Structure of Ionic Liquids

The Structure of a Room-Temperature Ionic Liquid with and without Trace Amounts of Water: The Role of C–H···O and C–H···F Interactions in 1-*n*-Butyl-3-Methylimidazolium Tetrafluoroborate**

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Room temperature ionic liquids (RTILs) have been considered as a "green", recyclable alternative to the traditional volatile organic solvents because of their chemical and physical properties, such as being liquid at room temperature, air and moisture stability, high solubility power, and virtually no vapor pressure.[1,2] Being hygroscopic, RTILs can absorb a significant amount of water. Their properties (e.g., solubility, polarity, viscosity, and conductivity) are not only changed by, but also are dependent on the amount of absorbed water.[1–3] Rates of chemical reactions and efficiencies of various processes in RTILs are, therefore, dependent on absorbed water.[1,2] As a consequence, information on the structures of RTILs and their interactions with water are important not only fundamentally but also for various industrial applications. Various studies have been made using either experimental techniques, such as FT-IR, Near-IR, fluorescence, viscosimetry, conductivity, and pulsed-gradient spin-echo NMR diffusion coefficient measurements,[3,4] or theoretical calculations.[5] Unfortunately, these techniques cannot provide direct information on the molecular level of structure of RTILs and their interactions with water. Herein we present direct experimental evidence of cation–cation, cation–water, and cation–anion interactions by NMR spectroscopy through intermolecular nuclear Overhauser enhancements (NOEs) on the model compound 1-*n*-butyl-3-methylimidazolium tetrafluoborate ($[BMIm]^+[BF_4]^-$ (**1**), Figure 1). Cation–cation interactions were investigated by homonuclear NOEs in the rotating frame (ROEs). The ROEs pattern of the pure liquid (**1a**) was compared with those of samples containing known amounts of water (**1b–g**, Table 1). Water was added to change the structure of the pure ionic liquid by introducing water–cation interactions. As a complementary picture, intermolecular water–cation ROEs were also observed and evaluated to provide details of 1) the type of water–cation interactions and 2) the site of interaction. Eventually, the role of the anion was investigated by heteronuclear steady-state $^1H\{^{19}F\}$ NOE difference spectra.

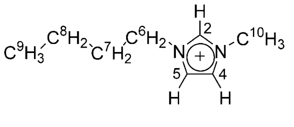

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Figure 1. Chemical structure and atom numbering for **1**.

Table 1: Composition of samples of compound **1**.

	1a[a]	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**
Water:**1** mole ratio	0	0.10	0.20	0.37	0.56	0.81	1.09
Water mole fraction	0	0.09	0.17	0.27	0.36	0.45	0.52

[a] Pure liquid, reference sample.

The analysis of intermolecular ROEs arising from cation–cation interactions was carried out by volume integration of the cross peaks attributed to intermolecular interactions.[6] The histogram of the relative intensities (Figure 2) shows two different trends: 1) ROEs intensity decreases with increasing water content for those interactions involving imidazolium ring protons H2, H4, H5; 2) the opposite (ROEs intensity increases with increasing water content) for interactions between H10 and the protons of the *n*-butyl group, H6, H7,

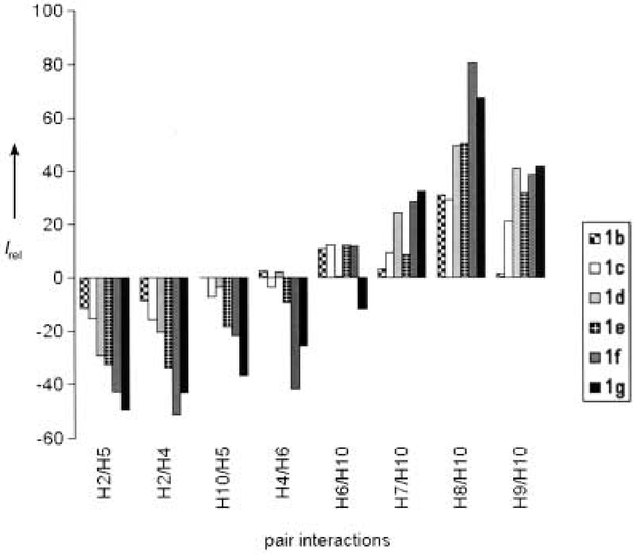

Figure 2. Relative intensity of intermolecular ROESY cross peaks in samples **1b–g**. The data reported were obtained as follows: relative intensity (%) $I_{rel} = [(V-V_0)/V_0]100$, where V_0 = integrated volume of a given cross peak in **1a** (pure ionic liquid) and V = integrated volume of the same cross peak in the sample containing known amounts of water (**1b–g**, Table 1). All volumes are internally normalized to the H2–H10 cross-peak volume set = 1.00 (arbitrary units). A negative bar for a given cross peak means a decreased relative intensity with respect to the same cross peak in the pure liquid.

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H8, H9. It was proposed that imidazolium ring protons may act as hydrogen-bond donors to F atoms of the counterion in ionic liquids with fluorine containing anion.[4c,d] In our case, the presence of water is likely to replace progressively the C(sp^2)-H···F interactions with hydrogen bonds involving water as an acceptor towards the cation and as a donor towards the $[BF_4]^-$ ion. The structure of pure ionic liquid **1a** is changed towards a different organization with a lower degree of ring stacking (or other types of piling) or, in other words, the presence of water makes the imidazolium–imidazolium associations looser, with consequent increase of intermolecular distances between ring protons and decrease of the related ROEs intensity. The increasing intensity of ROEs between H10 and the protons of the *n*-butyl chain is consistent with the methyl group shifting progressively towards the most hydrophobic part of the imidazolium ion, namely the *n*-butyl chain, as the water content raises. The observed trends for the H6–H4 and H10–H6 interactions may be due to the superposition of the factors mentioned above and others, for example, conformational changes at the *n*-butyl/imidazolium junction.

The ROESY spectra of samples **1b–g** allowed us to detect small but significant intermolecular cross peaks of imidazolium protons with the broad signal arising from water at about $\delta = 3$ ppm, thereby providing evidence of water–imidazolium cation interactions. The results of the integration of ROESY cross peaks relating to water–imidazolium protons for **1b–g** (Figure 3), seem to indicate that at very low water content (sample **1b**) the interaction of water is specific and localized at H2, H4, and H5, namely at those C(sp^2)-H protons capable of establishing hydrogen bonds with water. This conclusion is in agreement with the mechanism proposed in the previous paragraph on the intermolecular ROEs involving the aromatic ring protons. It also substantiates the role of water as a disturbing agent with respect to ring–ring assembly. At higher water content (e.g. samples **1f**, **1g**) the interaction of water with the other protons (H6, H7, H8, H9, and H-10) increases considerably and does not show any preference. This might be due to the system passing from a regime of selective interaction to a less defined, nonselective solvation.

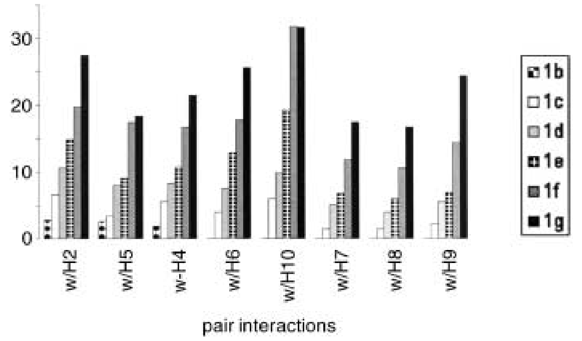

Figure 3. Relative intensity of ROESY cross peaks relating to water (W)–imidazolium cation interactions in samples **1b–g**. The data are normalized to the H2–H10 cross-peak volume set = 1.00 (arbitrary units).

The effect of the imidazolium counterion on the short-range structure of some ionic liquids has been recently investigated by the analysis of NMR chemical shift variations[7] in some 1-*n*-butyl-3-methylimidazolium salts as a function of solvent polarity, and also by homonuclear anion–cation NOE in 1-*n*-butyl-3-methylimidazolium tetraphenylborate.[8] This latter study showed NOE between H2 of the cation and H_{ortho} of one of the phenyl groups of the anion as a result of weak C(sp^2)-H···π attractive interactions. This finding, in turn, was found to be consistent with the presence of tight ion pairs even in the presence of solvent. We gained information on the cation–anion interactions in **1** by detecting heteronuclear $^1H\{^{19}F\}$ NOEs (Figure 4). Only the peaks assigned to H2, H5, and H4 appear as positive peaks in the NOE difference spectrum (3.6, 3.3, and 3.3 % enhancement, respectively). These results provide evidence for positive NOEs between fluorine atoms of the anion and the aromatic protons of the cation. The detection of heteronuclear anion–cation NOEs lends credence to the presence of an ion pair with short H···F contacts. The latter can be associated with attractive interactions of type C(sp^2)-H···F. These results are coherent with recent findings of Dölle and co-workers on the dynamic behavior of the $[BMIm]^+[PF_6]^-$ system.[9] Remarkably, a small positive NOE (1.5 %) is also detectable on the water signal, which seems to suggest that water can act as hydrogen-bond donor towards the $[BF_4]^-$ ion. We repeated the NOE experiments in the presence of a strong competitor at the hydrogen-bond site, such as DMSO[10] in an attempt to validate the hypothesis of C(sp^2)-H···F hydrogen bonds. Surprisingly, the same pattern of NOEs was found even in a sample containing 55 mg of pure **1** dissolved in 500 μL of [D$_6$]DMSO. The enhancements, once again observed for H2 (1.3 %), H5 (1.0 %), and H4 (1.1 %), are consistent with short H···F contact even for this sample where **1** was in a different molecular environment.

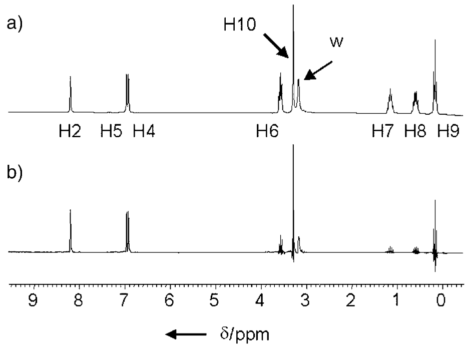

Figure 4. $^1H\{^{19}F\}$ NOE difference experiment carried out on compound **1e**. Trace a) reference spectrum ("off resonance"). Trace b) $^1H\{^{19}F\}$ NOE difference spectrum (vertical scale magnified 32 times with respect to (a)). The signals of H2, H4, H5, and water (w) are in pure absorption because of heteronuclear NOE. The other signals are subtraction artifacts.

The ROESY approach made it possible for us to detect intermolecular contacts of two types: cation–cation and water–cation. Increasing water content was found to appreciably change the structure of the ionic liquid through the participation of water in C(sp^2)-H mediated hydrogen bonds. The heteronuclear experiments on **1** indicated the existence of tight ion pairs in the pure liquid even in the presence of small amounts of water and, in a second set of experiments, even in DMSO solution. The heteronuclear NOE experiments provided direct evidence of the importance of the C(sp^2)-H···F interactions in governing the short-range structure of this class of ionic liquids. Experiments on other molten salts such as $[BuMIm]^+[PF_6]^-$ and $[BuMIm]^+[Tf_2N]^-$ (Tf = bis(trifluoromethyl)sulfonyl amide) are currently being performed in order to gain deeper insight into the hierarchy of intermolecular interactions.

Experimental Section

1-*n*-Butyl-3-methylimidazolium chloride ($[BuMIm]^+Cl^-$) was synthesized according to reported procedures.[11] Compound **1** was prepared from $[BuMIm]^+Cl^-$ by metathesis using the reported methods,[12] dried under vacuum at 70 °C overnight, and kept either under nitrogen or in a vacuum desiccator to protect it from moisture.

Suitable amounts of **1** were accurately weighted in glass vials. HPLC grade water was added by microsyringe. The resulting solutions were transferred into 5-mm NMR tubes equipped with coaxial capillary tube containing [D$_6$]DMSO. The external deuterated solvent provided both lock frequency and ^{1}H spectrum reference (central peak = 2.50 ppm). NMR spectroscopy experiments were carried out on a Bruker Avance 500 instrument at 305 K (nominal). Two-dimensional correlation experiments by dipolar coupling in the rotating frame (ROESY) were performed by using a pulse sequence proposed for off-resonance ROESY with adiabatic rotation.[13] All cross-peak volumes were normalized to the volume of H2–H10 cross peak.[14] The heteronuclear steady-state ^{1}H{^{19}F} NOE difference spectra were carried out by using a standard pulse sequence modified for the second radio frequency channel.[15] Expansion of the ROESY spectrum of **1e**, Tables of cross-peak volumes related to Figures 2 and 3, and the ^{1}H{^{19}F} NOE difference spectrum of **1** in [D$_6$]DMSO are available as Supporting Information.

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[14] The reason this choice are: 1) The H2–H10 interaction was assumed to be mainly, if not purely, intramolecular[6] and, therefore, not influenced by the added water; 2) the average distance between H2 and H10 can be considered to be independent of the intermolecular interactions and conformation of the cation of **1**, which is assumed to be planar.

[15] Selective saturation of fluorine signals was achieved by a suitably attenuated decoupler pulse on resonance on the ^{19}F signal of the ionic-liquid anion (spectrum “on resonance”). Control spectra (“off resonance”) were recorded by setting the decoupler frequency off resonance. NOE difference spectra were obtained by subtracting the “off resonance” spectrum from the “on resonance”.