POTENTIAL DEPENDANT ANALYSIS OF 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE IONIC LIQUID ON PLATINUM ELECTRODE BY SUM FREQUENCY GENERATION SPECTROSCOPY

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ABSTRACT

Sum Frequency Generation vibrational spectroscopy, SFG, of 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF₆], on a polycrystalline platinum electrode was used to determined the molecular orientation at the liquid-electrode interface under the influence of varied potentials. Cyclic voltammetry was used to identify the electrochemical window of 3V which define the potential range to be analyzed. The peaks intensities were slightly affected as the potential was increased from 0 mV to +1000 mV and more drastically at potentials of -500 mV and +1500 mV. No peaks were observed for a potential of 2000 mV. The changes in the intensity of the peaks for the CH₃(sym) at 2880 cm⁻¹, CH₃(asym) and N-CH₃(sym) at 2970 cm⁻¹ and H-C(4)C(5)-H(sym) at 3170 cm⁻¹ indicate a change of the ionic liquid orientation which is due to the surface charge.

INTRODUCTION

Room-temperature ionic liquids are liquids composed only of ions and are similar to molten salts like NaCl(I). However, a weak interaction between the ions allows them to be liquid at room-temperature.¹ Due to the high ionic conductivity, non-volatility, low vapor pressure, thermal stability, hydrophobicity, and wide electrochemical window that ionic liquids possess, these compounds have become a novel solution to problems encountered with organic solvents and make these molecules a prospective solution to the limitations encountered in electrochemical systems.²,³ Since the electrochemical window of the pure ionic liquids depends on the electrochemical stability of the cation and/or anion, understanding the ion behavior at the electrode surface leads to improvement and implementation of the ionic liquid to the desired system.⁷

Ionic liquids have been used in different systems such as electrochemical cells,²,³,⁸,⁹ fuel cells,¹⁰,¹¹ solar cells,¹²,¹³ liquid-liquid extraction¹⁴,¹⁵, and in biphasic catalysis.¹⁶,¹⁷ These systems depend on the interactions at the interface for their performance; unfortunately, the interfacial properties are not well characterized. To enhance the performance of the ionic liquids and expand their applications it is necessary to understand their behavior at the interface. The electrochemical behavior of haloaluminate ionic liquids have been widely studied, but since their applications are
limited due to their moisture sensitivity the attention has been recently focused on more stable ionic liquids such as those containing imidazolium based cations (Figure 1) and anions such as hexafluorophosphate, tetrafluoroborate, and others.$^7,18-20$

Sum frequency generation vibrational spectroscopy was used to determine the molecular orientation of [BMIM][PF$_6$] on a platinum electrode under potential control. These experiments suggest the imidazolium ring (Figure 1) reorients at the surface in response to the surface charge with the ring orienting more parallel to the surface at negative surface charge.

**BACKGROUND**

The most extensive work on ionic liquid structure near the metal electrode surface is from results in molten salt systems;$^{21}$ specifically, those of liquid mercury, magnesium,$^{22}$ and liquid lead electrodes in contact with metal halide salts.$^{23,24}$ Experimentally, the interfacial structure is inferred from electrocapillarity and capacitance measurements. The results must be interpreted in terms of a model—an equivalent circuit—which can be quite complicated.$^{22}$ The ions in a molten salt near an electrode surface generally exhibit a layered (alternating ion) structure. Surprisingly, the potential of zero charge (PZC) of the metal/molten salt system is similar to the corresponding ions in an aqueous solution.$^{23}$ To our knowledge, there has yet to be any detailed electrochemical impedance spectra (EIS) on room-temperature ionic liquids based on imidazolium cations from which the interfacial structure is deduced.

A molecular-level description on the arrangement of ions at the metal/ionic liquid interface is needed. The problem arises of how does one envision double-layer structure and the potential of zero charge, PZC, in a pure liquid electrolyte. By far, most experimental and theoretical work on the double layer structure is from aqueous systems using models such as Gouy-Chapman-Stern.$^{25-27}$ This model assumes ions are surrounded by solvation shells (of water) and have a non-uniform concentration distribution at the electrode surface that forms the diffuse double layer. This model is barely applicable to concentrated aqueous electrolytic solutions, and is not valid in the ionic liquids where there is no solvent. Further, the results from the molten salts (as stated above) is likely to be only an approximation to the room-temperature ionic liquids discussed in this paper since these are molecular ions and their chemical structure is likely to be important to the bonding and orientation at the surface. The first assumption is ions are directly adsorbed to the surface, as in an inner Helmholtz layer. Also, several layers of ions may extend into the liquid to compensate the excess surface charge. This model makes intuitive sense since the ions in the ionic liquid are relatively ordered due to high coulombic forces. According to the Gouy-Chapman-Stern model, the PZC is considered to be the state where the surface concentration of ions is the same as the bulk concentration.$^{21,27,28}$ However, in a pure ionic liquid with no solvent the ion concentration is essentially the same throughout the system and only in the inner Helmholtz layer is there a possible difference. There are theoretical treatments of capacitance data that show it is possible to have surface excess of ions at an electrode interface in a molten salt.$^{27}$

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**Bulk ionic liquid structure**

Measurements on the bulk structure of ionic liquid are useful to understanding the ion interactions at the electrode surface. From the crystallographic data of 1-alkyl-3-methyl imidazolium salts containing hexafluorophosphate\(^2\), it is known that the anion is centered on the cation ring. The peak shift of the aromatic hydrogen in NMR and IR spectroscopy has been used to study the interaction of ions in the ionic liquid. The results indicate that there is a slight preference for the anion toward the C(2)-H bond, however, the anion interacts with the other ring protons and thus is mostly centered on the imidazolium ring.\(^{31-34}\) Computer modeling of the bulk of the ionic liquid also indicate this relative positioning of the ions.\(^{35,36}\) The ion attraction is dominated by an electrostatic interaction but also influenced by hydrogen bonding and van der Waals, which are determined by the anion identity.

To probe the molecular-level information of the ions at the electrode/ionic liquid interface, a surface specific spectroscopic technique is used. SFG is a second order nonlinear spectroscopy technique sensitive to molecules in a noncentrosymmetric environment. Most molecules in the liquid state are considered to be in an isotropic environment and as a consequence SFG will not be generated in the bulk, but only from the liquid/electrode interface where the centrosymmetry is broken. The theory of SFG will not be covered in detail; instead, the reader is referred to different reviews.\(^{38-40,41-44}\) The intensity of the SFG signal is proportional to the square of the induced polarization:

\[
E_{\text{SF}} \propto P^{(2)} = \left| \chi^{(2)}E_{\text{vis}}E_{\text{IR}} \right| \quad \text{Equation 1}
\]

\[
\chi^{(2)} = \chi_{\text{res}}^{(2)} + \chi_{\text{nr}}^{(2)} \quad \text{Equation 2}
\]

\[
\chi_{\text{res}}^{(2)} = \sum \frac{N\langle \beta^{(2)} \rangle}{(\omega_{\text{IR}} - \omega_q + i\Gamma_q)} \quad \text{Equation 3}
\]

where \(E\) refers to the electric field of the visible and infrared incoming beams and \(\chi^{(2)}\) is the second order susceptibility tensor which relates the interface response to the input light fields. The \(\chi_{\text{nr}}^{(2)}\) arises from the non-resonant background of the surface and the \(\chi_{\text{res}}^{(2)}\) contains the molecular hyperpolarizability, \(\beta^{(2)}\), with the Raman polarizability and the IR dipole transition, which are averaged over the molecule orientation indicated by the brackets, \(\langle\rangle\). \(N\) indicates the number of molecules contributing to the SFG signal, \(\omega_{\text{IR}}\) and \(\omega_q\) refers to the frequency of the incoming IR and the normal mode, respectively, and \(\Gamma_q\) is the damping constant for the \(q\)th vibrational mode.

**EXPERIMENTAL**

**Sample synthesis and preparation**

The synthesis and characterization of 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF\(_6\)], is similar to that published by Grätzel et al. 1-methylimidazole is mixed with 1-chlorobutane in a 1:1.1 molar ratio and refluxed under
nitrogen at 65°C for 52 hrs. The 1-butyl-3-methylimidazolium chloride, [BMIM][Cl], is washed three times with ethyl acetate and dried under vacuum at a temperature of ~70°C. [BMIM][Cl] is then mixed with the acid of the desired anion in a 1:1.1 molar ratio and stirred for 24 hrs. The final [BMIM][PF₆] compound is simply washed with water until no chloride is detected in the water. After [BMIM][PF₆] is dried under vacuum at a temperature of ~70°C, the chloride concentration is detected directly in the ionic liquid using an ion selective electrode; for a chloride concentration ≤ 18 ppm.

All chemicals are from Aldrich and used without further purification. The water is deionized in a Millipore A10 system with a resistivity of >18 MΩ·cm and organic concentration of < 3 ppb. H-NMR, LC-MS, and FT-IR are used for characterization, and an ion selective electrode was used for the chloride determination. Cyclic voltammetry is used to estimate the water concentration (Figure 2).

The working electrode is made of polycrystalline platinum 10 mm thick by 0.25 inch in diameter and is prepared by flame annealing in a hydrogen-air flame for ~10 minutes. The electrode is cooled in a glass chamber flowing with argon gas for 10 minutes. Immediately upon removal from the cooling chamber a drop of ionic liquid is placed on the surface of the Pt electrode. The electrode is then introduced into the SFG electrochemistry cell. The procedure is analogous to the preparation of well-characterized electrodes used in aqueous electrochemistry by Clavilier where it produces a clean surface as determined by CV and UHV techniques.

The SFG-electrochemistry cell is an important development to accomplishing these experiments. The cell is vacuum-tight to >2×10⁻⁵ Torr, which is possible because the Pt working electrode is held in the cell with a ¼ inch Teflon® Swage fitting attached to the Kel-F shaft, (Figure 3). The entire cell is fabricated of only inert polymers (Kalrez o-rings, Teflon, or Kel-F parts) and glass, permitting aggressive cleaning in 50/50 nitric acid/sulfuric acid mixtures. The cell is thoroughly rinsed in water from a Millipore A10 water system. The counter electrode is a Pt wire and the reference is Ag/AgBF₄ or Ag/AgPF₆ that has a potential of ~ -200 mV vs. NHE (Normal Hydrogen Electrode).

Once the electrode with the ionic liquid drop on it is introduced into the cell, the cell is evacuated to its base pressure for ~4 hours at 60-70°C. Next, a vessel containing the ionic liquid is pressurized to just over an atmosphere pressure with argon gas. A stopcock connecting the vessel to the SFG cell is opened transferring the ionic liquid into the SFG cell without contact to air. The cell is able to maintain the ionic liquid in an anhydrous state for approximately 10 hours, as determined by cyclic voltammetry. The cell allows for control of potential during the SFG experiment as well as the measurement of the CV.

Spectroscopy
An Ekspla 20 Hz picosecond Nd:YAG laser is used to pump the optical parametric generation/amplification system, OPG/OPA (LaserVision). The OPG/OPA is composed of a set of KTP/KTA crystals which are used to generate the second harmonic (532 nm) and the tunable infrared beams (2000-4000 cm⁻¹). The visible beam is at an angle from the surface normal of 33° and the infrared was at an angle of 38° at the ionic liquid/Pt interface with energy densities of 30 mJ/cm² and 20 mJ/cm², respectively.

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Polarization control of the visible beams is accomplished by a $\lambda/2$ waveplate anti-reflection coated for 532 nm (CVI). The tunable infrared polarization was changed using a zero-order phase retardation plate ($\lambda/2$) supplied by ALPHALAS GmbH. Glan-Laser polarizers (CVI) are used for polarization selection in these experiments.

Optical access to the electrode surface is possible in the thin-layer cell design. The laser beams pass through an infrared quartz window, through a thin layer of ionic liquid (~ 10 $\mu$m thick), then to the Pt electrode. The generated SF signal is reflected out of the cell to the detection system described below. To verify that the SF signal is from the Pt/ionic liquid interface and not the infrared quartz/ionic liquid interface, two tests are performed. First, the Pt electrode is backed away from the window, -0.5 mm, so the infrared is completely adsorbed by the ionic liquid. Under these conditions there is no SFG detected using $ssp$ or $ppp$ polarizations. Second, the SFG signal exhibits a potential dependence, which only occurs at the Pt/ionic liquid interface.

RESULTS

The SFG spectra of [BMIM][PF$_6$] for $ppp$ and $ssp$ polarization are shown below in Figure 4 and 5 respectively. Qualitatively, the spectra are relatively complicated. There are several resonances observed as well as an intense non-resonant background, therefore, only the major peaks in the spectrum are assigned and used in the analysis. The results exhibit several vibrations in the C-H stretching region that are polarization and potential dependent. Peaks intensities were slightly affected as the potential was increased from 0 mV to +1000 mV and more drastically at potentials of -500 mV and +1500 mV.

In the $ppp$ spectrum (Figure 4), six resonances are observed. Peaks at 2870 cm$^{-1}$ and ~2935 cm$^{-1}$ are assigned to the CH$_3$(sym) and the N-CH$_3$(sym) of the butyl chain$^{48-50}$ while the peak for the CH$_2$(asym) is at ~2910 cm$^{-1}$. It is observed how the peak intensity changes as different potentials are applied. The imidazolium ring peak H-C(4)C(5)-H(sym) not only changes its intensity but also the peak shifted from 3200 cm$^{-1}$ to ~3170 cm$^{-1}$ when the potential changed from +1000 mV to -500 mV. The C(2)-H vibration is also observed at 3130 cm$^{-1}$ for an applied potential of -500 mV but seems to drastically decrease its intensity and shifted to ~3100 cm$^{-1}$ when a potential of +1000 mV is applied. The anion-cation interaction peak is also present in the spectra around 3030 cm$^{-1}$.

For the $ssp$ polarization the spectrum has four peaks. The CH$_3$(sym) resonance is at 2870 cm$^{-1}$ while resonances at 2915 cm$^{-1}$ and 3190 cm$^{-1}$ are from the CH$_2$(asym) and the H-C(4)C(5)-H(sym), respectively (Figure 5). The resonance at 2965 cm$^{-1}$ is due to the CH$_3$(asym) on the butyl chain.$^{48-30}$

The cyclic voltammetry of the ionic liquid, shown in Figure 2, is similar to the CV reported by Xiao and Johnson,$^8$ and Conboy et al.$^{51}$ and indicates there is no redox processes at these potentials. The potentials selected for the analysis are kept well below the oxidation and reduction limits.
DISCUSSION

The peaks in the SFG spectra indicate that the imidazolium ring is oriented with the C2 axis (Figure 1) along the surface normal. These results seem consistent with recent FTIR experiments.52

Orientation analysis is performed by the same method as that used by Hirose et. al. 41-44 Simulations of peak intensity vs. tilt angle (of the C2 axis) are plotted for several twist angles for [BMIM][PF6] (Figure 6). The H-C(4)C(5)-H peak at 3190 cm⁻¹ is used to determine orientation of the imidazolium ring. The intensity ratio (Table 1) for the H-C(4)C(5)-H of the imidazolium ring experimentally determined in ppp/ssp spectra are also plotted with the simulation. The intersection of the experimental ratio with the calculated ratio indicates the possible tilt and twist angles for the imidazolium ring. For this ionic liquid the tilt orientation is relatively constant from -500 mV to +1000 mV and is about 12-26° at -500 mV and 23-34° at +1000 mV. However, the twist angle changes dramatically from -0-35° at -500 mV to about 65-90° at +1000 mV. (Figure 6)

For a completeness of the orientation analysis the orientation of the butyl chain was also determined. The orientation found for the methyl group suggests the butyl chain is more parallel to the surface >60° at +1000 mV, while it is less than 40° at -500 mV. This indicates that as the imidazolium ring twists from parallel to perpendicular at the surface the alkyl chain projects toward the bulk of the ionic liquid with more degrees of freedom.

This interpretation assumes a delta function distribution and that the oriented cations do not form more than one monolayer, i.e. a Helmholtz layer at the surface. From previous electrochemical studies using capacitance and electrocapillarity, this model is reasonable.53

The PZC of 1-ethyl-3-methylimidazolium cation with a combination of different anions was determined by Koch et. al,53 and found to be similar for the different ions combinations with a value around ~0.5 V vs. Ag/AgCl (~Ag/AgPF6). Therefore a PZC of -0.5V for [BMIM][PF6] is used to estimate the coverage of imidazolium on the electrode from cyclic voltammetry. By integrating the double-layer current from PZC to a given potential in the Pt electrode, the charge accumulation is estimated. For [BMIM][PF6], integration from ~0.5 V to 1V is approximately 0.9x10⁻⁴ C/cm², assuming an atomically flat surface (otherwise a roughness factor of 2-3 should be applied)25. This charge value is compared to those calculated for [EMIM][BF4] from differential capacitance and found to be in agreement. The capacitance at the Hg/[EMIM][BF4] is on the order of 1x10⁻⁵ F/cm²,53 which is a surface charge of about 1x10⁻⁴ C, or 0.5 monolayer of electric charge (~2x10⁻⁴ C/monolayer). Using this estimate on the amount of surface charge it seems reasonable to envision that the ions adsorb to the surface as a single layer and multilayers are not present at the surface. This is consistent with a Helmholtz model of the interface.

The SFG data suggests that at high positive potential the cation, [BMIM]⁺, is tipped with the imidazolium ring along the surface normal and the ring becomes more parallel to the surface at more negative potentials (Figure 8). Previous results have
shown the cation charge is mostly centered on the aromatic ring $^{54,55}$ and thus this would be the lowest energy situation considering the electrostatic energy only. To screen the charge, the ring orients parallel to the surface. At positive surface charge the anion will move into the inner Helmholtz layer for charge compensation and the cation will then occupy the outer Helmholtz layer. This model suggests that the cation is tipped along the surface normal to make room for the anion to approach the surface at potentials positive of PZC.

In the case of negative surface charge, the imidazolium ring is relatively parallel to the electrode surface, presumably to screen the surface charge. However, when the surface charge becomes positive the ring tips from the surface to allow space for the anion to enter the Helmholtz layer and shield the electrode charge (Figure 8). For [BMIM][PF$_6$] the tilt angle is not changing as a function of potential, but instead is changing with respect to the twist angle. These results suggest that [BMIM]$^+$ changes its twist angle to allow [PF$_6$]$^-$ access the surface.

CONCLUSION

Sum frequency generation has been used to study the adsorption and orientation of ions in a room-temperature ionic liquid at the platinum electrode surface. The results indicate that the cation has a preferred orientation that changes as a function of applied potential. At relatively negative surface charge the imidazolium ring is nearly parallel to the surface, while it twist along the surface normal at more positive potential.

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Figure 1 Structure of 1-butyl-3-methyl imidazolium cation, [BMIM]$^+$, with numbering scheme and pseudo C2 symmetry axis of the imidazolium ring.

Figure 2 Cyclic voltammetry of neat [BMIM][PF$_6$] on Pt electrode. Scan rate = 100 mV/sec.
Figure 3 Thin-layer electrochemical cell for SFG studies. The reflected IR is sent to the reference channel for normalization of the SFG signal.
Figure 4: SFG ppp polarized spectra of [BMIM][PF6] at the platinum electrode under different potentials. Reference potential is Ag/AgPF6. Line is a fit to the line shape equation.
Figure 5: SFG ssp polarized spectra of [BMIM][PF6] at the platinum electrode under different potentials. Reference potential is Ag/AgPF6. Line is a fit to the line shape equation.
Table 1: Amplitude values for peaks in the SFG spectrum of [BMIM][PF₆] on Pt electrode at -500 mV and +1000 mV vs. Ag/AgPF₆ reference. The number in parentheses is the percent error of the amplitude.

|          | -500mV | +1000mV |
|----------|--------|---------|
| CH₃(sym) | 3.1(32)| 2.5(31) |
| CH₁ (asym) | 0.004(5000) | 2.0(70) |
| N(3)CH₃(sym) | 3.5(45) | 1.9(75) |
| CH₃(asym) | 0.018(722) | -0.86(100) |
| C(2)-H | 15(13) | 27(10) |
| H-C(4)C(5)-H | 13(10) | 23(3) |
| NR | -2.1 | -1.5 |

Figure 6: Simulation of SFG signal intensity ratio ppp/ssp for the H-C(4)C(5)-H symmetric stretch for [BMIM][PF₆]. (■) are the experimentally determined ratio.
Figure 7: Orientation analysis of the terminal CH3 group on the butyl chain of [BMIM][PF6]. Solid line is the theoretical curve. Data points (■,▲) are experimentally determined ratio.

Figure 8: Graphic of the molecular orientation suggested for the changes in potential from -500 mV to +2000 mV.