

Probing Electric Fields at the Ionic Liquid–Electrode Interface Using Sum Frequency Generation Spectroscopy and Electrochemistry

Steven Baldelli*

University of Houston, Department of Chemistry, Houston, Texas 77204

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The arrangement of ions at the platinum electrode in the room-temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate has been determined using sum frequency generation vibrational spectroscopy (SFG), electrochemical impedance spectroscopy (EIS), and the vibrational Stark effect. The results indicate that CO adsorbed on the Pt electrode has a Stark shift of 30–35 cm^{-1}/V in the ionic liquid. The potential of zero charge (PZC) of the ionic liquid–Pt system is approximately –500 mV (vs Ag wire), with a capacitance of 0.12 F/m^2 . Further, polarization-dependent SFG experiments suggest the ions reorganize at the surface depending on the electrode charge. In combination, all these results indicate that the ions of a neat ionic liquid are organized in a Helmholtz layer at the electrified metal electrode interface.

Room-temperature ionic liquids are promising electrolytes for electrochemical systems including batteries, light-emitting diodes –OLED, super capacitors, fuel cells, and solar cells.^{1–13} However, while the interface between metal electrodes and dilute aqueous electrolytes has been studied extensively,^{14–18} there are no established molecular-level models for the ionic liquid–metal interface.^{17,19–23} This letter presents results using sum frequency generation (SFG) vibrational spectroscopy and electrochemical impedance spectroscopy (EIS) to probe the organization of ions at the room-temperature ionic liquid–platinum interface. The results suggest that the arrangement of ions at the interface of an ionic liquid and metal electrode is one layer thick (i.e., the Helmholtz layer).

The structure of the electrified interface is a very important topic in physical and surface chemistry because of its ubiquitous appearance in nature. Aqueous electrolyte–metal interfaces have been studied in detail including the classic studies of Grahame, Frumkin, and Gouy. However, models such as Gouy–Chapman–Sterns that are somewhat successful in dilute aqueous electrochemistry are not at all appropriate for describing the ionic liquid–metal interface because of the strong Coulombic forces involved.^{16,17,21,22,24–26} Since the structure at the interface dramatically influences the electron-transfer reaction, detailed knowledge of the interfacial layer is required.²⁷ Information such as electric field strength, double layer thickness, and orientation of species at the interface is very helpful in describing this system.

One method used to probe this interface is differential capacitance (C).²⁸ With this technique, the interface is described as a parallel plate capacitor where one plate is the metal electrode and the other is the double layer/bulk liquid electrolyte boundary. Since the potential drop occurs across the double layer, the capacitor thickness is equal to the double layer thickness (d), so that $C \propto 1/d$.

The vibrational Stark effect is an effective probe of local electric fields, E_{loc} , at the surface. Field strengths on the order of 10^6 V/cm are common, since the voltage drop is ~ 1 V and the double layer thickness (d) is < 1 nm. The intense fields cause a shift of vibrational frequency as a function of field strength. The double layer thickness can be estimated by probing the electric field at the interface. The strength of the electric field in the double layer is determined by observing the vibrational Stark effect on CO adsorbed to the Pt electrode.²⁹ The magnitude of the electric field is related to the distance between the plates and the electrode potential, (ϕ). Since the CO vibrational frequency (ν_{CO}) is also related to the strength of the electric field, by measuring $d\nu_{\text{CO}}/d\phi$, the thickness of the double layer can be estimated.

The SFG spectrometer at the University of Houston has been described previously.³⁰ The results presented here are for ppp-polarized light fields, where the index indicates the orientation of the electric field vector of light, where p-polarized is in the plane of incidence. The potential is set to the desired voltage and SFG spectra are acquired: three scans at 1 cm^{-1}/s , averaged and corrected for variations in laser energy. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄] (see inset Figure 2), is synthesized in this lab³⁰ ($[\text{Cl}^-] < 20$ ppb, $\text{H}_2\text{O} < 10^{-7}$ mole fraction). Cyclic voltammetry (CV) indicates no Faradaic current between –1000 mV and +2000 mV vs Ag quasireference electrode (QRE). The polycrystalline platinum electrode and electrochemical cell are prepared as previously reported.³⁰ Carbon monoxide is adsorbed at –200 mV for 20 min.

The SFG spectra for CO adsorbed to the Pt electrode in the neat ionic liquid [BMIM][BF₄] are presented in Figure 1. The CO peak between 2000 and 2150 cm^{-1} is due to top-site coordinated CO, CO bonded to one Pt atom.³¹ The frequency shift of ν_{CO} is from ~ 2040 cm^{-1} at –800 mV to ~ 2110 cm^{-1} at +1600 mV, ~ 30 – 35 cm^{-1}/V . This tuning rate ($d\nu_{\text{CO}}/d\phi$) is consistent with previous studies in aqueous and nonaqueous

* SBaldelli@UH.EDU.

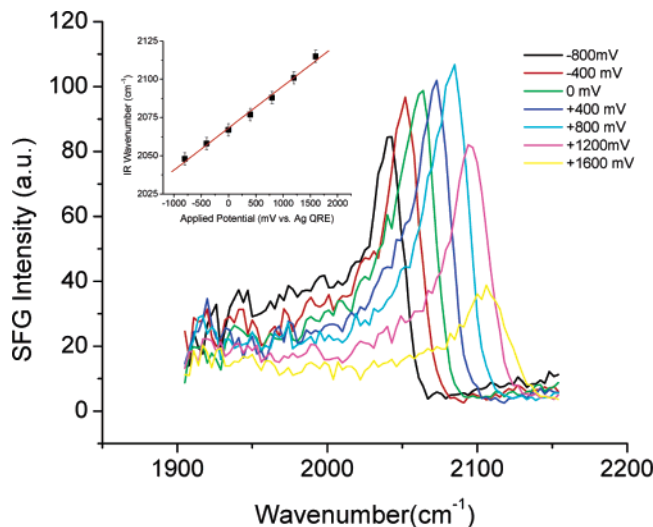


Figure 1. SFG spectra of CO on Pt electrode in [BMIM][BF₄] ionic liquid electrolyte. Potential range is -800 mV to $+1600$ mV vs Ag wire (QRE). Inset: plot of peak position vs electrode potential.

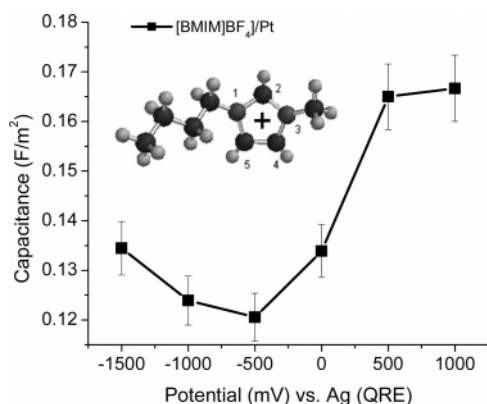


Figure 2. Capacitance vs applied potential for neat [BMIM][BF₄]-Pt system. Inset: Structure of cation [BMIM]⁺.

electrolyte.^{32–37} The intensity changes as a function of potential reaching a maximum near $+800$ mV; this is also due to the Stark effect.³⁸

The EIS measurements have been conducted to obtain the double layer capacitance information. Capacitances vs potential measurements for the [BMIM][BF₄] platinum system are shown in Figure 2. The minimum is approximately -500 mV vs Ag (QRE), which suggests this is the potential of zero charge^{21,22} and is where the double layer thickness is at a minimum.³⁹

By combining the information from the vibrational Stark effect, EIS/capacitance data, and previous results from the orientation of the cation, [BMIM]⁺, on platinum, a model of the interface is proposed.

The Stark tuning rates observed here are compared with previous calculations and measurements. CO on transition-metal surfaces in aqueous electrochemical systems (i.e., CO/Pt(111)) typically has a Stark tuning rate of $d\nu_{\text{CO}}/d\phi = 30\text{--}45$ cm⁻¹/V,^{34,40–43} which corresponds to a double layer thickness near 3 Å.⁴⁴ For CO/Pt in ionic liquid, the measured $d\nu_{\text{CO}}/d\phi$ is 33 ± 3 cm⁻¹/V (Figure 1, inset). The local electric field Stark effect $d\nu_{\text{CO}}/dE_{\text{loc}}$ for CO/Pt is $\sim 1 \times 10^{-6}$ cm⁻¹/(V/cm),⁴⁰ thus by relating the local electric field to the applied voltage, a double layer thickness is estimated^{38,44,45}

$$\left(\frac{d\nu_{\text{CO}}}{dE_{\text{loc}}} \frac{d\nu_{\text{CO}}}{d\phi} \right) = d = 3.3 \times 10^{-10} \text{ m}$$

This suggests the double layer is one-ion-layer thick. Capacitance data ($C = 0.12$ F/m²) also indicate a one-ion-thick double layer where the interface is modeled with a Helmholtz capacity. The $\epsilon \approx 7$ and ϵ_0

$$d = \frac{\epsilon\epsilon_0}{C} = 5 \times 10^{-10} \text{ m}$$

are the relative and vacuum permittivities, respectively, and d is the distance between the capacitor plates (double layer). The value of ϵ is chosen on the basis of dielectric saturation near the metal surface where the dielectric constant is approximately an order of magnitude less than the bulk dielectric constant.⁴⁶ The dimensions of [BMIM]⁺ are approximately $10 \times 4 \times 1$ Å³ in the conformation shown in Figure 2 (inset).⁴⁷ These results suggest that the double layer structure at the electrode surface of an ionic liquid is very thin, one-ion-layer thick, and is essentially a Helmholtz-type layer. This is supported by recent capacitance measurements of Kiszka of simple molten salts.²³ The results from SFG and EIS rule out a multilayer structure of ions, since this would increase d , decreasing the capacitance, and consequently leading to a decrease in the magnitude of the Stark effect.

For example, if another layer of ions was organized in the double layer (L1), the capacitance would add in series and $1/C_{\text{total}} = 1/C_{\text{Helmholtz}} + 1/C_{\text{L1}}$. The total capacitance would be 0.072 F/m², and the corresponding thickness is about 1 nm. This would give a Stark shift of 10 cm⁻¹/V, much lower than the observed value. This supports the model that the double layer is one-ion-layer thick.

Molecular dynamics calculations by Madden and Lanning on the screening of surface charge by a molten salt indicate that the potential drops to a very low value close to the surface.¹⁹ This is also consistent with the results here, since the potential drop is complete within $3\text{--}5$ Å of the metal surface. It is interesting to note that the Stark effect of CO/Pt observed here is similar to that in aqueous and nonaqueous systems,^{37,48–51} despite the very different nature of the ionic liquid electrolyte. No water is detected in this system either by SFG or CV.

These results correlate to the previous study of cation, [BMIM]⁺, orientation at the platinum electrode. In that study, the C_2 axis of the cation adopts a tilt angle from the surface normal of $\sim 60^\circ$, which is consistent with the Helmholtz model for single-ion-layer adsorption.³⁰ The situation would change at higher surface charge densities where multilayers of alternating charge are possible.¹⁹

SFG and EIS measurements are used to investigate the structuring of ions at the surface of a metal electrode and room-temperature ionic liquid. The results indicate a Helmholtz layer one ion thick.

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