

# Influence of Water on the Surface of the Water-Miscible Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate: A Sum Frequency Generation Analysis

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Sum frequency generation spectroscopy (SFG) was used to study the influence of water on the surface of the water-miscible ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate. The orientation of the cation at the gas–liquid interface was analyzed as a function of ionic liquid concentration in water for concentrations from 0 to 1 mole fraction of the ionic liquid. The cation was found to be oriented with the imidazolium ring nearly parallel to the surface plane with a tilt angle  $\geq 70^\circ$  when the ionic liquid was dry. Furthermore, no noticeable change in the orientation was observed when high concentrations of water were mixed with the ionic liquid. The cation butyl chain is projecting into the gas phase with a  $\text{CH}_3$  tilt angle of  $54 \pm 2^\circ$  when the ionic liquid is dry and  $46 \pm 4^\circ$  when mixed with water. Water is oriented at the surface only for concentration  $\leq 0.02$  mole fraction of the ionic liquid. At higher ionic liquid concentrations (mole fractions  $\geq 0.05$ ) the gas–liquid interface resembles that of the pure ionic liquid.

## Introduction

Ionic liquids are salts with a melting point close to room temperature, producing a liquid of pure ions without the use of extremely high temperatures. By selecting a different combination of ions, a tunable range of physical properties is obtained, which, combined with their low vapor pressure, provide a good substitute for volatile organic compounds in various applications.<sup>1–3</sup>

Over the past few years, there has been an increased interest in the determination and understanding of the physical properties of ionic liquids and their effect on performance. The purity of ionic liquids is extremely important in the determination of the physical properties such as melting point, viscosity, and conductivity. It is also known that the purity of ionic liquids may alter rate, as well as efficiencies, of chemical reactions and the solubility of other chemicals in ionic liquids.<sup>4</sup>

The most common impurities are halide ions and water. Alkyl halides are used in the synthesis of some ionic liquids, and special care has to be taken to ensure complete purification of the final product. However, even though halide ion impurities are more difficult to clean from some ionic liquids than others, once the ionic liquid is halide free it would stay clean, unless more halide ions are directly added into the system. On the other hand, water is ubiquitous in salts. The presence of water in ionic liquids is unavoidable.<sup>5</sup> As a result, water contamination is a common issue when working with ionic liquids and, consequently, is an area of general importance to study.

A promising application of ionic liquids is in the separation of gases and gas capture from flue stacks.<sup>6–10</sup> This capability is due to the selectivity that ionic liquids have shown for the absorption of specific gases. The uptake of gas molecules is determined by the interaction of the first layer of molecules in contact with the gas at the gas–liquid interface. Therefore, to understand the detailed mechanisms of the gas absorption in an ionic liquid, the interfacial structure must be known at the

molecular level. In addition, the physical properties of ionic liquids are highly influenced by the presence of water in the system;<sup>11,12</sup> hence, it is important to understand how water affects the interface and how this effect depends on the water miscibility of the ionic liquids.

Previously an interesting water effect was observed by our group.<sup>13,14</sup> The different imidazolium-based ionic liquids studied were found to have a similar surface orientation when they were dried at a pressure  $\leq 2 \times 10^{-5}$  Torr independent of the anion.<sup>15</sup> The ionic liquids analyzed were found to have results consistent with the imidazolium ring parallel to the surface plane. This orientation was determined due to the lack of the ring vibrational modes in the SFG spectra, although it should be noted that SFG is also not sensitive to randomly oriented functional groups as well. However, when low concentrations of water vapor were introduced into the system, only those ionic liquids nonmiscible with water were affected. The absorbance of water vapor by the nonmiscible ionic liquids was enough to cause a tilt of the imidazolium ring, which was represented by the appearance of the H–C(4)C(5)–H vibrational modes in the SFG spectra, while there was no water effect observed in the SFG spectra of the miscible ionic liquids.<sup>13</sup>

Studies on the effect of water on the physical properties of ionic liquids, as well as the interaction between water and the ions, have been performed by several groups.<sup>12,13,16–19</sup> An exciting result was found by Bowers from surface tension measurements of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) as a function of water concentration.<sup>19</sup> The behavior of the ionic liquid was found to resemble that of a surfactant, with a critical micelle concentration of 800 mM/dm<sup>3</sup>, which corresponds to a 0.0166 mole fraction of [BMIM][BF<sub>4</sub>], at which there was an aggregate formation of the ionic liquid. The same aggregate formation was found from thermodynamic analysis by Koga,<sup>20,21</sup> who observed that at concentrations higher than 0.5 mole fraction the ionic liquid formed clusters, as in the pure state, and water molecules interacted with the clusters without interacting among themselves. Koga reported a higher concentration than that reported by Bowers; however, the reader should keep in mind that Koga is describing

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the bulk of the ionic liquid and Bowers the surface. In addition, some ionic liquids possess a surface activity similar to that of surfactants; as a result, even though a concentration of 0.016 mole fraction is reported, it refers to the bulk of the liquid, which is expected to be lower than the concentration at the surface.

Cammarata used ATR-IR analysis of [BMIM][BF<sub>4</sub>] as a function of water to describe the state of water when absorbed into ionic liquids.<sup>12</sup> The position of the vibrational mode of water was used to identify its interaction with the ions. For [BMIM]-[BF<sub>4</sub>] the peak observed by ATR-IR was positioned at 3640 cm<sup>-1</sup> and identified as the antisymmetric mode of a weakly hydrogen-bonded water molecule. Cammarata concluded that water molecules were not interacting with themselves and can be considered as free water molecules interacting with the BF<sub>4</sub><sup>-</sup> anion of the ionic liquid.

Kim et al. performed an SFG analysis of [BMIM][BF<sub>4</sub>] as a function of water concentration focused on the butyl chain orientation.<sup>18</sup> The conformational flexibility of the butyl chain does not permit a correlation of the orientation of the butyl chain with the overall molecular orientation, specifically the imidazolium ring. Previously our group found that changes in the orientation of the imidazolium ring did not affect the orientation of the butyl chain.<sup>14</sup> In this report sum frequency generation was performed on [BMIM][BF<sub>4</sub>], for concentrations from 0 to 1 mole fraction of the ionic liquid (*X*<sub>IL</sub>). For a complete understanding of the water's effect on the surface of water-miscible ionic liquids, the vibrational spectra were analyzed over the C-H as well as the water O-H vibrational frequencies, from 2800 to 3800 cm<sup>-1</sup>, to monitor the reorientation of the imidazolium ring and the presence and orientation of water at the interface. We have correlated the results with the surface tension measurements found by Bowers<sup>19</sup> to establish a model of the water's influence to the surface structure of [BMIM]-[BF<sub>4</sub>] as well as the state of water at the surface.

Sum frequency generation (SFG) is a nonlinear vibrational spectroscopic technique sensitive to molecules in a noncentrosymmetric environment, such as the interface between two phases. A detailed description of the SFG theory is well reviewed by other groups.<sup>22-25</sup>

For the acquisition of the SFG spectra, a fixed frequency visible beam and a tunable infrared beam are overlapped at the surface, where, due to the nonlinear properties of the interface, a third beam is generated as a sum of the incident beams frequency:

$$I_{\text{SF}} \propto |P^{(2)} = \chi^{(2)} \cdot E_{\text{vis}} E_{\text{IR}}|^2 \quad (1)$$

$$\chi^{(2)} = \chi_{\text{nr}} + \sum \left[ \frac{N \langle \beta^{(2)} \rangle}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \right] \quad (2)$$

The SFG intensity is proportional to the square of the induced polarization (*P*<sup>(2)</sup>) (eq 1), where *E*<sub>vis</sub> and *E*<sub>IR</sub> refers to the electric field of the visible and infrared input beams respectively, and  $\chi^{(2)}$  is the second-order susceptibility tensor, which is dependent on the surface properties. The second-order susceptibility tensor (eq 2) is formed by a nonresonant part,  $\chi_{\text{nr}}^{(2)}$ , and a resonant susceptibility due to the vibrational modes of the surface molecules. The resonant susceptibility contains the hyperpolarizability,  $\beta^{(2)}$ , described by the Raman polarizability and the infrared dipole transition, which are averaged over the molecular orientation indicated by the brackets ( $\langle \rangle$ ). *N* is the number of modes contributing to the SFG signal,  $\omega_{\text{IR}}$  and  $\omega_q$  refers to the frequency of the incoming IR and the normal mode of vibration respectively, and  $\Gamma_q$  is the damping constant for the *q*th vibrational mode.

Selecting different polarization combinations of the input and output light provides information of the susceptibility tensor,  $\chi^{(2)}$ , Cartesian components. Since the magnitude of  $\chi^{(2)}$  is sensitive to the degree of the polar orientation of the molecules (eq 2), polarization analysis of the interface allows a determination of the molecular orientation with respect to the surface normal.<sup>23-25</sup> The analysis performed here is based on a delta function distributions of orientations; therefore, the error bars represent the experimental uncertainties and not the physical range of orientational angles.

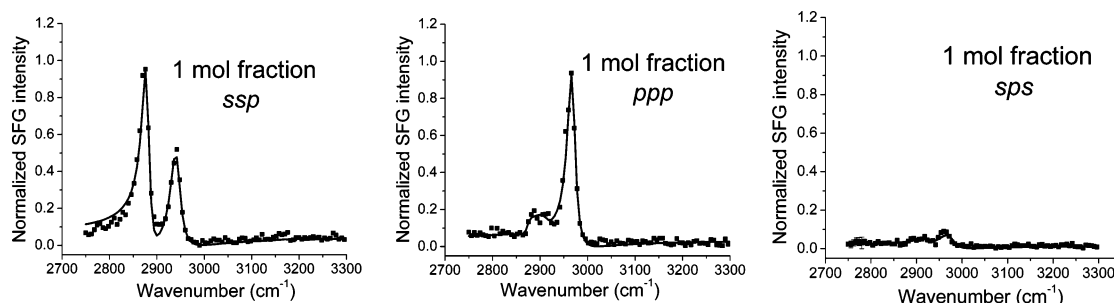
## Experimental Section

All chemicals were from Sigma-Aldrich and used without further purification. To synthesize the water-miscible ionic liquid [BMIM][BF<sub>4</sub>], an equimolar mixture of 1-methylimidazole and 1-chlorobutane was stirred and refluxed under nitrogen at ~65 °C for approximately 72 h. The product, 1-butyl-3-methylimidazolium chloride, was purified by liquid-liquid extraction, using ethyl acetate, while the system was kept warm to avoid the crystallization of the salt. After drying under vacuum for around 5 h, while being stirred and heated at ~70 °C, a small volume of water was added to the [BMIM][Cl] for dilution and mixed with HBF<sub>4</sub> in a 1:1.1 molar ratio. The mixture was stirred overnight (~15 h) at room temperature. The [BMIM][BF<sub>4</sub>] was then cooled in an ice bath and an equal volume of cold dichloromethane was added. Once cold, the ionic liquid was washed with ice-cold deionized water until no chloride was detected in the water (five washings, water volume was half of the volume of the dichloromethane/[BMIM][BF<sub>4</sub>] mixture). The final compound was cleaned with activated charcoal, filtered, and dried under vacuum for around 48 h, while being stirred and heated at ~60 °C, until a pressure  $\leq 2 \times 10^{-5}$  Torr was reached. Once the ionic liquid was clean and dry, the chloride content was again measured using an ion selective electrode and found to be <100 ppm. The final characterization was performed by <sup>1</sup>H NMR, LC-MS, and FT-IR.

For the sample preparation prior to analysis two different approaches were used.

**(A) 1–0.7 Mole Fraction of [BMIM][BF<sub>4</sub>].** The ionic liquid was transferred to a glass spectroscopy cell with Kalrez O-rings, Teflon stopcocks, and IR-quartz windows. The cell was attached to a glass vacuum line with liquid nitrogen traps and dried to a vapor pressure  $\leq 2 \times 10^{-5}$  Torr, which is considered the 1 mole fraction (1*X*<sub>IL</sub>). Once the ionic liquid reached the base pressure, water vapor was introduced into the system and the system equilibrated for at least 1 h. To introduce water into the system, a reservoir of water was attached to the vacuum line, degassed prior to each experiment by the freeze-pump-thaw method, and equilibrated to the desired temperature. Water vapor pressure was controlled with the temperature at which water was equilibrated by using a slush bath.<sup>26</sup> The concentration of water in [BMIM][BF<sub>4</sub>] was determined by Henry's Law using the values previously established by Brennecke.<sup>27</sup>

**(B) 0.5–0.0002 Mole Fraction of [BMIM][BF<sub>4</sub>].** For higher water concentrations, a known volume of liquid water, instead of vapor, was mixed with the ionic liquid. A septum was adapted to the spectroscopy cell to perform the mixing of water with [BMIM][BF<sub>4</sub>] in a clean manner. The cell was filled with acid and let stand overnight before being rinsed. After rinsing the cell with Millipore water (18 MΩ cm, TOC  $\leq 7$  ppb), it was directly attached to the Millipore system and water was continuously flowed through the cell for around 5 min. Subsequently, the cell was filled with water and the SFG spectrum verified for cleanliness. The cell was repeatedly rinsed



**Figure 1.** SFG spectra of dry [BMIM][BF<sub>4</sub>] for the different polarization combinations.

until a clean SFG water spectrum was obtained.<sup>28–32</sup> Once the water spectra resembled that of pure water, ionic liquid was introduced to the cell through the septum using a syringe. The mixture was first stirred and then permitted to equilibrate for 30 min. To ensure consistent cleanliness of the system, the SFG *ssp* spectrum of pure water (*s* for the sum frequency, *s* for the visible, and *p* for the infrared polarization) was first acquired prior to each experiment.

The spectroscopy system used in this analysis consisted of an Ekspla picosecond Nd:YAG laser, which pumped an optical parametric generation/amplification system (OPG/OPA). The OPG/OPA system generated the fixed visible (532 nm) and tunable infrared beam (1900–4000 cm<sup>-1</sup>). The surface was probed at 50° and 60° angle from the surface normal by the visible and IR beams, respectively.

Each spectrum was averaged over 10 scans for concentrations from 0 to 0.02*X*<sub>IL</sub> and five scans for higher concentrations. Data were collected for an average of 20 shots/point at a rate of 1 cm<sup>-1</sup>/s and corrected for fluctuations in the infrared. For the spectra in which water vapor was introduced to the system, the intensity was normalized to the CH<sub>3</sub>(sym) peak in the *ssp* spectrum. When the ionic liquid was introduced to the water, the intensity was normalized to the free O–H peak of water in the *ssp* spectrum. To obtain the frequency and amplitude of the peaks, the spectra were curve-fitted using eq 2 as the fitting function.

## Results and Discussion

When the ionic liquid is dried to  $\leq 2 \times 10^{-5}$  Torr the *ssp* spectra exhibits peaks at 2880 and 2945 cm<sup>-1</sup> (Figure 1) identified as the CH<sub>3</sub> symmetric and Fermi resonance (FR) of the methyl group at the end of the butyl chain.<sup>15</sup> For the *ppp* and *sps* polarization a peak at 2970 cm<sup>-1</sup> is from the CH<sub>3</sub>(asym) mode of the butyl chain and the peak at 2895 cm<sup>-1</sup> is from the antisymmetric vibrational mode of CH<sub>2</sub>.<sup>33</sup> No peaks from the ring were observed in any of the polarizations analyzed, which would appear between 3150 and 3200 cm<sup>-1</sup> and have been observed previously.<sup>14</sup> Absence of the ring modes in the SFG spectra are an indication of a lack of polar orientation of the imidazolium ring, implying a ring plane parallel to the surface plane.

The butyl chain conformational flexibility allows its orientation, to some extent, to be independent of that of the ring. Previously, our group observed that even with significant changes of the ring orientation at the surface, the butyl chain was only slightly affected.<sup>13,14</sup> The appearance of the ring modes when the water concentration was varied is considered an indication of a reorientation of the cation ring. Also, the emergence of water peaks in the spectra is an indication of oriented water at the surface.

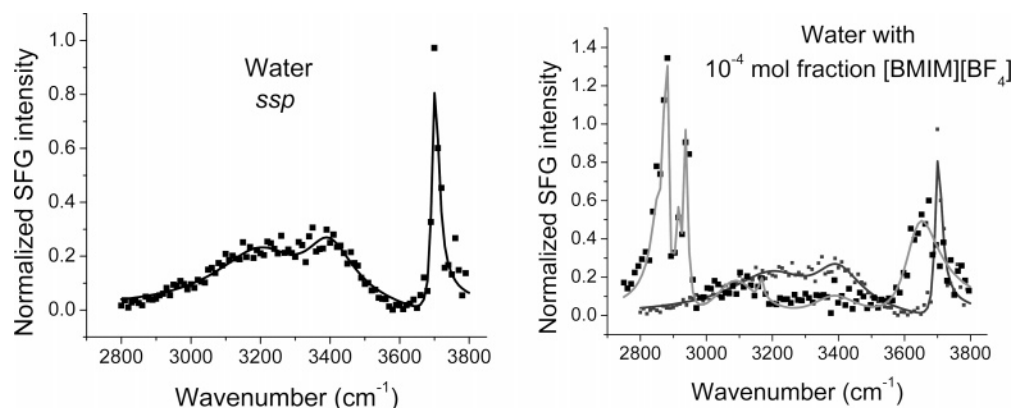
When the water vapor pressure is increased from  $2 \times 10^{-5}$  to 24 Torr (0.7*X*<sub>IL</sub>) no changes are observed in the SFG spectra

for any of the polarization combinations. With the presumption that the amount of water added by vapor was not enough to solvate the ions at the surface, higher concentrations of water were analyzed. There have been several SFG studies of water and the effect that different contaminants have on its surface structure.<sup>28–32</sup> For this analysis a direct addition of liquid water is necessary and the purity of the water is of extreme importance. Therefore, to ensure that the water used in the analysis was clean, a pure water spectrum was acquired prior each experiment. A pure water spectra contains two broad peaks at 3200 and 3400 cm<sup>-1</sup>, due to the different types of hydrogen bonding formed by water at the surface, and a sharp peak at  $\sim 3700$  cm<sup>-1</sup>, from the surface free O–H. The latter is sensitive to the presence of any surface-active contaminant; hence, in this analysis it is used to determine the cleanliness of the system and to analyze the ionic liquid interaction with water.

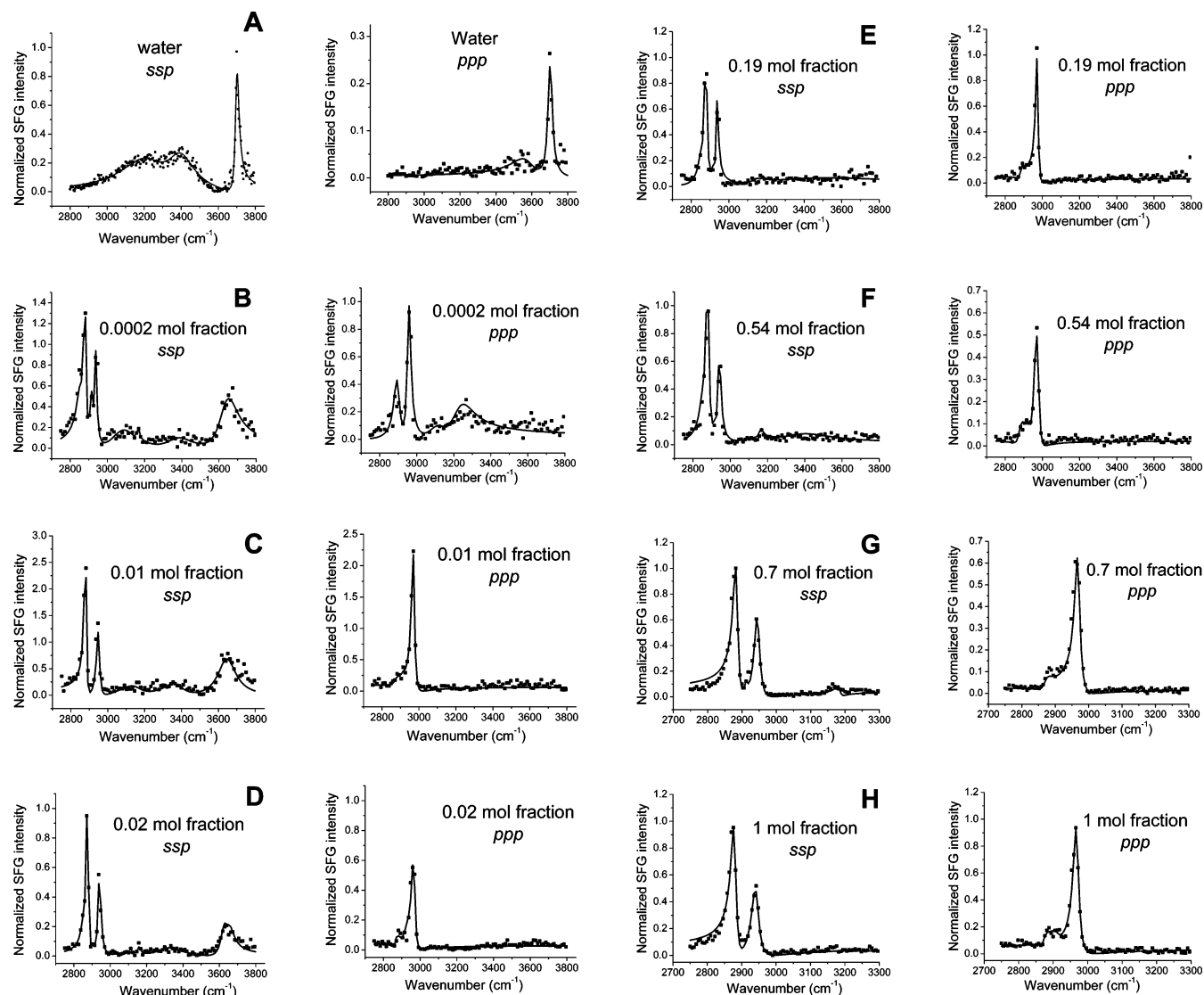
Once a pure water spectrum is acquired, the desired amount of ionic liquid is introduced into the system for a concentration range from 0.0002*X*<sub>IL</sub> to 0.5*X*<sub>IL</sub>. A value of 0.0002*X*<sub>IL</sub> is enough to perturb the water structure at the surface and clearly show the C–H peaks from the cation, about 1.4 times more intense than the water free OH, indicating an oriented [BMIM]<sup>+</sup> at the liquid surface, as shown in Figure 2. The intensity of the 3200 and 3400 cm<sup>-1</sup> peaks decreases drastically, while the peak at 3700 cm<sup>-1</sup> disappears with a new peak present at  $\sim 3650$  cm<sup>-1</sup> (Figure 2). In the aromatic C–H region, 3000–3200 cm<sup>-1</sup>, not only the H–C(4)C(5)–H modes are observed but also the peak for the interaction of [BF<sub>4</sub>]<sup>-</sup> with the ring C(2)–H.<sup>34</sup> However, given the low concentration of [BMIM][BF<sub>4</sub>], the intensity of the ring modes is overwhelmed by the hydrogen bond interaction peaks. As the concentration of the ionic liquid increases, the peaks from the butyl chain become more prominent, while the water peaks decrease until no longer observed for *X*<sub>IL</sub>  $\geq$  0.05 (Figure 3). Furthermore, the hydrogen-bond interaction peaks as well as the ring vibrational modes decrease, indicating a reorientation of the imidazolium ring.

As soon as some ionic liquid is added to the water (0.0002*X*<sub>IL</sub>) the butyl chain peaks dominate the spectra. The same surfactant behavior was observed by Bowers from the surface tension measurements, although at concentrations as low as 0.0002*X*<sub>IL</sub>, a significant change in the surface tension of the mixture was not yet observed.<sup>19</sup> At 0.0002*X*<sub>IL</sub> the CH<sub>2</sub> symmetric and Fermi resonance vibrational modes are observed at 2850 and 2915 cm<sup>-1</sup>, respectively, in the *ssp* spectra, while for higher concentrations a defined peak cannot be accounted for. The appearance of the CH<sub>2</sub> modes in the *ssp* spectra is an indication of gauche defects in the chain, given that the low concentration of ions at the surface decreases the aliphatic interactions by the alkyl chains, allowing the gauche defects to be formed.<sup>25,33</sup>

From surface tension measurements of [BMIM][BF<sub>4</sub>] as a function of water concentration, Bowers found the formation of aggregates of ionic liquids at 0.0166*X*<sub>IL</sub>.<sup>19</sup> This result



**Figure 2.** SFG spectra of pure water and after the first addition of [BMIM][BF<sub>4</sub>].



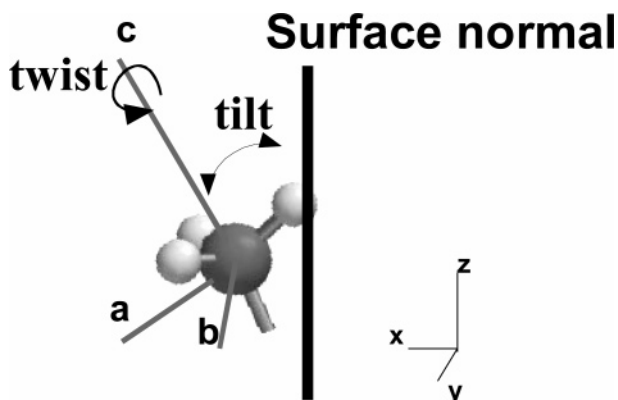
**Figure 3.** SFG spectra of water ionic liquid mixture for 0–1 mole fraction of [BMIM][BF<sub>4</sub>].

compares with the highest concentration at which the water peak was observed in our SFG analysis,  $0.02X_{IL}$ , as seen in Figure 3. The aggregate formation observed by Bowers would induce a change in the interaction of water with the ions, which would explain the disappearance of the water peak in the SFG spectra. Koga also found the formation of ionic liquid clusters, simulating interactions of ions as that of the pure state, wherein the water interacted with the ionic liquid without interacting with other water molecules.<sup>20,21</sup> Cammarata concluded that water can

be considered as free water molecules interacting with the  $BF_4^-$  anion.<sup>12</sup> More importantly Cammarata used a peak at  $3640\text{ cm}^{-1}$  to describe this type of interaction, correlating well with the water peak observed in the SFG spectra. The water peak observed for the mixture in the SFG spectra is at  $\sim 3650\text{ cm}^{-1}$  and can be attributed as a result of the interaction of water with the ionic liquid.

Hamaguchi further performed single-crystal X-ray crystallography and near-infrared Raman spectroscopy of 1-butyroni-





**Figure 4.** Description of the molecular coordinates axes (*a*, *b*, *c*) and surface coordinate axes (*x*, *y*, *z*).

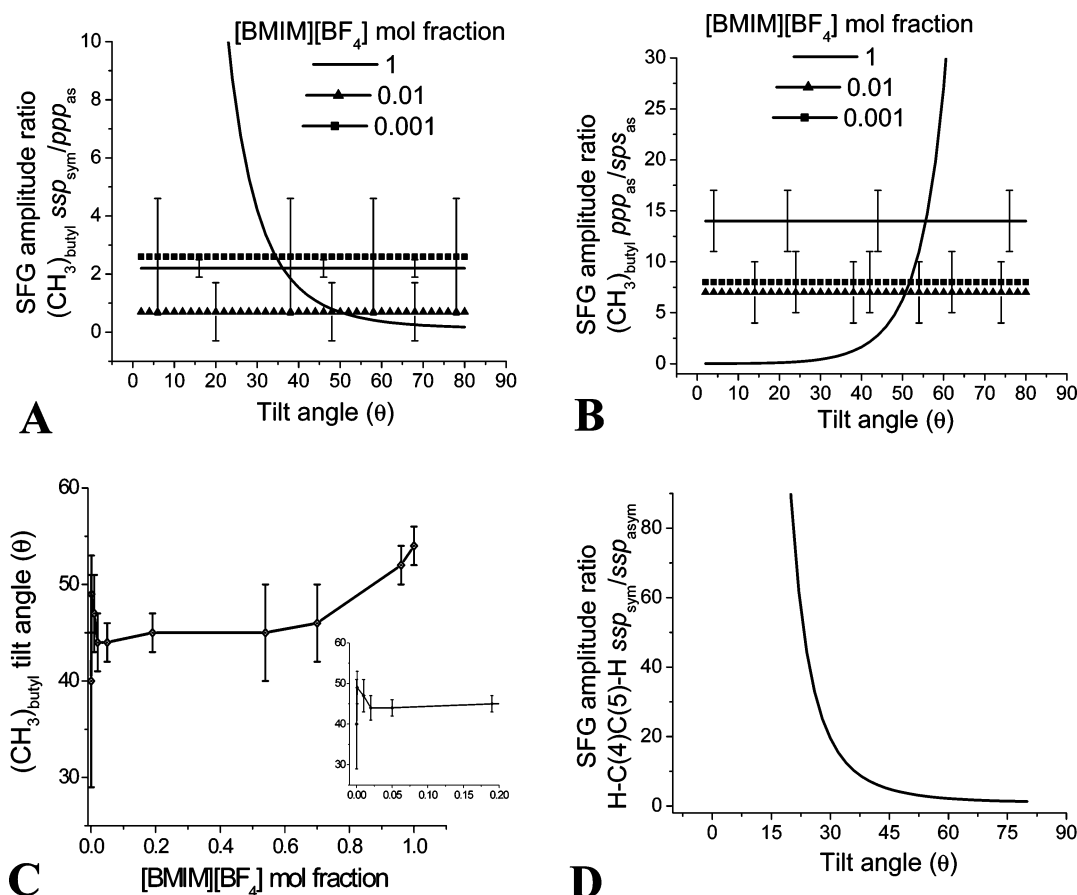
trile-3-methylimidazolium halide, in the presence and absence of water.<sup>35</sup> His finding correlates well with the small changes observed in the SFG for [BMIM][BF<sub>4</sub>], since water was reported to be bonded solely to the anion. In addition, although a change on the conformation of the *n*-butyronitrile side chain was observed, it was reported that this effect was not encountered for [BMIM]<sup>+</sup> ionic liquids.

**Orientation.** Using the same coordinate definition as Hirose,<sup>36,37</sup> the molecular coordinate (*a*, *b*, *c*) is correlated to the surface coordinate (*x*, *y*, *z*) (Figure 4). The *x*–*y* plane is defined as the surface plane with the *x*–*z* plane as the plane of incidence of the laser beams. The *a*–*c* plane corresponds to the  $\sigma_v$  plane for the C<sub>3v</sub> methyl with the *c* axis along the C<sub>3</sub> axis (Figure 4).

With these axis definitions the orientation of the molecule for a  $\delta$ -distribution function is expressed by the tilt ( $\theta$ ) angle of the *c* axis with respect to the *z* axis and the twist ( $\varphi$ ) along *c*. Orientation in the *x*–*y* plane (defined by the  $\chi$  angle) is assumed to be isotropic for liquids and therefore is not referred to in the molecular orientation description.

To determine the molecular orientation at the surface, a simulation of the SFG intensity as a function of the molecular orientation is performed. The values of the refractive indices used for the simulation are 1.43 for the ionic liquid and 1.2 for the interface. The simulated intensity ratios for the different polarization combinations are compared to the experimental intensity ratios, as seen in Figure 5, indicating the molecular orientation as the overlap of both curves. The CH<sub>3</sub> of the butyl chain is described only with respect to its tilt ( $\theta$ ) angle, since a free rotation along the C<sub>3</sub> axis is assumed and a twist angle cannot be assigned.

The cation ring is estimated to be tilted >70° to the surface normal, which is nearly parallel to the surface plane, for the 1X<sub>IL</sub>–0.7X<sub>IL</sub>. This orientation is assigned given a peak is barely observed in the spectra. From the simulation curve there is a limit at which the tilt angle of 70° is hardly distinguishable of that of 90° (see Figure 5D). For lower concentrations of ionic liquid, although the H–C(4)C(5)–H symmetric peak is observed for the *ssp* spectra, it is not present in any of the other polarization combinations. As a result, an accurate orientation could not be determined. Knowing that the *ssp* symmetric peak intensity decreases with the increase of the tilt angle,<sup>33</sup> the weak intensity of the H–C(4)C(5)–H symmetric peak observed can



**Figure 5.** (A) Comparison of simulated and experimental values for symmetric and antisymmetric peaks ratio in the *ssp* and *ppp* spectra, respectively. (B) Comparison of simulated and experimental values for the antisymmetric peaks ratio in the *ppp* and *sp* spectra. (C) Plot of the CH<sub>3</sub> tilt angle as a function of [BMIM][BF<sub>4</sub>] mole fraction. (D) Simulated curve for symmetric and antisymmetric peaks ratio in the *ssp* spectra for the H–C(4)C(5)–H of the imidazolium ring.

be related to a slight change on the ring tilt still close to the surface plane. A small change in the orientation can be supported by comparing the H–C(4)C(5)–H symmetric peak with the previous analysis performed for the water nonmiscible ionic liquids.<sup>13,14</sup> A tilt angle of  $47 \pm 7^\circ$  was reported for the water nonmiscible imidazolium ring when water was introduced into the system.<sup>14</sup> This orientation gave rise to an intense symmetric peak and a weak antisymmetric peak. Therefore, the presence of the weak H–C(4)C(5)–H symmetric peak for [BMIM][BF<sub>4</sub>] is considered an indication that the absorption of water does not have a drastic effect on the imidazolium ring orientation.

A common practice in SFG orientation analysis is the comparison of the symmetric mode in different polarization combinations, but in our results the symmetric peak is solely present in the *ssp* spectra. Previously our group found that comparison of the symmetric with the asymmetric peaks does not provide a consistent orientation analysis. This inconsistency is due to the use of the bond additivity model to describe the molecular hyperpolarizability. This model takes into account the addition of each particular C–H bond but does not take into account the perturbation due to the C–H coupling effect of the antisymmetric modes.<sup>24,38</sup> Therefore, the same vibrational mode should be used when comparing peak intensities in different polarization combinations. That is, a symmetric or antisymmetric mode can only be compared to the same mode at a different polarization combination. A comparison of the *ppp* and *sps* antisymmetric peaks provides a more consistent analysis than when the *ssp* symmetric peak is compared to the *ppp* and *sps* antisymmetric peaks, which do not agree between each other, as seen in Figure 5A,B.<sup>15</sup> This observation was corroborated by performing null angle analysis of CH<sub>3</sub>-(sym).<sup>24,39,40</sup>

From the orientation analysis it is observed that the dilution of the ionic liquid does not have a significant effect in the CH<sub>3</sub> orientation. For a pure ionic liquid an orientation of  $54 \pm 2^\circ$  is found. As the ionic liquid becomes more diluted there is a slight decrease in the tilt angle, as seen in Figure 5C. The first minimum is observed for the  $0.02X_{\text{IL}}$  with an orientation of  $44 \pm 3^\circ$ . As the concentration is decreased, the orientation slightly increases until the last concentration ( $0.0002X_{\text{IL}}$ ), where a second minimum is observed with an orientation of  $40 \pm 11^\circ$  (Figure 5C). The large uncertainty obtained is due to the weak SFG signal.

When this analysis is compared with Kim and Bowers' results, a minimum tilt angle is found at the same concentration at which the surface tension measurements showed a minimum,  $0.02X_{\text{IL}}$ . From SFG analysis, Kim also found a decrease on the CH<sub>3</sub> tilt angle from  $40^\circ$  for a pure ionic liquid to  $30^\circ$  for the  $0.02X_{\text{IL}}$ . Even though the angle found for the methyl group differs from our results, there is a consistent  $10^\circ$  decrease in the tilt angle, as the  $54^\circ$  found in this analysis decreases to  $44^\circ$  for the same concentrations observed by Kim.

From the surface tension measurements performed by Bowers<sup>19</sup> and Kim,<sup>18</sup> the minimum at  $0.016X_{\text{IL}}$  can be related to that at  $0.02X_{\text{IL}}$ , where the water peak is last observed in the SFG spectra as well as the minimum CH<sub>3</sub> tilt angle (Figure 3D and 5C). Bowers attributes this minimum to the formation of aggregates by the cation and Kim ascribes it to the point at which the anion starts populating the surface. Combining Bowers and Kim surface tension results with the SFG spectroscopy, at concentrations lower than  $0.02X_{\text{IL}}$ , the liquid–gas interface is mostly occupied by weakly associated ions interacting with the water molecules. However, as the [BMIM][BF<sub>4</sub>]–water mixture approaches the aggregation concentration of

$0.02X_{\text{IL}}$ , the interaction between the ions dominates the interface, displacing the water from the surface to resemble the surface of pure ionic liquid with the water mostly in the bulk of the liquid.

## Conclusion

Comparing the SFG results here reported with the surface tension measurements found by Bowers, water has no drastic effect on the surface orientation of [BMIM][BF<sub>4</sub>] cation for concentrations from  $0.0002X_{\text{IL}}$  to  $1X_{\text{IL}}$ . Diluting the ionic liquid up to  $0.5X_{\text{IL}}$  presents a similar orientation to that of pure ionic liquid, with a CH<sub>3</sub> tilt angle of  $54 \pm 2^\circ$  when dry and  $46 \pm 4^\circ$  in the presence of water. A sudden minimum in the orientation, for a CH<sub>3</sub> tilt angle of  $44 \pm 3^\circ$ , is found for a concentration of  $0.2X_{\text{IL}}$ . This change occurs at the same concentration at which water occupies the surface, indicating the solvation of the surface ions. Water is found to be interacting with the ionic liquid as a single water molecule identified by the water peak observed at  $\sim 3650 \text{ cm}^{-1}$ .

This analysis presents a preference of water to solvate the ions in the bulk without significantly effecting the surface for the water-miscible [BMIM][BF<sub>4</sub>], differing in the effect of water on nonmiscible ionic liquids.<sup>13,14</sup> This result correlates to the fact that water has a greater effect on the bulk properties of the water-miscible ionic liquids rather than the nonmiscible ones,<sup>41</sup> for which water preferred to solvate the ions at the surface rather than the bulk.

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