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**Interfacial Fields Measured by Vibrational Sum Frequency Generation at  
Electrode-Electrolyte and Electrode-Ionic Liquid Interfaces**

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# Interfacial Fields Measured by Vibrational Sum Frequency Generation at Electrode-Electrolyte and Electrode-Ionic Liquid Interfaces

Jahan Dawlaty, University of Southern California

## Publications Supported by this Award:

1. Interfacial Polarization and Ionic Structure at the Ionic Liquid–Metal Interface Studied by Vibrational Spectroscopy and Molecular Dynamics Simulations, Matthew J. Voegtle, Tanmoy Pal, Anuj K. Pennathur, Sevan Menachekanian, Joel G. Patrow, Sohini Sarkar, Qiang Cui, and Jahan M. Dawlaty, *J. Phys. Chem. B*, 125, 10, 2741–2753 (2021).
2. Strong Propensity of Ionic Liquids in Their Aqueous Solutions for an Organic-Modified Metal Surface, A. Pennathur, M. Voegtle, S. Menachekanian, J. Dawlaty, *J. Phys. Chem. B*, 124, 34, 7500–7507 (2020).
3. Electric Fields at Metal-Surfactant Interfaces: A Combined Vibrational Spectroscopy and Capacitance Study, S. Sarkar, A. Maitra, S. Banarjee, S. Thoi, J. Dawlaty, *J. Phys. Chem. B*. (2020).
4. Electrodes as Polarizing Functional Groups: Correlation Between Hammett Parameters and Electrochemical Polarization, S. Sarkar, J. Patrow, M. Voegtle, A. Pennathur, J. Dawlaty, *J. Phys. Chem. C*, 123, 8, 4926 (2019).

## Abstract

The goal of this project was to understand the details of interfacial electric fields at the metal electrolyte junctions, with particular emphasis on ionic liquids (ILs). The main experimental approach was to use vibrational Stark shift molecules tethered on the metal as probes of the interface. The most common probe used in our studies was benzonitrile, whose nitrile stretch served as the Stark probe. We achieved four goals using this approach. First, in our study of IL-metal junction we found out that the measured electric fields depended on the size of anions within a family of ILs. Further computational work revealed that this arises due to a balance between packing density and surface electrostatics. Second, we found that ILs outcompete water by a large margin for adhesion to a metal. We noted that in mixtures of IL and water, the mole-fraction of bulk water had to exceed very large values (>0.95) for the water to overwhelm and dissolve the interfacial structure. Third, we studied the electric field at the junction of metals and surfactants, which are closely related to ILs. We found out that the solvation structure of the surfactant head is crucial in determining the magnitude of the interfacial field. Finally, in a more fundamental work, we established a connection between the organic chemistry concept of Hammett parameter and interfacial polarization using benzonitrile Stark shift probes. All of these projects have given us a more molecular understanding of the ionic structure and interfacial fields at metal-IL junctions, and can help in designing tailored ILs for electrochemical applications.

## Introduction

Understanding the details of electric fields at interfaces is significantly important for several branches of chemistry, physics, and engineering. For example, electric fields at p-n junctions is at the heart of photovoltaic action, fields at electrode-electrolyte interfaces are expected to influence the kinetics and thermodynamics of electrochemical and thermochemical reactions, and fields within enzyme cavities are hypothesized to influence reaction barriers. With this in mind, our goal was to study the electric field at electrode-electrolyte junctions using vibrational spectroscopy of Stark-shift probes that were installed at such junctions. We implemented the above approach to three problems: metal-ionic liquid (IL) junction, metal-IL junction in the presence of water, and metal-surfactant junctions. The highlights of our findings are summarized below.

### Electric Fields at Metal-Ionic Liquid Junction: The Role of Ion Size and Ion Packing

Ionic liquids (ILs) have both fundamental and practical value in interfacial science and electrochemistry. However, understanding their behavior near a surface is challenging because of strong Coulomb interactions and large and irregular ionic sizes, which affect both their structure and energetics. To understand this problem, we used a combined experimental and computational study (joint with Prof. Qiang Cui, Boston University) using a vibrational probe molecule, 4-mercaptobenzonitrile, inserted at the junction between a metal and a variety of ILs. The vibrational frequency of the nitrile in the probe molecule reports on the local solvation environment and the electrostatic field at this junction. Within

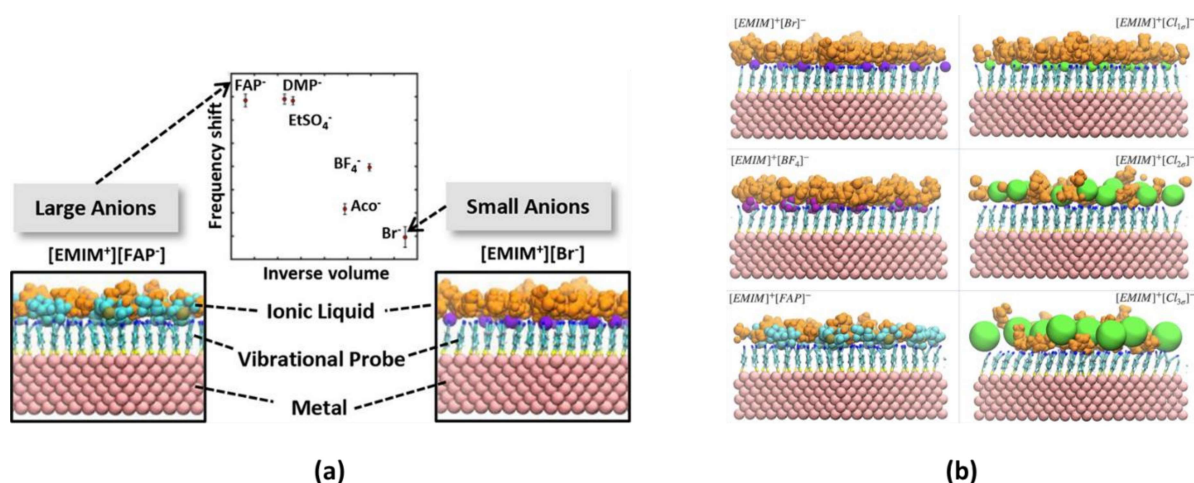


Figure 1. Summary of our results on ionic structure and interfacial polarization at the junction of a metal and ionic liquids. (a) We used a nitrile vibrational probe between a metal and a number of ionic liquids with varying anion sizes. We discovered that frequency shift (and correspondingly the electric field) scales inversely with anion sizes. This observation could not be explained by mean-field response of the ionic liquids, and required molecular dynamics simulation of the interface. (b) MD simulations of the interface revealed that anions intercalate within the vibrational probe monolayer. Smaller anions intercalate deeper, while larger ones can not. This results into denser packing of cations for smaller anions near the surface and correspondingly a larger frequency shift. This intricate balance between electrostatics and packing is relevant for engineering the interfacial field for driving chemical reactions.

the ethylmethyl imidazolium (EMIM<sup>+</sup>) cation family of ILs, we varied the anions over a range of sizes and types (figure 1). Complementing our surface spectroscopy, we also ran molecular dynamics simulations of these interfaces to better understand the ionic structures that produced the measured fields. The magnitude of the frequency shifts, and thereby fields, shows a general correlation with the size of anions, with larger anions corresponding to smaller fields. We found that the source of this correlation is partial intercalation of smaller anions into the probe monolayer, resulting in tighter packing of ionic layers near the surface. Larger anions reduce the overall lateral ion packing density near the surface, which reduces the net charge per unit area and explains the smaller observed fields. The insight from this work is important for developing a fundamental picture of concentrated electrolytes near interfaces and can help with designing ILs to create tailored electric fields near an electrode.

### Threshold for Breakdown of Ionic Structure by Water:

Understanding ionic structure and electrostatic environments near a surface has both fundamental and practical value. In electrochemistry, especially when room temperature ionic liquids (ILs) are involved, the complex ionic structure near the interface is expected to crucially influence reactions. We found evidence that even in dilute aqueous solutions of several ILs, the ions aggregate near the surface in ways that are qualitatively different from simple electrolytes. We used a vibrational probe molecule, 4-mercaptobenzonitrile (MBN), tethered to a metal surface to monitor the behavior of the ionic layers. The characteristic nitrile vibrational frequency of this molecule has distinct values in the presence of pure water ( $\sim 2232\text{ cm}^{-1}$ ) and pure IL (for example,  $\sim 2226\text{ cm}^{-1}$  for ethylmethylimidazolium tetrafluoroborate, [EMIM][BF<sub>4</sub>]). This difference reflects the local electrostatic field and the hydrogen-bonding variations between these two limiting cases. We tracked this frequency shift as a function of IL concentration in water all the way from pure water to pure IL. We report two important findings. First, only one nitrile peak is observed for the entire concentration range, indicating that at least on the length

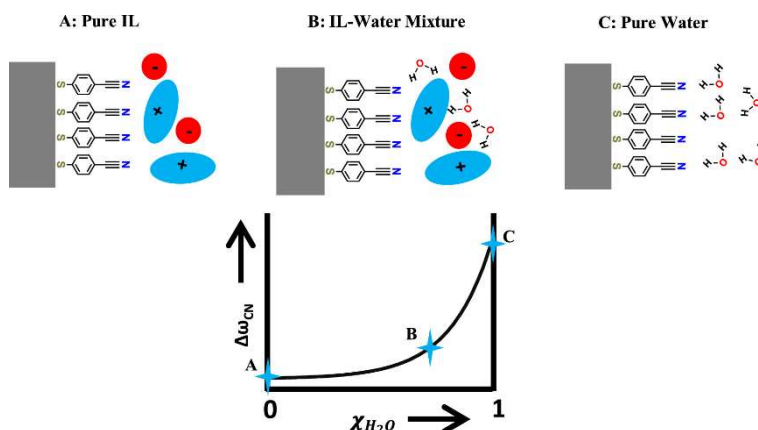


Figure 2. The concept of using a vibrational probe to investigate surface hydration. The CN stretch is sensitive to water (due to hydrogen bonding) and exhibits a blue shift, while it always red-shifts in the presence of ILs. Therefore, tracking the CN stretch is a measure of hydration of the interface. We find that increasing the mole fraction of water in the bulk does not result into a linear increase in the frequency shift of the CN at the interface. Rather, the ionic structure at the interface resists introduction of water until a threshold high concentration is reached (as shown in figure 3).

scale of the probe molecule water and ILs do not phase separate within the interface, and no heterogeneously distinct electrostatic environments are formed. Second, and more importantly, we find that even up to a significant mole fraction of bulk water ( $x \sim 0.95$ ), the nitrile frequency does not change from that indicative of a pure IL for [EMIM][BF4], indicating preferential aggregation of the ions near the surface. Because this behavior is very similar to surfactants, we chose an imidazolium cation with a longer side chain which resulted in behavior expected from a surfactant, with a preferential layer of the ions on the surface even in dilute water solutions ( $x \sim 0.995$ ). This observation indicates that even those ILs that are not nominally categorized as surfactants have a strong tendency to aggregate at the surface. Because ILs serve as electrolytes in a range of electrochemical reactions, including those requiring water, our results are likely useful for mechanistic understanding and tuning of such reactions.

#### Interfacial Fields at Metal-Surfactant Junctions:

Surfactants are known to influence electrochemical selectivity and reactivity. A prime example is suppression of the parasitic hydrogen evolution during CO<sub>2</sub> reduction by cationic surfactants. The origin of this selectivity is debated, but one of the hypotheses is that the interfacial electric field that is generated by the surfactants heads prevents or competes with the delivery of the positively charged proton carriers such as hydroniums to the surface. Given the importance of this selectivity, we sought to measure and model such interfacial fields. We used our nitrile Stark shift probes tethered on the surface of an electrode and in contact with an aqueous surfactant solution to measure such fields.

Our major finding was that the quaternary ammonium family induced the largest negative fields, while the anionic surfactants with sulfate head groups exerted a smaller positive field (figure 1). The neutral surfactants did not show a change. The reason for the anionic surfactants smaller field is due to the stronger solvation of the head group. At a high bulk surfactant concentration, the surface field reaches a terminal value, suggesting the formation of a full layer, which is also supported by impedance spectroscopy.

An important insight into problem came from a simple electrostatic model of the interfacial field. The fields in the vicinity of surfactant layer within distances smaller than the surfactant-surfactant separation is inhomogeneous. Therefore, a continuum capacitor model for the head-group interaction

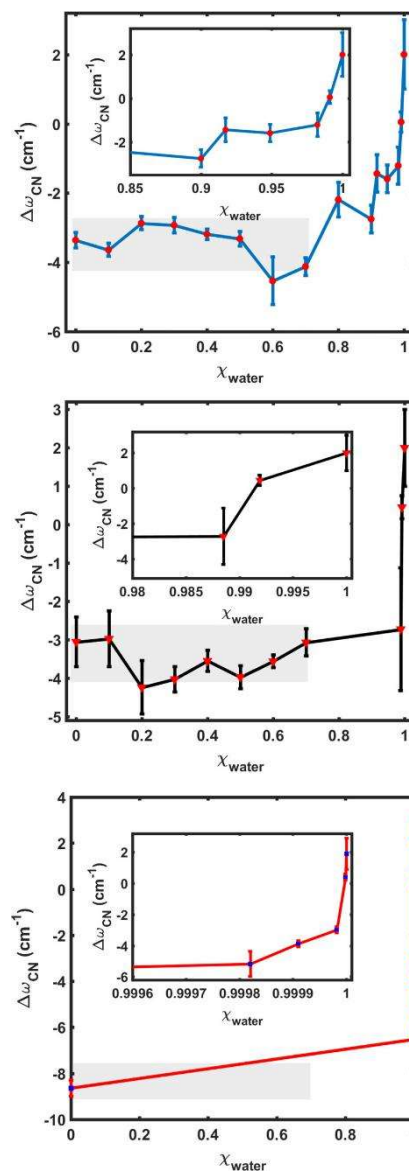


Figure 3. Frequency shift of nitrile as a function of water mole fraction in the bulk for three ionic liquids. As explained in figure 2, water penetrates the interface only after a critical concentration is reached. This critical concentration can be higher than 0.95 for all ionic liquids studied here.

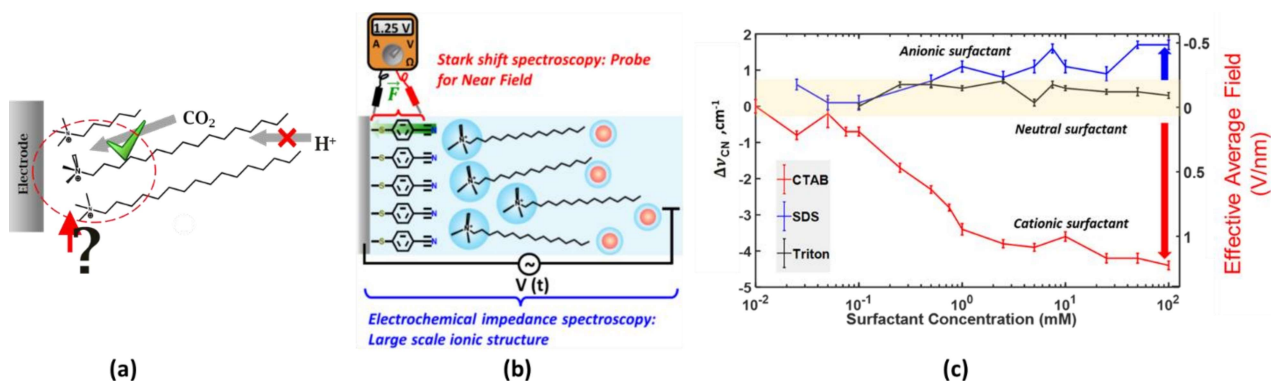


Figure 4. Summary of our work on surfactant-induced interfacial fields. (a) The motivation for the work comes from electrochemical literature showing that surfactants affect reaction selectivity (e.g. suppression of hydrogen evolution in favor of CO<sub>2</sub> reduction). The details remain unknown and often ascribed to interfacial electrostatics. (b) Our designed experiment to address this issue by measuring the electrostatic field induced by surfactants using vibrational Stark shift probes and electrochemical impedance spectroscopy. (c) Our results indicating measured vibrational Stark shifts and the corresponding effective fields in the presence of cationic, anionic, and neutral surfactants.

with the surface, while is useful for explaining the overall electrical properties of the interface, is not suitable for understanding the chemical influence of the layers over molecular length scales.

### The Analogy Between Molecular and Electrochemical Polarization:

Bridging the concepts of homogeneous and heterogeneous reactions is an important challenge in modern chemistry. Toward that end, here, we connect the homogeneous chemistry concept of the Hammett parameter, used by organic and organometallic chemists to quantify the electron-withdrawing capability of a functional group, to the electrochemical concept of polarization induced by a biased electrode. Because these two effects share similar origins, a theoretically motivated and experimentally verifiable link between them can be established. A convenient experiment that links the two is measuring the shift of vibrational frequency that is induced by these factors. To achieve this, first, we have measured the vibrational frequency of the nitrile stretch of 4-R-benzonitrile for a series of functional groups R spanning the Hammett parameter range  $-0.83 \leq \sigma_p \leq +1.11$ .

Because the nitrile stretch is sensitive to molecular polarization, its frequency depends on the Hammett parameter of the polarizing functional groups. Second, we have measured the nitrile vibrational frequency of 4-mercaptobenzonitrile tethered on a gold electrode and polarized in an electrochemical cell as a function of potential from  $-1.4$  to  $+0.6$  V versus Ag/AgCl. Comparison of the nitrile-stretch frequency between

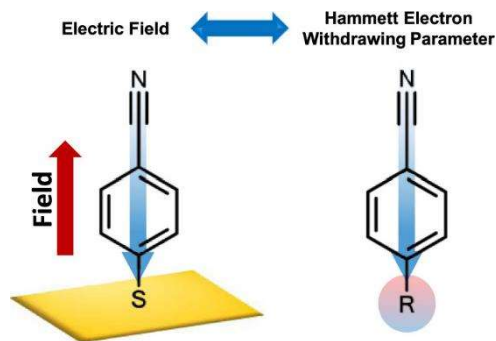


Figure 5. We proved and quantified that a similarity exists between the electron-withdrawing effect of an organic substituent and the polarizing electric field applied by an electrode. This opens opportunities to merge and systematize the knowledge in the synthetic

the two experiments allows us to correlate the polarization caused by a functional group to that induced by the electrode. The data suggest equivalence between the Hammett parameter  $\sigma_p$  and the local electric field at the electrode interface, therefore allowing a polarizing electrode to be treated as a functional group. Computational work supports the experimental results and allows for a quantitative relation between the interfacial electric field and  $\sigma_p$ . We anticipate the benefits of this correlation, in particular, in linking concepts between homogeneous and heterogeneous reactions.

This work was later cited by a high-profile publication (J. Heo et al, Electro-inductive effect: Electrodes as functional groups with tunable electronic properties, *Science* 2020, 370 (6513) , 214-219) which demonstrated that interfacial polarization, even in the absence of a Faradaic current, can influence the thermodynamics of some interfacial reactions.

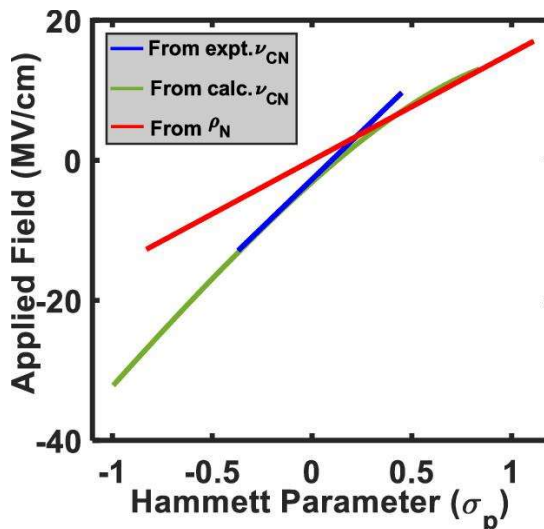


Figure 6. Relation between  $\sigma_p$  and electric field based on experimental frequency changes (blue), computational frequency changes (green), and charge density changes on nitrogen  $\rho_N$  (red).