraction equilibria toward neutral complex formation. For hydrophobic ILs, this high acidity also counteracts solvent loss via cation exchange.^{2,9} Unfortunately, under such conditions the solvent becomes saturated with nitric acid (even in the absence of the ionophores), and this extracted HNO₃ makes the electrolytic deposition of the metals (and/or electro-reduction in general) problematic. It appears that the one-pot concepts might require denitrification of the IL solvent, for which no method currently exists.

Yet another implication of our results concerns the radiation stability of the ILs contacting aqueous solutions containing decaying radionuclides.^{5,6,26–31} The hydronium readily scavenges the electrons generated by ionizing radiation arising from the extracted radionuclide ions, yielding reactive H• atoms that readily abstract hydrogen from the aliphatic arms of the cations and add to the π-rings of aromatic cations or react with HNO₃ to yield NO₂• + H₂O,^{28,29,32} and the NO₃• can trap both the electrons and electron deficiencies (“holes”),^{27,29,30} forming the reactive NO₃^{2•} and NO₃• radicals.^{29,32} The formation of such radicals may significantly increase the extent of radiation damage to the IL solvents^{26–29} and ionophores^{27,30} during nuclear separations.

ACKNOWLEDGMENT

We thank C. Hussey, J. F. Wishart, S. Dai, and H. Luo, and for stimulating discussions and J. Muntean and A. Tisch for technical assistance. The work at Argonne was supported by the US-DOE Office of Science, Division of Chemical Sciences, Geosciences, and Biosciences under Contract No. DE-AC02-06CH11357. Programmatic support via the DOE SISGR “An Integrated Basic Research Program for Advanced Nuclear Energy Separations Systems Based on Ionic Liquids” is gratefully acknowledged.

REFERENCES

- (1) Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, 37, 123–150. Ha, S. H.; Menchavez, R. N.; Koo, Y.-M. *Korean J. Chem. Eng.* **2010**, 27, 1360–1365.
- (2) Dietz, M. L.; Dzielawa, J. A.; Jensen, M. P.; Beitz, J. V.; Borkowski, M. In *Ionic Liquids IIIb: Fundamentals, Progress, Challenges and Opportunities: Transformations and Processes*; American Chemical Society: Washington, DC, 2005; Vol. 902, pp 2–18.
- (3) Nash, K. L. In *Separations for the Nuclear Fuel Cycle in the 21st Century*; Lumetta, G. J., Nash, K. L., Clark, S. B., Friese, J. L., Eds.; American Chemical Society: Washington, DC, 2006; Vol. 933, pp 21–40. Visser, A. E.; Swatoski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. *Ind. Eng. Chem. Res.* **2000**, 39, 3596–3604. Chun, S.; Dzyuba, S. V.; Bartsch, R. A. *Anal. Chem.* **2001**, 73, 3737–3741. Nishi, N.; Murakami, H.; Imakura, S.; Kakiuchi, T. *Anal. Chem.* **2006**, 78, 5805–5812. Vendilo, A. G.; Ronkkomaki, H.; Hannu-Kuure, M.; Lajunen, M.; Asikkala, Y.; Petrov, A. A.; Krasovsky, V. G.; Chernikova, E. A.; Oksman, P.; Lajunen, L. H. J.; Popov, K. I. *Russ. J. Coord. Chem.* **2008**, 34, 635–640. Vendilo, A. G.; Ronkkomaki, H.; Hannu-Kuure, M.; Lajunen, M.; Asikkala, J.; Krasovsky, V. G.; Chernikova, E. A.; Oksman, P.; Lajunen, L. H. J.; Tuomi, T.; Popov, K. I. *J. Incl. Phenom. Macrocycl. Chem.* **2010**, 66, 223–230.

- (4) Stepinski, D. C.; Young, B. A.; Jensen, M. P.; Rickert, P. G.; Dzielawa, J. A.; Dilger, A. A.; Rausch, D. J.; Dietz, M. L. In *Separations for the Nuclear Fuel Cycle in the 21st Century*; Lumetta, G., Nash, K. L., Clark, S. B., Friese, J. I., Eds.; American Chemical Society: Washington, D.C., 2006; pp 233.
- (5) Wishart, J. F. *J. Phys. Chem. Lett.* **2010**, *1*, 3225–3231.
- (6) Wishart, J. F.; Shkrob, I. A. In *Ionic Liquids: From Knowledge to Application*, Rogers, R. D., Plechkova, N. V., Seddon, K. R., Eds.; American Chemical Society: Washington, DC, 2009; pp 119–134.
- (7) Venkatesan, K. A.; Srinivasan, T. G.; Rao, P. R. V. *J. Nucl. Radiochem. Sci.* **2009**, *10*, R1–R6. Giridhar, P.; Venkatesan, K. A.; Subramaniam, S.; Srinivasan, T. G.; Rao, P. R. V. *J. Alloys Compd.* **2008**, *448*, 104–108.
- (8) Chen, P. Y.; Hussey, C. L. *Electrochim. Acta* **2004**, *49*, 5125–5138. Tsuda, T.; Hyssey, C. L.; Kuo, H.; Dai, S. *J. Electrochem. Soc.* **2006**, *153*, D171–D176.
- (9) Dietz, M. L. *Sep. Sci. Technol.* **2006**, *41*, 2047–2063. Dietz, M. L.; Stepinski, D. C. *Green Chem.* **2005**, *7*, 747–750. Dietz, M. L.; Dzielawa, J. A.; Laszak, I.; Young, B. A.; Jensen, M. P. *Green Chem.* **2003**, *5*, 682–685. Dietz, M. L.; Dzielawa, J. A. *Chem. Commun.* **2001**, 2124–2125.
- (10) Luo, H.; Dai, S.; Bonnesen, P. V.; Haverlock, T. J.; Moyer, B. A.; Buchanan, A. C., III. *Solvent Extr. Ion Exch.* **2006**, *24*, 19–31. Luo, H.; Dai, S.; Bonnesen, P. V. *Anal. Chem.* **2004**, *76*, 2773–2779. Dai, S.; Ju, Y. H.; Barnes, C. E. *J. Chem. Soc., Dalton Commun.* **1999**, 1201–1202. Luo, H.; Dai, S.; Bonnesen, P. V.; Buchanan, A. C., III. *J. Alloys Compd.* **2006**, *418*, 195–199.
- (11) Rickert, P. G.; Stepinski, D. C.; Rausch, D. J.; Bergeron, R. M.; Jakab, S.; Dietz, M. L. *Talanta* **2007**, *72*, 315–320.
- (12) Giridhar, P.; Venkatesan, K. A.; Srinivasan, T. G.; Rao, P. R. V. *J. Nucl. Radiochem. Sci.* **2004**, *5*, 21–26. Giridhar, P.; Venkatesan, K. A.; Srinivasan, T. G.; Rao, P. R. V. *J. Radioanal. Nucl. Chem.* **2005**, *265*, 31–38.
- (13) Thomazeau, C.; Olivier-Bourbigou, H.; Magna, L.; Luts, S.; Gilbert, B. *J. Am. Chem. Soc.* **2003**, *125*, 5264–5265.
- (14) Yasaka, Y.; Wakai, C.; Matudayashi, N.; Nakahara, M. *Anal. Chem.* **2009**, *81*, 400–407.
- (15) Gjokaj, M.; Brockner, W.; Namyslo, J.; Adam, A. *CrystEngComm* **2008**, *10*, 103–110.
- (16) Chaumont, A.; Wipff, G. *J. Phys. Chem. B* **2010**, *114*, 13773–13785.
- (17) Chenevert, R.; Rodrigue, A.; Beauchesne, P.; Savoie, R. *Can. J. Chem.* **1984**, *62*, 2293–2298. Chenevert, R.; Rodrigue, A. *J. Chem. Educ.* **1984**, *61*, 465–466.
- (18) Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 418–454.
- (19) Nockemann, P.; Thijs, P.; Parac-Vogt, T.-N.; Van Hecke, K.; Van Meervelt, L.; Tinant, B.; Hartenbach, I.; Schleid, T.; Ngan, V. T.; Nguyen, M. T.; Binnemans, K. *Inorg. Chem.* **2008**, *47*, 9987–9999.
- (20) Wang, Y.; Li, H.; Han, S. *J. Phys. Chem. B* **2006**, *110*, 24646–24651. Tsuzuki, S.; Tokuda, H.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 16474–16481. Dong, K.; Zhang, S.; Wang, D.; Yao, X. *J. Phys. Chem. A* **2006**, *110*, 9775–9782.
- (21) Shchori, E.; Jagur-Grodzinski, J. *J. Am. Chem. Soc.* **1972**, *94*, 7957–7962. Kolthoff, I. M.; Wang, W.-J.; Chantooni, M. K., Jr. *Anal. Chem.* **1983**, *55*, 1202–1204. Amini, M. K.; Shamsipur, M. *J. Solution Chem.* **1992**, *21*, 275–288. Chantooni, M. K., Jr.; Kolthoff, I. M. *J. Solution Chem.* **1992**, *21*, 683–697.
- (22) Dietz, M. L.; Bond, A. H.; Clapper, M.; Finch, J. F. *Radiochim. Acta* **1999**, *85*, 119–129.
- (23) Atwood, J. L.; Alavanipour, A.; Zhang, H. *J. Cryst. Spectrosc. Res.* **1992**, *22*, 349. Selig, H.; Sheshinski, H.; Cohen, S.; Columbus, I.; Shoham, G. *J. Fluorine Chem.* **1991**, *54*, 359.
- (24) Chénevert, R.; Rodrigue, A.; Chamberland, D.; Ouellet, J.; Savoie, R. *J. Mol. Struct.* **1985**, *131*, 187–200.
- (25) Heo, G. S.; Bartsch, R. A. *J. Org. Chem.* **1982**, *47*, 3559.
- (26) Berthon, L.; Nikitenko, S. I.; Bisel, I.; Berthon, C.; Faucon, M.; Saucerotte, B.; Zorz, N.; Moisy, P. *Dalton Trans.* **2006**, 2526–2534. Bosse, E.; Berthon, L.; Zorz, N.; Monget, J.; Berthon, C.; Bisel, I.; Legand, S.; Moisy, P. *Dalton Trans.* **2008**, 924–931. Le Rouzo, G.; Lamouroux, C.; Dauvois, V.; Dannoux, A.; Legand, S.; Durand, D.; Moisy, P.; Moutiers, G. *Dalton Trans.* **2009**, 6175–6184.
- (27) Yuan, L. Y.; Peng, J.; Xu, L.; Zhai, M. L.; Li, J. Q.; Wei, G. S. *J. Phys. Chem. B* **2009**, *113*, 8948–8952. Qi, M.; Wu, G.; Chen, S.; Liu, Y. *Radiat. Res.* **2007**, *167*, 508–514. Yuan, L. Y.; Peng, J.; Xu, L.; Zhai, M. L.; Li, J. Q.; Wei, G. S. *Radiat. Phys. Chem.* **2009**, *78*, 737–739. Yuan, L. Y.; Peng, J.; Xu, L.; Zhai, M. L.; Li, J. Q.; Wei, G. S. *Dalton Trans.* **2008**, 6358–6360. Yuan, L. Y.; Xu, C.; Peng, J.; Xu, L.; Zhai, M. L.; Li, J. Q.; Wei, G. S.; Shen, X. H. *Dalton Trans.* **2009**, 7873–7875.
- (28) Shkrob, I. A.; Chemerisov, S. D.; Wishart, J. F. *J. Phys. Chem. B* **2007**, *111*, 11786–11793.
- (29) Shkrob, I. A.; Marin, T. W.; Chemerisov, S. D.; Wishart, J. F. *J. Phys. Chem. B* **2011**, DOI: 10.1021/jp2003062.
- (30) Shkrob, I. A.; Marin, T. W.; Dietz, M. L. *J. Phys. Chem. B*, published online March 16, <http://dx.doi.org/10.1021/jp200307h>.
- (31) Allen, D.; Baston, G.; Bradley, A. E.; Gorman, T.; Haile, A.; Hamblett, I.; Hatter, J. E.; Healey, M. J. F.; Hodgson, B.; Lewin, R.; Lovell, K. V.; Newton, B.; Pitner, W. R.; Rooney, D. W.; Sanders, D.; Seddon, K. R.; Sims, H. E.; Thied, R. C. *Green Chem.* **2002**, *4*, 152–158.
- (32) Katsumura, Y.; Jiang, P. Y.; Nagaishi, R.; Oishi, T.; Ishigure, K.; Yoshida, Y. *J. Phys. Chem.* **1991**, *95*, 4435–4439. Mezyk, S. P.; Bartels, D. M. *J. Phys. Chem. A* **1997**, *101*, 6233–6237.