Communication

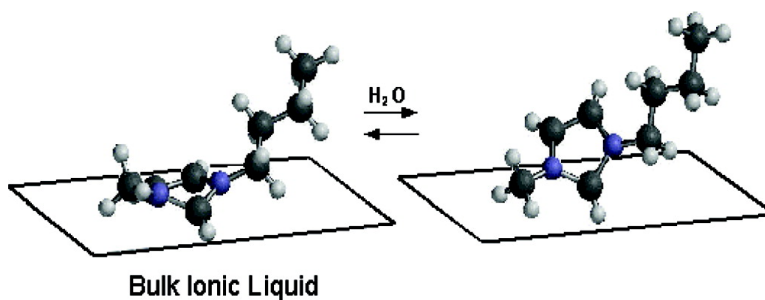# Influence of Water on the Surface of Hydrophilic and Hydrophobic Room-Temperature Ionic Liquids

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Bulk Ionic Liquid

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Influence of Water on the Surface of Hydrophilic and Hydrophobic Room-Temperature Ionic Liquids

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Ionic liquids are finding increasing use in many areas of technology and science. Many of these applications involve interfacial chemistry; therefore, obtaining information on the molecular details of these new materials is important to improving their properties and performance. Further, the activity of these materials is strongly influenced by the presence of water as an impurity.[1] Water is often present as a contaminant (up to ~0.2 mol fraction) in hydrophilic as well as in hydrophobic ionic liquids, highly affecting their physical properties.[2,3]

This communication reports the influence of water on the surface orientation of hydrophilic (water miscible) and hydrophobic (water immiscible) classes of room-temperature ionic liquids. The room-temperature ionic liquids discussed in this communication are based on the imidazolium cation (Figure 1). The miscibility of an ionic liquid with water is mostly determined by the associated anion. Anions such as halides, pseudo-halides, BF_4^-, methyl sulfate, NO_3^-, ClO_4^-, etc., are miscible, while PF_6^-, AsF_6^-, bis(perfluoroalkyl)-imides (imide), and $[C_4F_6SO_3]^-$ are immiscible.

The gas−liquid interface of the ionic liquid is investigated using surface-sensitive vibrational spectroscopy sum frequency generation (SFG). The results indicate that when the ionic liquid is dry the cation is oriented with the imidazolium ring parallel to the surface plane for both hydrophilic and hydrophobic ionic liquids. However, the cation reorients with respect to the surface for the hydrophobic liquid when water is added, while the orientation in the hydrophilic liquid is unaffected.

Ionic liquids are synthesized using a procedure previously established[4] and then transferred to a spectroscopy cell. Prior to each experiment, the samples are evacuated to ~10^{-5} Torr with stirring while being heated at 70 °C. Water vapor is introduced and equilibrated for more than 2 h, and the SFG analysis is then performed. Water concentration in the ionic liquids is determined by Henry's law using the coefficients previously established by Brenecke,[5] Rogers,[6] and Welton.[7] The SFG spectroscopy is conducted according to previous practice.[4]

The SFG spectra of the ionic liquids have several notable features (Figure 2). First, for the dry samples, both hydrophobic and hydrophilic ionic liquids only display aliphatic C−H modes of the butyl chain. These are seen at 2880 and 2935 cm^{-1} and are due to the terminal methyl group.[8,9] This assignment has been confirmed by isotopically labeling the butyl chain with deuterium where the two peaks are then absent. Their appearance suggests that these are the only groups oriented along the surface normal at a tilt angle of ~20° from normal (Figure 2F). Furthermore, the aromatic ring must be nearly parallel to the surface plane.

Upon addition of water to the system, new features appear in the spectrum of the hydrophobic ionic liquids. At as little as 10^{-4} Torr water partial pressure, two new peaks are present in the spectrum for [BMIM][imide] at 3150 and 3170 cm^{-1}, respectively. The peaks increase in intensity until a maximum ~P_{H2O} = 20 Torr. These peaks do not appear in the water-miscible ionic liquid spectra.
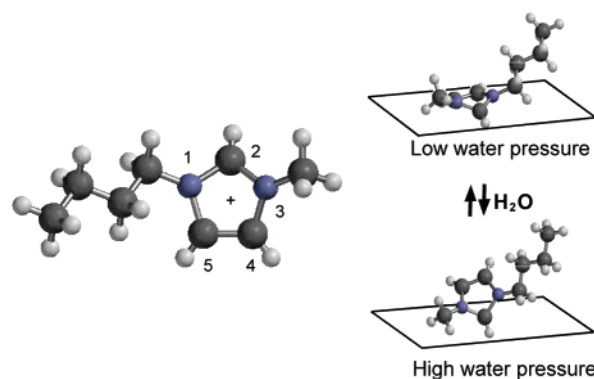

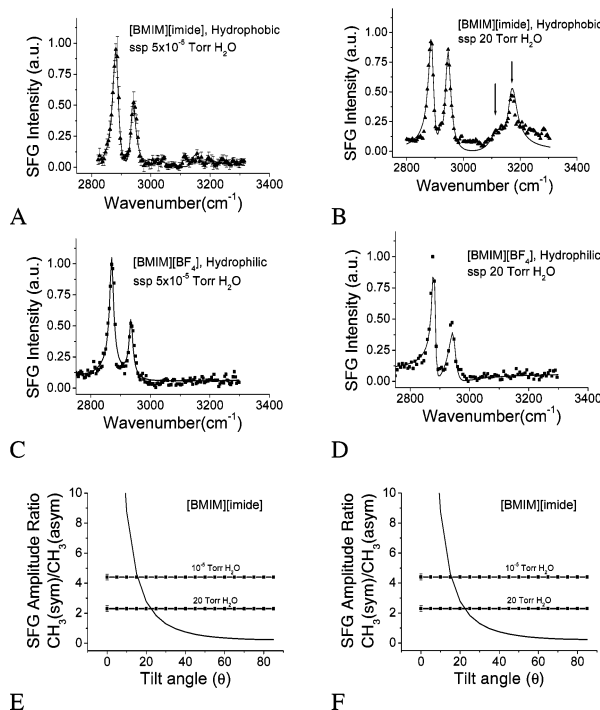**Figure 1.** Structure of [BMIM]$^+$ with numbering scheme. Model of cation reorientation at gas−liquid interface.

Figure 2. SFG spectra of (A, B) [BMIM][imide] and (C, D) [BMIM]-[BF4] at water partial pressure of 5×10^{-5} Torr and 20 Torr. Polarization is ssp. (E) Simulation of SFG signal as a function of imidazolium orientation and (F) methyl group orientation.

These peaks are assigned to the anti-symmetric and symmetric stretch of the H−C(4)C(5)−H modes on the imidazolium cation, respectively[10,11] (Figure 1). The intensity of the peaks from the methyl group is only slightly affected by the addition of water. In addition, there are no features in these spectra that are due to the added water, which are expected at 3200, 3450, and/or 3700 cm^{-1}.[12−14]

The orientation of the cation has been estimated by measuring the polarization dependence of the SFG spectra.[4,15−17] Some of the results of this analysis are present in Figure 2E,F. The orientation angle is determined by where the experimental data points intersect the theoretical curves. They indicate that the imidazolium ring has tipped with the C(2)−H bond directed toward the bulk liquid and the H−C(4)C(5)−H projecting out of the interface at an angle of 30−50° from the surface normal. Further, the data are consistent with a twist of the ring around the pseudo C2 axis of 0−45° projecting the N(1) nitrogen (with the butyl chain) toward the gas phase. The orientation of the butyl chain (Figure 2F) is relatively unaffected by this reorientation because of chain flexibility.

Why Does Water Affect the Surface of Hydrophobic Ionic Liquids and Not Hydrophilic Ones? In the bulk of the water-miscible ionic liquids, the water molecules are stabilized by favorable intermolecular interactions such as hydrogen-bonding and dipole−dipole forces,[5,7,18−20] and thus it is less favorable to partition water to the surface where solvation is incomplete.

However, water-immiscible ionic liquids display a dramatic reorientation at the gas−liquid interface as water is added to the system. This observation seems reasonable since in the bulk ionic liquid water is less stable and therefore is forced to the surface. This is evidenced by the appearance of the C−H stretching mode on the imidazolium ring in [BMIM][imide].

The tilting of the cation on the surface is likely due to the interaction of water with the C(2)−H; calculations show some preference of the anion to associate with the C(2)−H.[21−24] Water will then be likely to interact at this point when solvating the ions in the ionic liquid. In fact, the bulk structure of imidazolium-based ionic liquid crystals shows that the water forms a disordered cluster with the anion and that the imidazolium cation can adopt a different orientation relative to the alkyl chain.[25] Where the plane of the ring will be, either parallel or perpendicular to the alkyl chain, is dependent on the protonation or methylation of the C(2) position. Since the tilt of the alkyl chain at the surface remains unchanged, this amounts to a tilting of the ring relative to the surface normal. Further, by having water interact with the C(2)−H, the C(2)−H bond will point into the bulk liquid where it will participate in hydrogen bonding.[21] The H−C(4)C(5)−H will be directed into the vapor phase.

The partitioning of water to the interface is also justified on a thermodynamic basis. The activity of water is higher in the hydrophobic ionic liquid than in the hydrophilic,[5] and thus water will partition to the gas−liquid interface of the [BMIM][imide] ionic liquid more than in [BMIM][BF$_4$]. Therefore, only the surface of the hydrophobic ionic liquid will be influenced by the added H$_2$O.

The preference for water to stay in the bulk liquid is due to the favorable solvation interactions that occur there.[5,7,19,26,27] These are observed in the bulk properties (such as viscosity, conductivity, and melting point) of the miscible ionic liquid being more affected by the added water than the immiscible ionic liquid.[6] However, the surface properties may be different. It is noted that the surface tension of the [BMIM][BF$_4$] is reported to be 46.6[6] or ∼41 mJ/

m^2 [28] and appears to be as low as 35mJ/m2 with added water.[29] For [BMIM][imide], the surface tension is 37.5 mJ/m^2 in the dry liquid and hardly changes for the water-equilibrated sample to 36.8 mJ/m^2.[6] Apparently, the addition of water influences the surface energy of the ionic liquid, and this may be related to the reorientation that is observed here.

Surface-sensitive vibrational spectroscopy has been used to determine the influence of water on the surface of a room-temperature ionic liquid. The results indicate that surface hydrophobic, nonmiscible ionic liquids are more sensitive to the addition of water than miscible, hydrophilic ones. The hydrophobic ionic liquids respond to the addition of water by reorienting their cations to help solvate the water molecules. Further, this effect is verified for other ionic liquids investigated in this laboratory.

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