DISCOVERING AND MODULATING LONG RANGE INDUCED CHARGE DENSITY GRADIENTS IN ROOM TEMPERATURE IONIC LIQUIDS

By

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ABSTRACT

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Room temperature ionic liquids (RTILs) are salts that are liquid at or below room temperature. The unique properties of RTILs such as low melting point, low vapor pressure, non-flammability and large electrochemical potential window have made them very promising in applications ranging from solvents for organic synthesis and electrolytes for energy storage devices to potentially novel electro-optic materials. Despite the broad utility of RTILs, understanding the fundamental interactions between constituents at the molecular scale, and the existence of long-range organization in these systems remains limited. Therefore, it is important to characterize the length scale of organization in RTILs because such order will bring with it the development of a variety of novel applications.

We used picosecond laser technologies and time resolved spectroscopic approaches to gain insight into the existence and length scale of molecular organization in RTILs. We have used time correlated single photon counting (TCSPC) detection with a confocal microscope for spatially resolved excitation and time-resolved emission collection to measure the rotational diffusion dynamics of three structurally similar chromophores (anionic, cationic and neutral) as a function of distance from the silica support. The results reflected the existence of a charge density gradient induced in the RTIL by the charge present on the silica surface. Control experiments were also performed for 1) identical measurements in ethylene glycol and 2) capping the silica support with Me₂SiCl₂ to prove this property is unique to RTILs in contact with charged surfaces. Second, we have used fluorescence anisotropy decay imaging (FADI) with a confocal microscope to measure the rotational diffusion dynamics of cationic chromophore cresyl violet as a function of distance from the conductive oxide support, FTO (fluorine doped tin oxide) or ITO (indium doped tin oxide). Using this experimental configuration, control over the bias and current applied to the support can be achieved, allowing the reorientation dynamics of the charged chromophores to vary with the potential difference between and the current across the FTO or ITO support. The effects of water on the induced charge density gradient in the RTILs were also explored. Data from those measurements showed that when ca. 25,000 ppm or more of water is added to the RTIL, the induced charge density gradient persists but with apparently diminished amplitude.

The results of this work have demonstrated a novel experimental method to study the local organization in RTILs. These findings represent an initial step for characterizing and modulating the long range order in RTILs, which will result in using this family of materials most effectively and providing a practical framework to better understand ionic liquids.

Copyright by KE MA 2019 To my parents, Yuling Du and Dianchun Ma, and my beloved wife, Weijing Liu

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CHAPTER 1: BACKGROUND AND MOTIVATION

1.1 INTRODUCTION

The development of "green" energy storage devices is fast becoming a critical issue for efficient use of renewable energy. To cater to the needs of a new generation of electric vehicles and large scale storage of electrical energy, technologies must be developed that can deliver increased energy density (the amount of energy stored in a given mass) and power density (controlled by the speed of energy release) with better safety, lower cost and without adverse effects on the environment. Electrochemical supercapacitors (ESs) are characterized by high power density and long cycle life (exceeding 1 million cycles¹). Such devices are already in use as an integral part of electric vehicles and back-up power supplies.²

Interfaces and surfaces are the regions where important events happen: energy storage, catalysis, molecular recognition, charge transfer, polymerization, and many other critical processes take place at the boundary between one medium and another.³ Central to the function of an interface is the structure and dynamics occurring in the interfacial region. The chemical composition of the interface region and the molecular arrangement at the interface can be very different from that in the bulk medium.

Charge storage in ESs occurs through the formation of an electric double layer (EDL) at the electrode–electrolyte interfaces. This device stores energy physically rather than electrochemically, and the chemical reactions that operate in rechargeable batteries during charging and discharging are not relevant. Compared to rechargeable batteries, the electric double layer capacitor (EDLC) has a remarkably long cycle-life and high power density.⁴ However, due to the narrow electrochemical window of water (ca. 1.23 V), the energy density of EDLCs in aqueous electrolytes is generally low (5– 10 Wh kg⁻¹).⁵ Therefore, in recent years,

developing non-aqueous EDLCs has become a matter of great interest for their comparatively wide potential window and higher power density.

For these reasons, room temperature ionic liquids (RTILs) have been identified as a useful family of materials. RTILs are a class of compounds that can be described as salts that melt at room temperature or lower.⁶ Most salts adopt a crystalline lattice structure where the ionic constituents reside at specific positions in a three-dimensional assembly. The stabilization energy of the resulting crystalline structures is well in excess of k_B T at room temperature. Typical melting points of salt crystals can be multiple hundreds of degrees. Such a structural motif is possible because the charged species are comparatively compact and the ionic charge is not shielded extensively. For systems characterized by larger and/or irregularly shaped ionic species, the electrostatic forces between the charged species still operate but their physical extent prevents close, ordered packing, resulting in a fluid lattice structure, which is termed room temperature ionic liquid (RTIL). The structures of some of the more widely-used RTIL cations, typically organic, and anions, typically inorganic, are shown in Fig 1.1.



Figure 1.1 Structures of commonly used RTIL cation (left) and anion (right) species.

Because of their unique properties, RTILs hold much promise for applications in areas ranging from electrolytes in supercapacitors⁷⁻⁸, novel solvents for organic synthesis⁹, green solvents for separations¹⁰, and potentially as novel electro-optic materials. Despite the wide use of these materials, much remains to be understood about their properties and the underlying chemical and physical principles that account for them. There are several characteristics of RTILs that are important for determining their properties: (1) low melting point so they exist as liquids at ambient temperature and have wide usable temperature range, (2) extremely low volatility as RTILs are thermally stable,do not have a significant vapor pressure¹¹ and are typically nonflammable, (3) RTILs have high ionic conductivity, and (4) organic ions allowing

for a broad range of structures and combinations.² RTILs having a wide electrochemical potential window (ca. 3.0 - 5.0 V) are presently being considered as promising electrolytes for developing high energy density supercapacitors.² The time scale of the formation and relaxation of electric double layers is ca. 10^{-8} s, giving ES a high power density.¹² RTILs are used as green electrolytes for those electrochemical supercapacitors because of their low volatility and high ionic conductivity, which are important properties for electrolyte solutions to exhibit.

It is clear from the above discussion that a key issue in the use of RTILs in energy storage applications is the nature and spatial extent of their organization at electrode surfaces. Macroscopic properties of interfaces, such as surface tension at liquid-solid interfaces, have been studied widely, however, the microscopic properties of interfaces have been more difficult to ascertain.¹³⁻¹⁵ Interrogating such organization poses an experimental challenge since the relevant length scale of such organization is presently not known. For solution phase electrolytes it is known that the electric double layer has a very limited spatial extent, but it is not clear whether this situation is relevant for ionic liquids based on their high charge density. One way to evaluate such organization of how such organization changes with distance from the charged support on a macroscopic (μ m) level. A detailed molecular understanding of RTIL interfaces and any transition from interfacial to bulk organization and dynamics is critical to understanding how RTILs behave macroscopically.¹⁶

Fluorescence spectroscopy is sensitive to microenvironments in liquid solutions and, therefore, is particularly useful for the study of solvation phenomena. Rotational diffusion measurements performed with time-resolved fluorescence spectroscopic techniques provide a means of measuring the motional properties of a probe molecule and elucidating information on

local organization in the medium. Through the use of optical spectroscopic techniques, a molecular scale understanding of RTIL-chromophore and RTIL constituent interactions is sought to increase our knowledge of RTILs as a means of achieving greater control over chemical processes like energy storage.

1.2 MOLECULAR SCALE ORGANIZATIONS IN IONIC LIQUIDS

Room-temperature ionic liquids (RTILs) hold promise as solvent-free electrolytes for supercapacitors, solar cells and batteries. For such applications, it is crucial to understand the structure of the RTIL-electrode interfacial region. The classical Gouy-Chapman-Stern model for dilute electrolytes has been used to interpret RTIL capacitance data.¹⁷

The Gouy–Chapman–Stern model predicts that as the electrode becomes more highly charged, the diffuse layer in aqueous solutions becomes more compact and its differential capacitance grows. In this theory, ions outside the compact layer are treated as point charges that occupy no volume. A consequence of this assumption is that the model is accurate only for dilute solutions and at potentials close to the potential of zero charge (PZC).¹⁸



Figure 1.2 Gouy-Chapman-Stern model for electrical double layer.¹⁹ The graph is adapted from Ref. 19.

However, the ions that comprise ionic liquids are often large, non-rigid, highly polarizable and chemically complex. Moreover, the relatively low melting point of ionic liquids also means a number of interionic forces, in addition to Coulombic forces, may act to affect the structure of these liquids. These include dispersion forces, dipole–dipole interactions and hydrogen bonding.¹⁸ The Gouy–Chapman–Stern model is still not comprehensive enough for explaining the EDLs at the interfacial region for RTILs.

Experimental and theoretical investigations of RTILs have revealed four length scales over which organization of some type has been observed. These are hydrogen bonded network organization, ca. 10 nm, ca. 1 μ m and ca. 100 μ m. The term "organization" is not well-defined, however, and the relationship between the phenomena with different characteristic length scales remains to be understood fully.

Hydrogen Bonded Network Organization. Dr. Jairton Dupont developed the concept in his review that pure 1,3-dialkylimidazolium ionic liquids can be described as polymeric hydrogen-bonded supramolecules.²⁰ Highly-ordered, hydrogen-bonded networks in the form of $([(DAI)_x(X)_{x-n})]^{n+} [(DAI)_{x-n}(X)_x)]^{n-}$ can be formed, where DAI is the 1,3-dialkylimidazolium cation and X the anion. This structural motif is a general trend for the solid phase and is maintained in the liquid phase to a significant extent and even in the gas phase.²⁰

X-ray studies on the structure of 1,3-dialkylimidazolium salts was reported by the Cambridge Crystallographic Data Center.²¹ One imidazolium cation surrounded by at least three anions and each anion is surrounded by at least three imidazolium cations in turn comprises the monomeric unit of the salts. There is a trend of such structures forming in the solid state, an extended network of cations and anions connected together by hydrogen bonds.

The structural trend of one imidazolium cation hydrogen bonded to at least three anions and one anion hydrogen bonded to at least three cations is a general trend in imidazolium salts. However, the number of anions that surround the cation (and vice-versa) can change depending upon the anion size and type of the N-alkyl imidazolium substituents.



Figure 1.3 Two-dimensional simplified solid-state model of 1,3-dialkyl imidazolium ionic liquids hydrogen bonds network between the imidazolium cation(C^+) and the anions (A^-) (one cation is surrounded by three anions and vice-versa). The graph is adapted from Dupont, J., On the solid, liquid and solution structural organization of imidazolium ionic liquids. *J Brazil Chem Soc* **2004**, *15* (3), 341-350. (Ref. 20).

By neutron diffraction analysis of 1,3-dimethylimidazoliumchloride (DMIM⁺Cl⁻) and its hexafluorophosphate analogue (DMIM⁺PF₆⁻) in both the solid and liquid phase, the Soper Group also provided strong evidence that the hydrogen-bonded network also existed in the liquid phase.²² Their model derived from the obtained data used Empirical Potential Structure Refinement indicated that significant charge ordering is present in the liquid phase and that the local order in these liquids resembles those found in the solid phase. Moreover, the Hamaguchi group performed Raman spectroscopic analysis of both crystalline and liquid state of 1-Butyl-3-methylimidazolium chloride (BMIM⁺Cl⁻),²³⁻²⁴ with similar results, indicating that three dimensional structure found in the solid state²⁵ is maintained in the liquid phase.

10 nm-Scale Organization. In an effort to understand the role of electrostatic screening in RTILs, the Israelachvili group has produced an elegant body of work where temperaturedependent surface force measurements²⁶ were used to infer information on the force exerted on a charged surface by a RTIL.²⁷⁻²⁸ This means of measuring forces of interaction has revealed the spatial extent of interaction between a RTIL layer and a charged (mica) plate. The result is that the characteristic effective Debye length, $(\kappa^*)^{-1}$, is on the order of 6 nm for 1-Ethyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM⁺NTf₂⁻) and 1-Propyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide (PMIM⁺NTf₂⁻), corresponding to an ion number density of $n^* \sim 10^{15} - 10^{16}$ cm⁻³. The physical origin of order over this length scale derives from the formation of organization analogous to the electric double layer in the RTIL due to its contact with the charged mica surface. Within the framework of the GCS model or some variant,²⁹ organization on the order of 10 nm requires a very low free ion density. Increased dissociation results in the higher ion density and thus the greater extent of charge screening. Limited dissociation leads to longer length scale effects due to the field(s) associated with quasipoint charges. The picture that emerges from this work is that the dominant form of the RTIL is Bjerrum pairs with a relatively small fraction of free ions.³⁰ The Israelachvili group reported no longer range organization.

 $1 \mu m$ -Scale Organization. The Shaw group has identified orientational order in RTIL films over distances of ~1 μm .³¹⁻³³ Using thin RTIL films, they measure the evolution of order

through changes in the vibrational spectra of the RTILs and, using second harmonic generation measurements, they make a compelling case for the evolution of (non-centrosymmetric) order developing throughout the film over a timescale of tens of minutes at room temperature. They also note that the extent of order depends on the identity of the anionic component of the RTIL. Taken collectively, these data imply that the dominant species present in RTILs is the dipolar contact ion pair. If the RTIL constituents existed as discrete ions, the resulting structure would be, necessarily, centrosymmetric in the bulk and therefore no evolution of second harmonic signal would be observed. We note that this finding is in conceptual agreement with the report of the Israelachvili group, albeit with a difference in length scale, which could be a consequence of the different techniques used by the two groups. It is also important to note that this work provides direct experimental evidence for second order nonlinear optical effects being operative in RTILs, a property we will exploit (*vide infra*).

While the Shaw group has provided a detailed interpretation of the vibrational spectra, which gives some insight into the structure of the organized media, a firm understanding of either the microscopic organization in these systems or the driving forces for the evolution of said organization is still lacking. The time-scale of organizational evolution in these RTIL films strongly suggests an annealing process to form an organized arrangement of dipoles where the stabilization energy of the "ordered" structure is on the order of k_BT . In contrast to the order seen on the 10 nm length scale, this "order" is consistent with that induced by interactions among dipoles in such a way as to produce a non-centrosymmetric structure. One way to reconcile the Shaw and Israelachvili groups' findings is to note that the Shaw group senses the Bjerrum pairs while the Israelachvili group senses the free ionic species. There is no reason *a priori* why these two different entities should be correlated in the characteristic length scale of their organization.

100 μm-Scale Organization. We have identified and characterized organization in RTILs over a range of ca. 100 μm that was induced by a (charged) planar silica support.³⁴ We also demonstrate the ability to control the induced organization.³⁵ Fluorescence anisotropy decay of the charged chromophores is measured using time correlated single photon counting system in the RTIL as a function of distance from the charged support.³⁶ Depth resolution is achieved with an inverted confocal microscope through mechanical control over the microscope stage position. The chromophores exhibit depth-dependent reorientation dynamics that vary with their ionic charge. The occurrence of spatially varying chromophore dynamics requires the RTIL to be in contact with the (charged) silica support. We have constructed a closed cell that confines the RTIL between two transparent conductive surfaces (indium doped tin oxide (ITO) or fluorine doped tin oxide (FTO)) in order to gain control over the surface charge density. The influences of water dilution of the RTIL on the long range induced charge gradient density is also studied. The details of our work will be described in the following chapters.

1.3 OBJECTIVES OF THE DISSERTATION

The fundamental interactions between RTIL constituents, and the existence of long-range organization in RTILs remains to be explored fully. One fundamental obstacle to understanding RTILs rests on the unresolved issue of the extent to which ionic liquids exist as ion-paired dipolar species and as dissociated ions, and the consequences of this equilibrium. Most attempts to model RTIL properties start from the premise that they can be treated as a fluid dielectric medium. Such a starting point cannot be fully accurate because of dissociation in RTILs and the dissociated ions function as carriers. RTILs, however, cannot be treated effectively as conductors. The essential questions of free ion density, the dielectric response of the ion-pairs, and the consequent screening effect(s) in RTIL media are not well understood.

The work contained in this dissertation has been focused on discovering and modulating the induced long-range charge density gradient in room temperature ionic liquid BMIM⁺BF₄⁻, and the possible theory and explanations behind the charge density gradient. Time Correlated Single Photon Counting (TCSPC) Microscopy and Fluorescence Anisotropy Decay Imaging (FADI) were employed as measurement techniques to examine the rotational diffusion dynamics of probe molecules in RTIL electrode systems, and provide a detailed description of the measurement science in Chapter 2. In Chapter 3, we report on the rotational diffusion behavior of three probe molecules cresyl violet (cationic), resorufin (anionic) and nile red (neutral) separately in the RTIL/silica system using FADI. Opposite trends of reorientation time constants (τ_{OR}) vs. distance from glass substrate surface for cresyl violet and resorufin were found, and this gradient persists for distances up to 100 µm from the silica support. It was also found that for nile red τ_{OR} is invariant with the distance from the support surface. Two sets of control experiments were done separately to further help us understand the reasons for our observations. In order to modulate the induced charge density gradient in the RTIL, BMIM⁺BF₄⁻, a sealed electrochemical cell was designed using indium doped tin oxide (ITO) or fluorine doped tin oxide (FTO) as the working electrode. The RTIL is confined between the two electrodes in a sandwich structure. Two different methods were used to change the surface charge density on the electrode in an effort to control the induced, counter balancing charge density gradient within the RTIL. The detailed results of the experiments are described in Chapter 4. In Chapter 5, the effects of water concentration in the RTIL sample on the induced charge density gradient using FADI and Karl-Fisher titration are reported. The use of optical techniques to examine the physical properties of the RTIL electrode system provides an opportunity to study the complex

dynamic properties of RTILs in the interfacial region in ways that have not been reported previously.

On physical grounds, ionic interactions and the extent of the field(s) associated with the cannot account for the long-range order seen in RTILs. This situation, combined with the knowledge that it can take minutes to hours for dipolar annealing to occur in thin RTIL films, leads to the central hypothesis of this dissertation that long-range order in RTILs can be understood in the same context as induced order in piezoelectric (solid) materials. Determining the validity of this hypothesis and the limits to which it holds is the central focus of this work. A deeper understanding of RTILs will result, which is a prerequisite for using this family of materials most effectively and provide an effective framework in which to understand ionic liquids.

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CHAPTER 2: EXPERIMENTAL TECHNIQUES FOR EXAMING LOCAL ORGANIZATION IN ROOM TEMPERATURE IONIC LIQUIDS

2.1 INTRUMENTAL METHODS

Due to the growing use of RTILs, and the recognition of the need for a deeper understanding of their properties, there is a rich literature on the bulk and interfacial structure of RTILs, with both experimental methods and computer simulations being reported. Many applications of RTILs involve physical or chemical processes at interfaces, such as lubrication¹⁻², electrical energy storage devices³⁻⁴, and catalysis.⁵⁻⁶ The interfacial structure of the RTILs|Support system influences or mediates many of these processes, and detailed knowledge of local organization in this region will afford new opportunities. The structure and organization of these systems are complicated because of the potentially high ionic strength of the medium and the unknown extent of dissociation. A major challenge is the need for *in situ* characterization of molecular and longer-scale organization in the proximity of the RTIL|Support interface. Gaining such information is hampered by the limited number of techniques available, the possible role of impurities in the ionic liquids, , and even a lack of consensus on what an ionic liquid is and what defines the interface. A major obstacle to describing the solid-liquid interface is the lack of experimental probes that are able to interrogate this condensed-phase system.⁷ While not an exhaustive list, the utility and limitations of the most common and widely used methods for study of bulk and interfacial structure of RTILs will be discussed briefly below.

Small-Angle Scattering (SAS). Small-angle X-ray scattering (SAXS) and Small-angle neutron scattering (SANS) are jointly referred to as SAS. SAXS is a non-destructive method that can reveal spatial correlations in RTILs on the order of tens of Angstroms.⁸ This method is based on analyzing the elastic scattering behavior of X-rays interacting with the sample by recording their scattering at small angles. Triolo *et al.*⁸⁻¹⁰ reported experimental evidence for the existence of nanoscale segregation of the alkyl chains of 1-alkyl-3 methylimidazolium

hexafluorophosphate ($C_nMIM^+PF_6^-$, $4 \le n \le 10$) into the charged matrix using SAXS. The size of these structural heterogeneities was found to depend linearly on the alkyl chain length. However, when the alkyl chain was too short (n < 4), it was difficult to identify the analogous structural heterogeneities using SAXS because they appear as a small shoulder on a much more intense X-ray diffraction amorphous halo.⁹

SANS is an experimental technique that uses elastic neutron scattering at small scattering angles to investigate the structure of various substances on a mesoscopic scale of 1–100 nm. Atkin *et al.*¹¹ demonstrated the existence of amphiphilic nanostructure for RTILs ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) using SANS. Their data appears to be the first experimental evidence of nanoscale heterogeneity in RTILs with alkyl chains less than C₄. However, for SANS there remain some disadvantages, such as neutron sources that are very expensive to build and maintain.

Fluorescence Correlation Spectroscopy (FCS). FCS is a correlation analysis of fluctuations of fluorescence intensity. It can monitor the motion of a small number of chromophores by measurement of spontaneous fluorescence fluctuations caused by Brownian motion of the chromophores. The observation volume can be extremely small (femtoliters) and it is determined by the focus of a confocal microscope.¹²⁻¹⁵ The technique is exquisitely sensitive, offering detection down to the single-molecule level.¹⁵ Guo *et al.*¹⁵ reported that heterogeneous liquid structures exist in N-alkyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (C_nMPy⁺Tf₂N⁻, n = 3,4,6,8 and 10). Rhodamine 6G (R6G) was used as the fluorescent probe molecule and FCS results revealed biphasic diffusion dynamics for all of the aliphatic chain lengths studied. The fast and slow diffusion rates for R6G are due to the diffusion within non-aggregated regions and self-aggregated domains, respectively. Despite the utility and sensitivity of this technique, there remain some limitations, including the appropriate treatment of experimental data under different conditions and the lack of models for data interpretation.¹⁶⁻²⁰

Second Harmonic Generation (SHG). SHG is a nonlinear spectroscopic technique in which two photons with the same frequency interact with a nonlinear material (in this case, RTILs), are "combined", and generate a new photon with twice the energy of the initial photons. The sum frequency signal intensity is related to the first hyperpolarizability and order of the material. The signal is zero for centrosymmetric systems but nonzero at interfaces or in materials that do not possess a center of inversion. Thus SHG can be used to detect the presence of interfaces or ordered structures in bulk non-centrosymmetric materials.²¹⁻²² Shaw *et al.*^{21, 23} reported the transformation of ionic liquid films from isotropic bulk to a fluid-ordered state over micrometer length scales through the application of a shearing force, and they sensed the order induced in the RTIL with SHG measurements. One advantage of SHG measurements is that the generation of second harmonic light does not require the use of a chromophore introduced into the RTIL. Rather, SHG senses organization in RTILs directly. More consideration of SHG measurements will be discussed in Chapters 5 and 6 of this dissertation.

Computer Simulations. The two main families of simulation that have been applied to RTILs are molecular dynamics (MD) and Monte Carlo (MC) simulations.²⁴ MD is a method for studying the physical movements of atoms and molecules. This method is now routinely used to investigate the structure, dynamics and thermodynamics of a variety of systems. For different imidazolium-based RTILs, a first sharp diffraction peak (FSDP) at low frequency in the X-ray and neutron scattering spectra can be observed.²⁵ FSDP has often been experimentally interpreted as indicative of mesoscopic organization of those RTILs.^{8, 10, 26-27} Annapureddy *et*

 $al.^{25}$ combined detailed MD simulations with evidence from published experimental data to clarify the geometrical origin of the FSDP in 1-alkyl-3-methylimidazolium (C_nMIM⁺, n=6, 8 and 10) based RTILs with spherical or pseudospherical anions. While the existence of complex morphologies is neither proved nor disproved by their study, they concluded that the geometric anisotropy in the cation is a necessary but not a sufficient condition for the nanoscale segregation of the cation alkyl chains. The FSDP can be explained by much simpler consideration of solvation shell asymmetry of the cations.

MC techniques can be used to compute the equilibrium properties of classical many-body systems.²⁸ They are useful for simulating systems with many coupled degrees of freedom, such as fluids, disordered materials, strongly coupled solids, and cellular structures. Shah *et al.*²⁹ carried out MC simulations on the RTIL 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM⁺PF₆⁻), and reported that PF₆⁻ anions preferentially cluster in two favorable regions near the cation. The highest probability location is in proximity to the cation C₂ carbon atom, both below and above the plane of the imidazole ring. These findings suggest but do not prove the existence of ion-paired species in RTILs.

MC and MD simulations act as a bridge between microscopic length and time scales and the macroscopic world of the laboratory. They also act as a bridge in another sense: between theory and experiment.²⁴

2.2 TIME RESOVLED FLUORESENCE SPECTROSCPY

Time-resolved fluorescence spectroscopy is a powerful method for investigations ranging from condensed matter physics and chemistry to the life sciences.³⁰ The measurement of time resolved anisotropy decay allows the study of molecular scale reorientation of chromophores in a

variety of matrices. In this section, information on fluorescence microscopy techniques used to examine the rotational diffusion behavior of a chromophore in a RTIL is provided. A brief explanation of the theory behind the rotational diffusion measurement techniques is described. The associated instrumental design is described in detail.

Fluorescence Anisotropy Decay Measurements. Fluorescence anisotropy is the phenomenon where the light emitted by a fluorophore has unequal intensities (*I*) along different axes of polarization. When the polarization of an incident (resonant) electric field is parallel to the transition dipole moment of a chromophore, the molecule will absorb the photon and be excited to a higher energy state. The molecule will relax rapidly and non-radiatively to the v=0 S₁ state. Subsequent radiative relaxation from this state will proceed according to first order kinetics, with a characteristic time constant that is the reciprocal of the rate constant for radiative relaxation. This time constant is referred to as the fluorescence lifetime. The emitted photon will have a specific polarization with respect to the molecule. By measuring the time-resolved intensity of fluorescence both parallel $I_{ll}(t)$ and perpendicular $I_{\perp}(t)$ to the initial excitation polarization , the fluorescence lifetime (eqn. 2.1) and anisotropy decay function (eqn. 2.2) of the chromophore can be formulated.³¹

$$I_{fl}(t) = I_{\parallel}(t) + 2I_{\perp}(t)$$
[2.1]

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}$$

$$[2.2]$$

The decay of R(t) is due to the rotational diffusion of the fluorescent probe molecule in the Chromophore|RTIL system. Although the R(t) function can contain up to five exponential components, for most systems only one or two component anisotropy decays are observed.³²⁻³³ Chuang and Eisenthal³¹ reported that the functional form of R(t) depends on the shape of the
volume swept out by the reorienting chromophore molecule. A series of equations were derived to relate the decay of R(t) to the Cartesian components of the rotational diffusion constant. The shape of the volume swept out by the rotating chromophore molecule is modeled as an ellipsoid. Chuang and Eisenthal related the Cartesian components of the rotational diffusion constant to the rotor shape as follows.³¹ If the π -system of the planar chromophore is assigned as the xy plane, with the x-axis being the long in-plane axis and the y-axis being the short in-plane axis, the z-axis is normal to the xy plane. For a prolate rotor, $D_x > D_y = D_z$, and for a oblate rotor, $D_z > D_x = D_y$.



Figure 2.1 Schematic of (a) prolate rotator and (b) oblate rotator.³⁴ The graph is adapted from Ref. 34.

For a prolate rotator with the excited and emitting transition dipole moments parallel to the dominant (x) axis of rotation, R(t) decays as a single exponential (eqn. 2.3). For an oblate rotator with the transition dipole moments parallel and in the x-y plane, R(t) exhibits a two-component exponential decay (eqn. 2.4). R(0) is related to the angle between the excited and emitted transition dipole moments of the chromophore molecule.

$$R(t) = 0.4exp(-6D_z t)$$
[2.3]

$$R(t) = 0.1exp(-(2D_x + 4D_z)t) + 0.3exp(-6D_xt)$$
[2.4]

The determination of rotational diffusion constant (D) is based on measuring its Cartesian components (eqn. 2.5). The information we extract from the function of R(t) is the angle between the excited and emitting transition dipole moments (R(0)) and the anisotropy decay time constant(s) (τ_{OR}). We focus on the decay time constant(s), which are inversely related to the Cartesian components of D. For a prolate rotor, where the only Cartesian component of D that is available is D_z, $\tau_{OR} = (6D_z)^{-1}$. For oblate systems, the decay time constants are related to the D_z and D_x components of D. Molecular motion is described by Debye-Stokes-Einstein (DSE) equation³⁵⁻³⁷ (eqn. 2.6).

$$D = \frac{1}{3}(D_{\chi} + D_{y} + D_{z})$$
[2.5]

$$\tau_{OR} = (6D)^{-1} = \frac{\eta V f}{k_B T S}$$
[2.6]

In eqn. 2.6, η is the viscosity of the bulk solution, k_B T is the thermal energy of the system, V is the hydrodynamic volume of the rotating entity, *f* is a boundary condition term used to describe the frictional contributions of the chromophore-solvent interactions, which can range from near zero in the slip limit to one in the stick limit,³⁸⁻³⁹ and S is a shape factor that accounts for the non-spherical shape of the rotating entity.⁴⁰

For the chromophores discussed in the following chapters, all of them can be modeled as a prolate rotator and R(t) can be fitted using a single exponential decay function.³²⁻³³

Fluorescence Anisotropy Decay Depth Profiling Instrument. The instrument used to acquire fluorescence anisotropy decay data of the chromophores in the RTIL BMIM⁺BF₄⁻ is based on the combination of a time correlated single photon counting (TCSPC) laser system

coupled to an inverted confocal laser scanning microscope (CLSM) (Nikon Eclipse Ti-U), shown in Fig. 2.2.



Figure 2.2 Schematic of the Fluorescence Anisotropy Decay Depth Profiling Instrument.

The light source for this instrument is a synchronously pumped cavity dumped dye laser (Coherent 701-3) excited by the output of a passively mode locked Nd:YVO₄ laser (Spectra Physics Vanguard). The pump laser produces 13 ps pulses at 80 MHz repetition rate at both 355 and 532 nm, with 2.5 W average power at each wavelength. The repetition rate of the dye laser is controlled by a cavity dumper. The output of the dye laser is characterized by ca. 5 ps pulses at a repetition rate typically of 4 MHz (it can range from 80 kHz to 80 MHz), and the average power at the sample is less than 0.5 mW. By changing the dye and optics used and the excitation wavelength, the output of the dye laser can be tuned from 430 nm to 850 nm. For the work

presented in this dissertation, the dye laser output is set to be 563 nm. The wavelength was selected based on the excitation spectra of the chromophores used in this work and the bandpass filters used in the confocal scanning system. The pulsed excitation light is passed through a polarizer selected to an angle of 0 degrees (vertical polarization), and sent to the confocal scanning head for delivery to the sample. Collected emission light is sent to a set of long-wavelength pass and bandpass filters, separated into vertical and horizontal polarization components, and then sent to avalanche photodiode detectors.

The confocal scanning device, connected to an inverted optical microscope, provides the requisite high focal depth resolution required to characterize the local organization of the RTIL $BMIM^+BF_4^-$ that is reported in this dissertation. In this configuration, which was designed initially for confocal imaging, the laser is focused on the sample at a selected position, and polarized emission transients are acquired at each laser position. Images are acquired pixel-bypixel by stepping the laser spot position in the focal plane. For the work reported here, the sample is homogeneous in the x-y plane for any given depth in the sample, and the acquisition of multiple pixels in a given focal plane serves as an efficient means of signal averaging. Detection of time-resolved data is achieved with a polarized dual channel confocal scanning instrument (Becker & Hickl DCS-120) attached to an output port of the microscope and controlled by a galvo-drive unit (Becker & Hickl GDA-120). The confocal scanner is equipped with a polarizing beam splitter and two avalanche photodiode detectors (APD) (ID-Quantique ID100) for the acquisition of fluorescence lifetime and anisotropy decay images. Polarized fluorescence transients are acquired using time-correlated single photon counting (TCSPC) detection electronics (Becker & Hickl SPC-152, PHD-400N reference diode).

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The main components for TCSPC detection electronics are constant fraction discriminators (CFD), electrical delays (DEL), the Time-to-Amplitude Converter (TAC), Amplifier (between the TAC and ADC), Analog-to-Digital Converter (ADC) and digital memory. TCSPC is a statistical method requiring a highly repetitive light source to accumulate a sufficient number of photon emission events for the required statistical data precision. The principle of TCSPC is the detection of single photons and the measurement of their arrival times in respect to a reference signal, usually the light source (in this work the picosecond laser source). TCSPC electronics can be compared to a fast stopwatch with two inputs (Fig. 2.3). The clock is started by the START signal pulse and stopped by the STOP signal pulse. The time measured for one START - STOP sequence will be represented by an increase of a memory value in a histogram, in which the channels on the x-axis represent time. Millions of START – STOP sequences can be measured in a short time with a high repetition rate laser source. The fluorescence intensity versus time can be represented through the resulting histogram counts versus channels. Thus fluorescence anisotropy decay function R(t) can be calculated through the resulting histogram. The photon rate is kept low in comparison to the rate of the exciting lamp (usually 5% or lower) in order to ensure that only one photon per light flash is detected, otherwise histogram statistics will be affected and erroneous measurement results will be generated through multi-photon events. The TCSPC system in our lab is operated in reverse time mode. The electrical delay unit moves the reference pulse to come after the emitted photons from the sample instead of turning on the TAC for every excitation pulse with the reference channel. The reason and advantage of reverse mode is that TAC unit runs much less often so that electronics can recover between individual TAC events, resulting in the time-to-amplitude conversion being linear in time. Thus, the reference channel acts as the "stop" channel at a fixed point in time and the signal channels

start the TACs at statistically determined times before the (fixed) reference pulse. An instrument response function of less than 100 ps FWHM can be achieved by the combination of the pulsed dye laser source and TCSPC electronics.



Figure 2.3 Illustration of a fast stopwatch with two inputs mechanism of TCSPC detection system.

Data obtained from the fluorescence anisotropy decay depth profiling instrument are used in subsequent chapters of this dissertation to understand the long range induced charge density gradient ρ_{f} , the modulation of ρ_{f} and the effects of water on ρ_{f} .

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CHAPTER 3: CHARGE-INDUCED LONG-RANGE ORDER IN A ROOM-TEMPERATURE IONIC LIQUID

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3.1 ABSTRACT

Charge-induced long range (ca. 100 μ m) order in the room temperature ionic liquid (RTIL) 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM⁺BF₄⁻), supported on a silica surface was examined. The rotational diffusion dynamics of anionic, cationic and neutral chromophores as a function of distance from a silica surface were measured. The results reflect the excess charge density gradient induced in the RTIL by the (negative) charge present on the silica surface. Identical measurements in ethylene glycol reveal spatially invariant reorientation dynamics for all chromophores. Capping the silica support with Me₂SiCl₂ results in spatially invariant reorientation dynamics in the RTIL. These data are understood in the context of the RTIL exhibiting a spatially-damped piezoelectric response mediated by RTIL fluidity and disorder.

3.2 INTRODUCTION

Room-temperature ionic liquids are a well-established class of materials that hold promise for a host of applications ranging from solvents for organic synthesis¹ to electrolytes in supercapacitors.²⁻³ The properties of RTILs that make them attractive are the characteristically wide temperature range over which they exist in the liquid phase, their large redox window, and their ability to solvate a wide variety of solutes. Despite the plethora of uses for RTILs, there remains only a limited understanding of this family of materials at the molecular scale.⁴⁻⁶ The primary reason for this situation is that RTILs are characterized by a very high charge density (5–6 M). As a consequence, the treatment of intermolecular interactions in RTILs has not been resolved fully, including issues such as whether these systems are best considered as ion pairs or as discrete ions. Also, because of the high charge density of RTILs, the Gouy–Chapman–Stern (GCS) model is of limited value.⁷ While there is significant literature pointing to the existence of ordering in RTILs for distances somewhat in excess of that seen for the double layer of a

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dilute solution, there remains no clear experimental means to resolve the actual length scale of any such organization. It is important to characterize the length scale of organization in RTILs because such order will mediate the physical and chemical properties of the RTIL.

There have been many experimental⁸⁻¹⁰ and theoretical/computational¹¹⁻¹³ studies of organization in RTILs, and it is typically held that order near an interface persists over 5 nm or less.^{4-7, 14} There is presently, however, no effective means of probing the extent and nature of such organization. Experimental methods, such as X-ray diffraction (XRD), neutron diffraction, or atomic force microscopy (AFM), are of limited utility because of the fluid nature of RTILs, and to this point, the methods available to interrogate organization at an RTIL–solid interface have been limited. The spatially resolved spectroscopic results reported on herein here reveal persistent organization over ca. 100 μ m from a charged silica support. This distance is quite long relative to the typical electric double layer seen in dilute solution (hundreds of nanometers at most).

Our approach to elucidating long range order at RTIL-solid interfaces is based on the use of spatially-resolved spectroscopic measurement of dilute fluorescent probe molecules. It is known that the linear spectroscopic properties of fluorescent probes are sensitive to their immediate environment, and the existence of charged probes similar in size to the RTIL constituents provides an opportunity to interrogate the local environment(s) formed by RTILs over a range of length scales. Three chromophores were used for this purpose in this chapter: Resorufin (R, anion), Nile Red (NR, neutral) and Cresyl Violet (CV, cation) (Fig 3.1). The rotational diffusion dynamics of these three chromophores are measured in BMIM⁺BF^{4⁻} as a function of distance from a planar silica support using a confocal microscope equipped with time-resolved, polarized fluorescence detection gear. Our data reveal opposing trends in the depth-dependent

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reorientation dynamics for R⁻ and CV⁺ and depth-independent reorientation for NR in the RTIL over a distance of ca. 100 μ m. For ethylene glycol, a viscous neutral solvent, chromophore reorientation dynamics are spatially invariant. When the (negatively charged) silica surface is capped with dimethyldichlorosilane (Me₂SiCl₂) prior to the introduction of RTIL, the reorientation dynamics of all chromophores are spatially invariant. We show in this chapter that the surface distance-dependence in the anisotropy decay dynamics for R and CV in the RTIL BMIM⁺BF₄⁻ reflects the free charge density gradient, ρ_f , in the RTIL, induced by the surface charge of the silica support. The mapping of ρ_f in the RTIL provides the first direct measure of the spatial extent of surface charge-induced organization in an RTIL. The fact that this induced order persists over ca. 100 μ m provides many potential opportunities for control of RTIL optical and electronic properties through externally controllable potential gradients.



Figure 3.1 Structures of the RTIL constituents BMIM⁺ and BF_4^- (top), resorufin, nile red, and cresyl violet (bottom, from left to right).

3.3 MATERIALS AND METHODS

Chemicals. Resorufin sodium salt and Nile Red were purchased from Sigma Aldrich and used as received. Cresyl violet perchlorate was purchased from Eastman Kodak Co. and used as received. Ethylene glycol (EG, \geq 99%, Macron Fine Chemicals) was used as received. Ethanol (\geq 99.5%, Sigma Aldrich) was used as received. Methanol (\geq 99.8%, Sigma Aldrich) was used

as received and chloroform (99.0 - 99.4%, Sigma Aldrich) was used as received. Water used in these studies was purified in-house with a Milli-Q filtration system (Millipore).

Purification of the RTIL. The preparation and purification of the RTIL has been described previously.¹⁵ As-received BMIM⁺BF₄⁻ (Sigma-Aldrich, neat concentration of 5.35 M) was first stored over activated carbon for 3 days. After this time, the RTIL was centrifuged to separate the carbon powder. Most of the BMIM⁺BF₄⁻ sample (several milliliters) was then carefully removed and (ca. 0.5 mL) heated to 70 °C for 50 min while purging with ultrapure Ar (99.9995%, Linde). This procedure was performed with the RTIL in an electrochemical cell in a N₂-purged vinyl drybox.

Preparation of ionic liquid solution. To prepare the chromophore containing RTIL sample, a stock solution of chromophore (*ca.* 5×10^{-4} mol L⁻¹) was prepared and used as follows. The chromophore (final concentration 5×10^{-5} mol L⁻¹) + BMIM⁺BF₄⁻ solution was prepared by transferring 0.1 mL of the chromophore stock solution into a 1 mL volumetric flask and then evaporating to dryness in an oven at 100 °C for 1 h. The volumetric flask was then filled to the mark with the purified BMIM⁺BF₄⁻. This solution was then stirred for 12 h before use.

All sample preparation procedures were performed inside a N₂-purged vinyl dry box (Coy Laboratories, Grass Lake, MI). The relative humidity in the box was $\leq 0.1\%$, as measured with a hygrometer. All purified BMIM⁺BF₄⁻ were stored over activated (heat treated at 400 °C in a furnace) 5 Å molecular sieves in a glass-stoppered bottle and kept in the dry box.

Fluorescence anisotropy decay depth profiling. The instrument used to obtain fluorescence anisotropy decay dynamics as a function of distance from the silica support has been described in detail in Chapter 2. Briefly, a Nikon Eclipse Ti-U inverted microscope is equipped with a confocal

scanning head (B&H DCS-120) equipped with two time-resolved, polarized detection channels, each with an avalanche photodiode detection (ID Quantique ID100). The time-resolved data are processed using time-correlated single photon counting electronics (B&H SPC-152) and are recorded using B&H software. The light source for the experiment is a cavity-dumped synchronously pumped dye laser (Coherent 702-2) operating at 563 nm (5 ps pulses, 4 MHz repetition rate). This dye laser is excited by the second harmonic output of a passively mode locked Nd:YVO₄ laser (13 ps pulses, 80 MHz repetition rate, 2.5 W average power at 532 nm).

3.4 RESULTS AND DISCUSSION

The primary purposes of this work described in this chapter are to characterize the spatial extent of persistent organization in RTILs in contact with a charged surface and to offer a framework within which to interpret these results. This organization is orders of magnitude in excess of the length scale expected for dilute solutions, where traditional double layer models apply.

The fluorescence anisotropy decay of selected chromophores in the RTIL as a function of distance above the silica support are measured.¹⁶ Depth resolution is achieved with a microscope stage and with the use of a confocal microscope to minimize the depth of focus for the individual measurements. For the chromophore concentrations used in this chapter (*ca.* 10⁻⁵ M), excitation transport contributes negligibly to the measured depolarization. The chromophores (Fig 3.1) exhibit different depth-dependent reorientation dynamics depending on their formal charge. The depth-dependent anisotropy decay time constants for Resorufin (anion, Fig 3.2a) and Cresyl Violet (cation, Fig 3.2b) as a function of distance from the silica support are showed in Fig 3.2. The most obvious features contained in these data are that the cationic and anionic chromophores exhibit opposing trends while the neutral NR chromophore exhibits a negligible depth-

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dependence (Fig 3.3a). The second feature of note is that the distance over which the anisotropy decay time constants change is ca. 100 μ m. The functional form of the depth dependence and the physical basis for these results are examined following verification of the role of surface and RTIL charge in these findings.





Figure 3.2 (cont'd)

the range of $0-500 \,\mu\text{m}$ was acquired using a $10 \times$ microscope objective (~2 μm depth of focus) with blue, green, and red data points representing individual depth profiles, and for the data acquired over the range of $0-100 \,\mu\text{m}$, a $40 \times$ microscope objective was used (ca. 0.9 μm depth of focus).



Figure 3.3 (a) Variation of anisotropy decay time constant with the distance from a silica support for resorufin (anion, red), cresyl violet (cation, blue), and nile red (neutral, black). (b) Variation of anisotropy decay time constant with the distance from a silica support treated with Me₂SiCl₂

Figure 3.3 (cont'd)

for resorufin (anion, red), cresyl violet (cation, blue), and nile red (neutral, black).

Given the opposing functional forms of the distance-dependent dynamics for the cationic and anionic chromophores, it is important to determine the contributions of RTIL and supporting surface charge to the data. Chromophore dynamics have been measured in ethylene glycol (EG) supported on the same silica surface. The results are found to be independent of the distance from the silica support (Fig 3.4). To evaluate the role of surface charge, the surface silanol functionalities were capped using dimethyldichlorosilane. Treating the silica surface with this reagent terminates the surface with neutral dimethylsilane functionalities, giving rise to depth-independent anisotropy decay dynamics for all chromophores (Fig 3.3b). The anomalous distance-dependent dynamics observed thus require the RTIL to be in contact with the (charged) silica support. We now turn to understanding the functional form of the data shown in Fig 3.2.



Figure 3.4 Depth dependence of the anisotropy decay time constant for resorufin (anion, red), cresyl violet (cation, blue), and nile red (neutral, black) in ethylene glycol. Data points at zero depth are displaced somewhat as a result of the interaction of the chromophores with the silica surface.

The induced orientational anisotropy decay of an ensemble of chromophores is derived from the

normalized difference between polarized emission transients (eqn 3.1) to produce the function,

R(t).

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}$$
[3.1]

Extracting chemical and physical information from R(t) has been treated extensively in the literature.¹⁷⁻²³ The modified Debye-Stokes-Einstein (DSE) model is useful for relating specific properties of the system to the observed experimental data.^{18, 21-22}

$$\tau_{OR} = \frac{\eta V f}{k_B T S}$$
[3.2]

where τ_{OR} is the decay time constant of R(t); η is the viscosity of the medium; V is the hydrodynamic volume of the reorienting entity; *f* is a frictional boundary condition term; k_B T is the thermal energy; and *S* is a shape factor to account for the ellipsoidal shape of the rotating species. The key question is which quantity in eqn 3.2 is responsible for the observed chargeand depth-dependent behavior in RTILs. The shape factors *S* of the chromophores are known to be on the order of 0.75 and the (rigid) chromophores will not change shape with distance from the support.²⁴⁻²⁵ Likewise, k_B T is uniform throughout the system. The frictional interaction term, *f*, is taken to be 1 for all measurements, which is typical for polar systems. The viscosity of the RTIL is on the order of 50 cP and there is neither evidence or precedent to suggest this term varies with proximity to a silica surface; it is a bulk property of the RTIL. The hydrodynamic volume of the rotating entity, however, can be used to account for the observed functional form of the τ_{OR} data (Fig 3.2).¹⁹

For the cationic and anionic chromophores, there is an equilibrium between free and ionpaired species. The chromophore is present at low concentration so the relevant ion-pairing will be between Resorufin⁻ and BMIM⁺ or between Cresyl Violet⁺ and BF_4^- ([BMIM⁺] = [BF_4^-] = 5.35 M).





Because the presence of a charged surface is required to produce the observed anisotropy decay gradient and this gradient is seen only in ionic liquids, it is asserted that the charged surface induces a compensating counter ion excess in the RTIL near the surface. This situation is analogous to that in the Gouy-Chapman-Stern model. The difference between an RTIL and a dilute solution is that for the RTIL, all molecules are charged and the movement of one charge ultimately requires the compensatory movement of an opposing charge to maintain bulk electroneutrality. Because the (charged) chromophores exist in an equilibrium between free ionic species and complexes with the dominant counter ion, and the presence of a surface charge induces a gradient in RTIL constituent concentrations, there will consequently be a gradient in the amounts of the free and complexed chromophores, reflected in the anisotropy decay time constant gradient as long as the rate constants for chromophore-RTIL association and dissociation are faster than τ_{OR}^{-1} . For a negatively charged surface, excess BMIM⁺ near the surface gives rise to an enrichment in resorufin-BMIM complex, leading to a relatively slow anisotropy decay time constant that becomes more rapid with distance from the surface. For the cationic cresyl violet chromophore, the relatively low density of BF₄⁻ near the interface yields a lower complex concentration, and the measured anisotropy decay time constant should be faster near the surface, slowing with distance from the surface.

Relationship of the Rotational Motion Gradient to the Free Charge Gradient. It is

instructive to relate the property we measure, the gradient in reorientation time constant, $\nabla \cdot \tau_{OR}$, to the displaced excess charge in the system and the surface potential of the silica plate. We accomplish this through the hydrodynamic volume of the reorienting moiety.

$$\nabla \bullet \tau_{OR} = \frac{\eta f}{k_B T S} \nabla \bullet V$$
[3.3]

At any given distance from the silica surface there will be an equilibrium between free and complexed chromophore (schemes 1 and 2) that is determined by the (RTIL) counter ion concentration,

$$[counter ion] = K_{eq} \frac{[complex]}{[free]}$$

$$V = X_{free}V_{free} + X_{complex}V_{complex}$$

$$V = \left(\frac{K_{eq}}{K_{eq} + [counter\ ion]}\right) V_{free} + \left(\frac{[counter\ ion]}{K_{eq} + [counter\ ion]}\right) V_{complex}$$
[3.4]

where the terms *X* are the mole fractions of free and complexed chromophores. $\nabla \cdot V$ is thus related to the counter ion gradient through $\nabla \cdot V = V_{free} \nabla \cdot X_{free} + V_{complex} \nabla \cdot X_{complex}$. In a system where every constituent molecule is charged, such a concentration gradient defines the gradient in displaced excess charge, *D*

$$\nabla \bullet \tau_{OR} = \frac{\eta f}{k_B T S} \nabla \bullet V = k' \nabla \bullet \mathbf{D}$$
[3.5]

where k' is a collection of constants, including those relating $\nabla \cdot V$ to $\nabla \cdot$ [excess counter ion].

The hydrodynamic volume of each species present in the systems under investigation can be determined using the method of van der Waals increments (Table 3.1).¹⁹

Species	Structure	V (Å ³)
Resorufin		165
Cresyl Violet	+H2N O NH2	217
Nile Red		250
BMIM ⁺		139
Tetrafluoroborate	Filme Brown F	50
R-BMIM complex		304
CV-BF ₄ complex		267

Table 3.1 Hydrodynamic volumes of system constituents.¹⁹

With f = 1, we estimate from the experimental anisotropy decay time constant data for resorufin, $X_{complex} = 0.46$ and $X_{free} = 0.54$ at the silica surface, while at 100 µm distance from the surface, $X_{complex} = 0.21$ and $X_{free} = 0.79$. Determining the actual excess BMIM⁺ concentration at the surface is complicated by the inability to quantitate the charge density at the silica surface. The

excess BMIM⁺ at the surface necessarily corresponds to a deficit in BF_4^- because all species present in the RTIL are charged. Quantitation of this charge gradient will require control over the charge density at the surface(s) of the RTIL. In the RTIL, the gradient in *D* is related to the surface potential of the silica through Poisson's equation,

$$\rho_f = \nabla \bullet \mathbf{D} = \varepsilon \nabla \bullet \mathbf{E} = -\varepsilon \nabla^2 \Phi$$

$$\nabla \bullet \tau_{OR} = -k' \varepsilon \nabla^2 \Phi \qquad [3.6]$$

where ε is the dielectric constant of the RTIL; ϕ is the scalar electric potential field arising from the surface charge; and ρ_f is the free charge gradient. The ability to characterize the free charge gradient in the RTIL provides direct insight into the spatial extent of the electric field induced by the surface charge through Poisson's equation (eqn 3.6). The distance over which the gradient is observed is not consistent with the predictions of the GCS model, and we are not aware of an existing theoretical framework in which to treat these data. RTILs are expected to deviate from the predictions of the GCS model because of the high density of charged species present. RTILs are also not crystalline materials because of the characteristic sterically induced disorder which leads to their existence in the liquid state at room temperature.

Analogy to Piezoelectric Behavior. The presence of the free charge gradient in the RTIL in response to the surface charge on the silica support is reminiscent of the response of piezoelectric materials to the presence of surface charge, except the spatial extent of the piezoelectric effect is damped in this instance by the molecular properties of the system. Piezoelectric materials manifest surface charge upon experiencing external stress. Lattice distortion results in the redistribution of charge within the material. The converse of this effect is that the application of charge to the surface of the material gives rise to a lattice distortion. These well-known effects

are seen in deformable crystals that possess an asymmetric unit cell. RTILs are obviously not crystalline materials, but they are characterized by strong ionic interactions that result in high viscosity and low volatility. Our observation of a free charge density gradient over *ca*. 100 μ m can be considered analogous to that seen in a piezoelectric material. We note that piezoelectric behavior is seen in a variety of biomaterials, including peptide nanotubes²⁶⁻²⁷ and viruses,²⁸ underscoring the fact that the effect is not limited to inorganic crystals.

The piezoelectric effect is described through the relationship between the application of a stress to a material and the resulting charge displacement, D^{29}

$$D = \varepsilon E + \delta T$$

$$S = sT + \delta^t E \tag{3.7}$$

where ε is the dielectric constant of the material; E is the electric field; δ is the matrix describing the piezoelectric effect; with δ^{t} being the converse, relating application of an E field to the strain induced in the system. T is the stress applied, which produces a strain, S; with *s*, the compliance, characterizing the proportionality between stress and strain. It is instructive to consider the molecular properties responsible for the effect we observe. The electric field is a property of the support and in future experiments will be a quantifiable and controllable experimental parameter. The matrix δ is a material property and will not vary with distance from the support. Likewise, the compliance of a material, *s*, is not expected to exhibit spatial variation for a nominally homogeneous material. The quantity in eqn 3.7 related to the molecular properties of the RTIL is the dielectric constant, ε . Although termed a constant, ε is frequency-dependent and related to the molecular polarizability through the Clausius-Mossotti relation.³⁰ Polarizability depends on molecular structure and orientation, and when considered in the bulk sense, the susceptibility is known to depend on the ordering within the material. For this reason, the potential gradient in the RTIL should manifest as a refractive index gradient ($\varepsilon = \mathbf{n}^2$).

Measurement of the dielectric response of a material can be challenging, especially when it changes over micrometer length scales. One way to evaluate the dielectric response of a material, at least qualitatively, is through the fluorescence lifetime of a probe molecule. The factors that contribute to the fluorescence lifetime of a chromophore are numerous, but it is well established that changes in the dielectric response of a material over short distances are reflected in changes in the fluorescence lifetime of a chromophore.³¹⁻³³ A gradient in τ_{fl} is observed for the chromophores examined here (Fig 3.5a), consistent with a gradient in the dielectric response of the RTIL. For the same RTIL systems supported on a silanized surface we do not observe the same fluorescence lifetime behavior (Fig 3.5b). We note that the lifetime depth-dependence and the anisotropy decay depth dependence are not identical, and hasten to note that there is no fundamental basis for the fluorescence lifetime and the anisotropy decay time to correspond directly. In fact, R(t) is normalized for fluorescence lifetime, rendering molecular motion measurements independent of changes in τ_{fl} .



Figure 3.5 (a) Variation of fluorescence lifetime with the distance from a silica support for resorufin (anion, red), cresyl violet (cation, blue), and nile red (neutral, black). (b) Variation of fluorescence lifetime with the distance from a silica support treated with Me₂SiCl₂ for resorufin (anion, red), cresyl violet (cation, blue), and nile red (neutral, black).

3.5 CONCLUSIONS

There are two immediate implications of the findings demonstrated in this chapter. The first is that by devising a means of characterizing ρ_{f} in RTILs, we have demonstrated for the first time a level of organization that exceeds previously reported gradients in this family of materials. The ability to relate this gradient to applied surface charge brings with it the possibility of controlling material properties such as refractive index gradients in RTILs. Perhaps of more fundamental value is that this family of materials can be understood in the context of piezoelectric materials where the bulk properties damp the spatial extent of the potential gradient owing to the disorder intrinsic to any liquid phase molecular system. Evaluating the dependence of ρ_{f} on the identity of the RTIL will help to determine the range of utility for this effect. Finally, the results give rise to a number of questions to consider about heterogeneous electron transfer of charged and neutral analytes in RTILs and how the redox probe molecule-RTIL complex has to reorganize for the electron transfer to occur. We believe our results to be fully consistent with observations of slow relaxation of the electric double layer in other RTILs.³⁴

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CHAPTER 4: MODULATION OF AN INDUCED CHARGE DENSITY GRADIENT IN THE ROOM-TEMPERATURE IONIC LIQUID BMIM⁺BF₄⁻

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4.1 ABSTRACT

In Chapter 3, we described in detail the existence of an induced charge density gradient, ρ_f , in a room temperature ionic liquid (RTIL, BMIM⁺BF₄⁻) normal to a charged planar silica surface. In this chapter, experimental control over the sign and magnitude of the gradient is demonstrated. The spatial extent of ρ_f can exceed 100 µm from the charged surface. ρ_f was characterized through the rotational diffusion time constant gradient of a cationic chromophore in the RTIL. The sign and magnitude of ρ_f in BMIM⁺BF₄⁻ is linked directly to the surface charge density of the electrode, which can be controlled. Transparent conductive electrodes (fluorine doped tin oxide (FTO) and indium doped tin oxide (ITO) coated on glass) were used as supports and it was demonstrated that control over the electrode surface charge carrier density can influence the magnitude and sign of ρ_f . There are limitations to this approach based on the FTO and ITO properties and these limits will be demonstrated experimentally in this chapter.

4.2 INTRODUCTION

Room temperature ionic liquids (RTILs) are a useful family of materials that have found application in a number of areas. Despite the utility of these materials, their physical and chemical properties have been challenging to understand, in large part because of the high charge density present in such systems (ionic strength 5 - 6 M), and the underlying inability to resolve the fundamental unit species, *i.e.* whether RTILs should be considered as discrete ions or as ionpaired dissociable molecules.¹ Recently, the Shaw group² (described in Chapter 2) and our group³ (described in Chapter 3) have independently identified organization in RTILs that extends over macroscopic distances. The Shaw group demonstrated that organization evolved slowly in RTILs at either gas or solid interfaces, where the media would organize into crystal-like (liquid)

media over periods of minutes to days, and this structural order persisted at least one micron into the bulk RTIL. This order was seen using infrared spectroscopy (IRRAS) and second order nonlinear spectroscopy. Their findings demonstrated clearly the (slow) evolution of crystal-like order in RTILs.

In Chapter 3, we discussed that exposing RTILs to a planar charged surface induced a charge density gradient in the ionic liquid normal to the charged surface plane, and the extent of the gradient was on the order of $100 \,\mu$ m. It is not clear if the order found by the Shaw group is related directly to that which we have found – theirs is structural and ours deals with a concentration gradient with no explicit structural order implied. These two separate and important findings, however, point to the fact that ionic liquids behave very differently than either ionic crystals or dilute solutions, and their propensity for exhibiting organization over macroscopic length scales renders them a unique class of materials. It is an ongoing effort to determine the relationship between the structural organization observed by the Shaw group and the induced charge density gradient observed by our group. Regardless, it is of central importance to determine if the induced charge density gradient seen in RTILs can be controlled and, if it can, what the limits of this control are.

In this chapter, a means devised by our group of controlling ρ_f in RTILs by controlling the excess surface charge density on FTO- or ITO-coated support surfaces in contact with the RTIL is introduced. We detail below our work demonstrating this control and describe how our approach to this problem differs from a capacitive approach to controlling surface charge density.

4.3 MATERIALS AND METHODS

Chemicals. Cresyl violet perchlorate (CV^+) was acquired from Eastman Kodak Co. and used without further purification. Ethylene glycol (EG, \geq 99%, Macron Fine Chemicals) and ethanol (\geq 99.5%, Sigma Aldrich) were used without further purification.

Purification of the ionic liquid. The preparation and purification of BMIM⁺BF₄⁻ has been described elsewhere.⁴ BMIM⁺BF₄⁻ (Sigma Aldrich, neat concentration 5.35 M) was stored over activated carbon for three days. The mixture was then centrifuged to separate the carbon powder from the RTIL. The majority of the BMIM⁺BF₄⁻ (several mL) was then removed and (*ca*. 0.5 mL) was heated to 70°C for 50 min while purging with ultrapure Ar (99.9995%, Linde). This procedure was performed with the RTIL in an electrochemical cell in a N₂-purged glove box.

Preparation of ionic liquid solutions. To prepare the RTIL sample containing CV^+ , a stock solution of CV^+ ($5 \times 10^{-4} \text{ mol } L^{-1}$) in ethanol was prepared. CV^+ (final concentration 5×10^{-5} mol L^{-1}) in BMIM⁺BF₄⁻⁻ was prepared by transferring 0.1 mL of the CV^+ stock solution into a 1 mL volumetric flask and evaporating it to dryness in an oven (100 °C, 1 hr). The cooled volumetric flask was then filled to the mark with purified BMIM⁺BF₄⁻⁻ and the solution was stirred for twelve hours prior to use. The solution was mounted in a cell configured as schematized in Fig 4.1.





Figure 4.1 (a) Schematic of cell holding RTILs configured as a capacitive device. The conducting coating is either ITO or FTO. For this cell, d = 1 mm. (b) Schematic of cell holding RTILs with the lower support configured as a resistive device. The conducting coating is either ITO or FTO. For this cell, d = 1 mm.

All sample preparation procedures were performed inside a N₂-purged vinyl dry box (Coy Laboratories, Grass Lake, MI). The relative humidity in the box was $\leq 0.1\%$ at room temperature, measured using a hygrometer. All purified BMIM⁺BF₄⁻ and solutions were stored over activated 5 Å molecular sieve in a glass-stoppered bottle and kept in the dry box. The molecular sieve was activated 400 °C. Water impurity levels after this pretreatment were estimated to be below 20 ppm, as measured by thermogravimetric analysis.

Electrode and cell preparation. Both FTO (Solaronix, TCO22-7, 7 Ω /sq) and ITO (Nanocs Inc., IT10-111-25, 10 Ω /sq) coated supports were sonicated in water containing detergent (Fisherbrand, Sparkleen 1), 18 M Ω water (Milli-Q) and then in isopropanol (Macron, 99.50%), for 15 min. each. The cleaned electrodes were removed from the isopropanol, washed with ethanol and oven-dried at 200 °C for 30 min. After the electrodes were cooled, they were cleaned using a UV/ozone cleaner for 20 min. and connections were applied to the FTO or ITO surface using conductive (silver-filled) epoxy (MG chemicals, 8331S-15G). The epoxy was cured at 120 °C for 30 min. prior to assembly of the cell. The cell spacer (*ca.* 1 mm thick) was cut from silicone rubber sheet (MSC Direct), and was sonicated in water containing detergent and 18 M Ω water (Milli-Q) for 15 min each. The cleaned spacer was washed with ethanol and then dried in flowing N₂ and air for 2 h prior to assembly of the cell.

Fluorescence anisotropy decay depth profiling. The instrument used to acquire depthdependent fluorescence anisotropy decay dynamics has been described in Chapter 2 and we provide only the essential details here. A Nikon Eclipse Ti-U inverted microscope is equipped with a confocal scanning head (B&H DCS-120) that has two time-resolved, polarized detection channels, each with an avalanche photodiode (ID Quantique ID100). The fluorescence transients are processed electronically using commercial time-correlated single photon counting gear (B&H SPC-152) and B&H software is used to operate the instrument and store the data. The light source is a synchronously pumped cavity-dumped dye laser (Coherent 702-2) operating at 563 nm (5 ps pulses, 4 MHz repetition rate). The dye laser is excited by the second harmonic output of a passively mode locked Nd:YVO₄ laser (Spectra Physics Vanguard) producing 13 ps pulses at 80 MHz repetition rate with 2.5 W average power at 532 nm.

4.4 RESULTS AND DISCUSSION

In Chapter 3 we demonstrated the existence of a free charge density gradient, ρ_{f} , in the RTIL, BMIM⁺BF₄⁻. The free charge density gradient existed over distances in excess of 100 µm from a planar charged surface (SiO_x) and was probed through measurement of the rotational diffusion time constant of charged chromophores as a function of distance from the (charged) surface. This unexpected finding lead naturally to the desire to control the free charge density gradient, for both fundamental reasons and because of the potential for practical applications stemming from such charge organization in RTILs. In this chapter, we report on the ability to control the charge density gradient in BMIM⁺BF₄⁻. Cationic chromophore Cresyl Violet (CV⁺) was used because of its favorable and well-characterized optical properties.

Before discussing control over ρ_f , it is useful to consider the magnitude of its spatial extent relative to known models of ionic species in the liquid phase. Most treatments of ionic species in solution at a charged surface are based on the Gouy-Chapman-Stern model⁵ or a variant to understand the electric double layer (EDL). The EDL forms in dilute ionic solutions in response to the presence of a charged interface, such as an electrode. While the details of the EDL have been the focus of a great deal of attention, the thickness of the counter-balancing solution layer in a concentrated electrolyte solution would be in the range of 1-100 nm depending on the excess

surface charge. All such treatments are based on the ionic species being present at relatively low concentrations, and for ionic liquids this is clearly not the case.^{1, 6-7} Recent capacitive electrochemical measurements in BMIM⁺BF₄⁻ however, are consistent with GCS behavior as well as the behavior expected for a molten salt,⁸ in contrast to theoretical predictions for RTILs.⁷, ⁹ There have been a number of investigations of interfacial organization of RTILs, both experimental and theoretical, with a common finding that organization, as measured by scattering or diffraction methods has a persistence length of 10 nm at most.^{5, 10-18} Such findings are apparently at odds with recent reports of long-range organization in RTILs, which show that spatial gradients can and do exist over um to sub-mm length-scales.²⁻³ It is instructive to consider that each of the methods used to acquire information on "organization" in RTILs sense a different property of the system. For example, the work of Anaredy and Shaw reports on molecular orientation using FTIR and second harmonic generation spectroscopies.² Other approaches, including electron diffraction, neutron diffraction, X-ray reflectivity and surface force measurements sense order at or near the RTIL surface.^{1, 14, 19-20} In our case the organization sensed is in the form of a charge density gradient and there is no specific implication of a spatial variation in the molecular orientation or organization of either cationic or anionic species, or any implication of quasi-lamellar structure as implied by scattering methods. The charge density gradient we report is, rather, a redistribution of discrete ionic species that is a systemic response to the imposition of a force and we have drawn the analogy of the effect we observe to the piezoelectric effect previously.³

In Chapter 3, a sample holder geometry was used where the RTIL was in contact with a planar silica window. There was no silica plate in contact with the top of the *ca*. 1 mm thick RTIL film (the RTIL was contained in a closed vessel). While this configuration was adequate

for demonstrating the existence of the induced charge density gradient, it was less than optimal if the goal is to demonstrate control over the direction and magnitude of the gradient. In order to achieve greater control we constructed a closed cell where both the top and bottom planar sheets that define the cell were glass coated with either ITO or FTO, transparent conductive oxides in contact with the RTIL (Fig 4.1).

As shown in the data presented in Fig 4.2, the direction of ρ_f , as sensed by CV⁺ demonstrates that these transparent conductive materials are characterized by positive ζ potentials, consistent with literature reports for pH values lower than 6.²¹ This finding is significant because of the implication that the pH experienced by the silica surface is below 6. The RTILs we use are anhydrous but there is expected to be an adlayer of water on the support surface owing to its hydrophilic nature. The thickness of this aqueous adlayer is unknown but small, and the extent to which this layer interacts preferentially with either the support (ITO or FTO) surface or the RTIL is not known. Our empirical data indicate that the effective pH of this interface is below 6 but more detailed information remains to be elucidated.



Figure 4.2 Depth dependent reorientation time constant, τ_{OR} , of CV^+ as a function of distance from the lower supporting FTO-coated plate. Data were acquired with the cell configured as shown in Fig 4.1a, capacitive mode. Voltages applied ($V_{bottom} - V_{top}$) are (a) from 0 mV to -1000 mV as indicated in the legend, and (b) from 0 mV to +1000 mV as indicated in the legend.

Initial efforts to control the charge density gradient were aimed at controlling the surface charge density, σ , present on the electrodes on each side of the RTIL. Such a configuration is,

schematically, a capacitor (Fig 4.1a) and a potentiostat can be used to control the potential difference across the electrodes. Experimental implementation of this means of controlling ρ_f in RTILs does not, however, produce the desired result. Potential differences of 1V between the plates, regardless of the direction of the polarization, did not yield any change in the experimental signal in either the magnitude or direction of ρ_f (Fig 4.2).

The reason for this apparent failure lies in the geometry of the cell used, which is itself a consequence of the length scale of the induced gradient discussed in Chapter 3. To understand the reason for our findings, it is instructive to estimate the amount of charge that can be stored in this configuration and determine how that induced charge compares to the ambient charge on the FTO (ITO) surfaces.

The capacitance per unit area of this cell is given by eqn 4.1

$$\frac{c}{A} = \frac{\varepsilon \varepsilon_0}{d}$$
[4.1]

where C/A is the capacitance per unit area; ε is the dielectric constant of BMIM⁺BF₄⁻ (ε = 11.7);²² ε_0 is the permittivity of free space (8.854x10⁻¹² F/m); and *d* is the distance between plates. For the cell shown in Fig 4.1a, *d* = 1 mm, yielding a capacitance of 10 pF/cm² for the 1 cm² ITO (FTO) plates used. This capacitance corresponds to $\sigma \sim 6x10^7$ charge carriers per electrode for |V| = 1V.

It is important to compare this achievable surface charge density σ to that present on an ambient silica surface, the support on which ρ_f was first found to exist. We assume that the charge density on an ambient ITO (FTO) surface will be similar to that of silica, and even if this assumption is not quantitatively correct, it will be within an order of magnitude of the actual

value. For silica, the surface silanol group density is *ca*. 5 μ mol/m² (3×10¹⁴ O⁻/cm²).²³ The silica surface has been studied extensively and the silanol groups are characterized by two pK_a values, one at *ca*. 4.5 (19%) and the other at *ca*. 8.5 (81%).²⁴⁻²⁵ For silica in contact with BMIM⁺BF₄⁻, it is not possible to estimate the pH of the surface. If we assume that the silanol groups characterized by a pK_a of 4.5 are deprotonated while those with a pK_a of 8.5 are fully protonated, the silica surface charge density is 6×10¹³ O⁻/cm².

Using a two-plate model (Fig 4.1a), with control over the potential applied to each plate, σ can thus be changed by *ca*. 1 ppm of its ambient value. It is for this reason that no change is seen in ρ_f with variations in the plate potentials. Among the important questions is whether or not this physical configuration could be used to control ρ_f if it were changed dimensionally. The operative equation is Q = CV. As noted above, |V| = 1V was used, and the value of C was 10 pF. Two quantities can be changed; these are the distance between plates and the potential difference applied. For practical reasons, the smallest value of *d* is on the order of 1 µm, yielding C = 10 nF. The second variable quantity is V. Assuming a potential difference of 100 V between the plates, a change of $\sigma = 6 \times 10^{12}/\text{cm}^2$ can be achieved. Such values would approach, if not exceed, the limits of the device and would provide for a change in surface charge of only *ca*. 10% of the ambient value of σ . For this reason, it is necessary to identify other means of controlling the charge density on the support plate(s).

There are other ways to control surface charge density. One of these is use of the individual ITO (FTO)-coated plates as resistors (*ca*. 10 Ω) and to pass current across them (*not* between them). This experimental configuration is shown in Fig 4.1b. By controlling the current passed through the ITO, σ can be controlled in a range that is on the same order as the ambient surface

charge density of silica. $\Delta V = (V_+ - V_-)$ and R_L (Fig 4.3b) can be controlled to control the current I passing through the electrode. This approach controls the steady state density of charge carriers, σ , in the ITO (FTO). From the definition of current, I = Q/t, the appropriate values of ΔV and R_L required to control I can be estimated and thus Q in a relevant regime. Based on Chapter 3's results showing a measurable τ_{OR} gradient, we need to be able to modulate the charge on the support by ca. $10^{14} e^{-1}$ cm² s, corresponding to $1.6 \times 10^{-5} C$ /cm² s. For a 1 cm² ITOor FTO-coated glass support ($\ell = 1$ cm), the requisite current is thus estimated to be 1.6×10^{-5} A. The applied voltage is under our experimental control, and we use $\Delta V = 200 \text{ mV}$ for illustrative purposes (we use a range of voltages in our experimental measurements, vide infra). For $\Delta V =$ 0.2 V, $R_L \cong 12.5 \text{ k}\Omega$. The circuit indicated in Fig 4.1b places the ITO-coated plate (10 Ω) in series with R_L, producing a voltage drop across the ITO plate of 0.16 mV. This is feasible based on the typical dopant density of ITO. The units of I are C/s and the actual current required depends on the residence time of an e^{-} on the ITO plate. The drift velocity of the electron is $v_d =$ (I/ne) and for the parameters given above, $v_d = 1$ cm/s. Thus, for a flux of 10^{14} e⁻/s, the residence time of the e^{-} on the 1 cm x 1 cm ITO-coated plate is 1 s, but actual material properties (e.g. thickness, grain boundaries, dopant density) can and do affect this value substantially (vide infra).



Figure 4.3 Depth dependent reorientation time constant, τ_{OR} , of CV^+ as a function of distance from the lower supporting plate. Data were acquired with the cell configured as shown in Fig 4.1b, resistive mode. Currents applied (a) ranged from 0 mA to 200 mA using FTO as the conducting film on the support plate and (b) ranged from 0 mA to 420 mA using ITO as the conducting film.

A note is in order regarding the comparison of these two means of controlling σ , the charge density on a planar surface. From Gauss's law, for a capacitor the E field between the plates is given by $E = \sigma/2\varepsilon_0$, and for a planar conductor, the E field perpendicular to the plate is given by $E = \sigma/\varepsilon_0$. The E field experienced by the RTIL is the same for both configurations (Fig 4.1), and from Chapter 3 the free charge density gradient in the RTIL $\rho_f = \varepsilon \nabla \cdot E$. The underlying issue is the range of σ that is accessible using the two experimental configurations. For the capacitor (Fig 4.1a) $\sigma = \varepsilon \varepsilon_0 V/d$, and for the resistor (Fig 4.1b) $\sigma = (V/R)^*(\ell/v_d)$, with the factor (ℓ/v_d) being required in the latter case because of current flow. As discussed above, owing to the spatial extent of ρ_f , control over σ is more facile using the configuration shown in Fig 4.1b.

In Fig 4.3, the experimental τ_{OR} gradients for CV⁺ in BMIM⁺BF₄⁻ as a function of current applied to the FTO (Fig 4.3a) and ITO (Fig 4.3b) supports (corresponding voltages and powers are given in Table 4.1) are shown. There are several important points to note regarding these data. The first is that the gradient for both FTO and ITO electrodes depends on the current across the lower conducting plate, demonstrating the validity of this means of controlling ρ_f . It is significant that the direction of the gradient can be changed with the application of *ca*. 150 mA across the plate. The current required to effect this change in gradient is significantly larger than that predicted theoretically. The reason for this is the finite thickness of the FTO or ITO material. It is the surface charge that mediates ρ_f , but due to finite plate thickness and the materials properties (*e.g.* dopant level, grain boundaries, defects), only a fraction of the current passes across the surface. The majority of the current passage is mediated by structure (*e.g.* grain boundaries, defects) that is buried within the oxide layer and is thus screened.

Table 4.1 Relationship between current and voltage across the bottom support plate thin film (ITO) and the change in temperature of ethylene glycol in the cell indicated in Fig 4.1b.

I (mA)	V (mV)	Power (mW)	ΔT (°C)
0	0	0	0
50	700	35	0.5
100	1700	170	2.5
200	3700	740	10.5
400	6300	2520	30

For this experimental configuration, control over the steady state charge density on the ITOcoated plate is easily achievable using conditions that should produce little Joule heating.²⁶⁻²⁷ It is important, however, to quantitate the extent to which Joule heating contributes to our experimental data. As can be seen in Fig 4.3, for the higher applied currents the CV⁺ anisotropy decay time is seen to decrease, with a loss of gradient.

One way to gauge the temperature of the medium in which CV^+ is reorienting is by modeling its behavior using the modified Debye-Stokes-Einstein equation (eqn 4.2),²⁸⁻³¹

$$\tau_{OR} = \frac{\eta V f}{k_B T S}$$
[4.2]

where η is the viscosity of the medium; *V* is the hydrodynamic volume of the probe;³² *f* is a frictional term to account for intermolecular interactions;³⁰ and *S* is a shape factor to account for the non-spherical shape of CV⁺.³¹ These quantities are known for CV⁺; *S* = 0.645, *V* = 216 Å³ and *f* = 1 in polar media.³³ While there are data on the viscosity of BMIM⁺BF₄⁻ available, and

information on its temperature dependence,³⁴⁻³⁶ we can use other solvents with thermal conductivity similar to that of the RTIL where the temperature-dependence of the solvent viscosity is equally well known.³⁷⁻³⁸ One such solvent is ethylene glycol, a comparatively viscous solvent whose temperature-dependent viscosity has been characterized in detail previously.³⁷ While these same measurements could be made directly using BMIM⁺BF₄⁻, we assert that using ethylene glycol is preferable because the rotational diffusion behavior of the CV⁺ probe has been examined more extensively in ethylene glycol than in any RTIL, and temperature-dependent changes in ρ_f cannot contribute to the measured CV⁺ rotational dynamics in ethylene glycol. By measuring the reorientation time of CV⁺ in the same sample cell used for the RTIL measurements as a function of current passed through the ITO (FTO) window, we can gauge the role of Joule heating in our measurements.

Using the parameters for CV^+ given above, τ_{OR} in ethylene glycol is calculated as a function of temperature using the temperature-dependent viscosity data from Bohne *et al.*³⁷ We compare the experimental data (Fig 4.4a) with the calculated temperature-dependence (Fig 4.4b) to determine the relationship between power applied and temperature of the cell (Fig 4.5). While it is possible to heat the sample significantly by means of Joule heating, it is clear from these data that the temperature change is less than 5 °C over the current range relevant to controlling the sign and magnitude of the free charge density gradient. We anticipate that with the use of thinner conductive layers the contribution of Joule heating will be even less.



Figure 4.4 (a) Dependence of CV^+ reorientation time constant, τ_{OR} , in ethylene glycol on current applied to the lower support plate conducting film. ITO was used as the thin film conductor for these measurements. Currents applied are as indicated in the legend and as shown in Table 4.1. (b) Dependence of CV^+ reorientation time constant, τ_{OR} , in ethylene glycol as a function of temperature, as determined from temperature-dependent viscosity data and eqn 4.2.



Figure 4.5 Temperature of the cell as a function of power applied. Red box indicates the power region and consequent maximum temperature change over which the sign of the free charge density gradient, ρ_f , changes sign.

These data also demonstrate that a temperature gradient does not exist across the thin film sample because the anisotropy decay time constant for CV^+ is depth-independent at each temperature measured (Fig 4.4). Because of the similar thermal conductivities of BMIM⁺BF₄⁻ (0.19 W/m-K)³⁹ and ethylene glycol (0.25 W/m-K),³⁷ the data shown in Fig 4.4 demonstrate that the ρ_f gradient we observe is not accounted for by a thermal gradient.

4.5 CONCLUSION

In this chapter, the ability to control the free charge density gradient, ρ_f , in the RTIL

BMIM⁺BF₄⁻ is discussed. The spatial extent of ρ_f and the physical properties of the ITO (FTO)

layer on the conducting support plates preclude the ability to control ρ_f by capacitive means. Steady state carrier density on the conducting support plates can be controlled by passing controlled current through them. This approach is successful because the drift velocity of the electrons in the ITO (FTO) is sufficiently low that the steady-state carrier concentration is directly proportional to the current applied. In this configuration there is a material-dependent difference between total current applied, which contributes to Joule heating, and the surface carrier density, which modulates ρ_f . The contribution of Joule heating to this effect has been shown experimentally. It is clear based on these findings that the development of thin conducting support layers will be useful in further minimizing the role of heating in these measurements, thereby allowing a greater range of control over ρ_f . REFERENCES

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CHAPTER 5: EFFECTS OF WATER ON THE INDUCED CHARGE DENSITY GRADIENT IN THE ROOM TEMPERATURE IONIC LIQUID BMIM+BF4 $^-$

5.1 ABSTRACT

In previous chapters, an induced charge density gradient ρ_f in the RTIL, BMIM⁺BF₄⁻, was reported on when it is in contact with a charged planar silica surface. The ρ_f gradient is normal to the silica surface and persists over ca. 100 μ m. The sign and magnitude of ρ_f in BMIM⁺BF₄⁻ is linked directly to the surface charge density of the electrode. By using indium doped tin oxide (ITO) or fluorine doped tin oxide (FTO) electrodes instead of silica as a support and passing current through (at least one of) the electrodes, we can control the steady- state carrier density on the conducting support plate(s). Thus, control was gained over the sign and magnitude of ρ_f in BMIM⁺BF₄⁻. In this chapter, the effect of water on ρ_f in BMIM⁺BF₄⁻ is discussed Controlled amounts of water were added to the RTIL/electrode system order to achieve concentrations up to ca. 25,000 ppm (2.5% w/w). The magnitude of ρ_f decreases with increasing water concentration, but the characteristic length scale appears to remain constant. When the water concentration reaches ca. 25,000 ppm, ρ_f is no longer observed using rotational diffusion experiments. This finding is unexpected based on the assumption that the dilute solution limit of RTIL behavior is described by the Guoy-Chapman-Stern model. There are essentially two possible reasons for this finding. Either the RTIL exhibits a structural anomaly that has not been described to date, or the addition of water is affecting the means we use to characterize ρ_{f} . To resolve this matter, other measurements can be performed in the future. One experimental method is secondharmonic generation measurements of BMIM⁺BF₄⁻ to characterize depth-dependent order in the RTIL in the absence of added chromophores. A second means is to change the anion of the RTIL to a hydrophobic one, thus maintaining the use of reorientation dynamics as a probe of ρ_{f} . The details of these approaches will be discussed below.

5.2 INTRODUCTION

Room-temperature ionic liquids (RTILs) are a useful class of materials with properties that include a large electrochemical potential window,¹ low vapor pressure,² nonflammability, and high thermal stability³. RTILs can be used in a variety of practical applications ranging from electrolytes for energy storage devices⁴⁻⁵ to novel solvent systems for organic synthesis⁶⁻⁷. Despite the potential of RTILs, understanding their properties on the molecular scale remains limited.⁸⁻¹¹ The reason for this limitation is the high charge density of RTILs (ca. 5-6 M) and the uncertainty associated with how to treat RTILs, either as ion pairs or discrete dissociated ions. The Gouy-Chapman-Stern (GCS) model does not describe the behavior of RTILs.¹² There have been experimental¹³⁻¹⁵ and theoretical studies¹⁶⁻¹⁸ of organization in RTILs ranging characteristic length scale from nanometers¹⁹⁻²¹ to micrometers.^{8, 22-23}

We have discussed in Chapter 3 that an induced charge density gradient ρ_f exists in RTILs in contact with a charged (planar) silica surface. The charge density gradient ρ_f is normal to the surface and persists for ca. 100 μ m. In Chapter 4, we discussed that the charge density gradient in RTILs can be modulated in both sign and magnitude by controlling the steady state carrier density in the ITO or FTO support material. These findings were predicted based on our initial experiments and underscored the fact that RTILs behave differently than dilute solutions and are a unique type of material. Further research on the molecular organization of RTILs and intermolecular forces that are operative in these materials will provide a better fundamental physical and chemical understanding of this class of materials.

The difference between hydrophilic and "hydrophobic" RTILs lies in the amount of water that can be absorbed when the the RTIL is exposed to atmosphere. Certain room temperature ionic liquids are known to be hygroscopic.²⁴⁻²⁷ It was found that even though many 1-butyl-3methylimidazolium based RITLs are "hydrophobic" (or less hydrophilic), such as 1-Butyl-3methylimidazolium hexafluorophosphate (BMIM⁺ PF_6^-) and 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM⁺TfN₂⁻), they are still very hygroscopic and can absorb water quickly when they are exposed to a humid environment.²⁸ It is thought that the RTIL anions interact more strongly with water molecules than the RTIL cations. The dominant wateranion interaction is assumed to be hydrogen bond formation. In many RTILs it is difficult if not impossible to avoid at least trace amounts of water being present, and sometimes water is added deliberately to reduce RTIL viscosity, increase conductivity and lower the high price of RTILs.²⁹ At the present time, however, the fundamental nature of the interactions of water with the RTIL constituents is not well understood, and the relationship between RTIL component structure, amount of water present and macroscopic properties is not predictable. There are currently no theoretical models describing the thermodynamic properties over the entire compositional range from pure RTILs to infinitely dilute RTILs solutions. The primary reason for this lack of models is the extremely complex molecular behavior of RTILs, both in their pure form and combined with water.²⁹ Understanding how H₂O interacts with RTILs and how the properties of RTILs are affected by the presence of H₂O is important in both scientific research and practical applications.

In this chapter, we discuss the effects of water in BMIM⁺BF₄⁻ on the induced charge gradient reported in Chapter 3. The water concentrations studied range from ca. 500 ppm to 25,000 ppm $(\chi_{H2O} \approx 0.006 \text{ to } 0.031 \text{ in mole fraction})$. Reorientation data for Cresyl Violet (CV⁺) show that the magnitude of ρ_f decreases with the increase of χ_{H2O} in the system. However, χ_{H2O} doesn't have a resolvable effect on the length scale of ρ_f . When χ_{H2O} reaches 0.031, ρ_f was no longer

observed in the RTIL|H₂O system. We describe below our results and consider possible reasons for the water-dependence we observe in these data.

5.3 MATERIALS AND METHODS

Chemicals. Cresyl violet perchlorate (CV^+) was purchased from Eastman Kodak Co. and used as received. Ethanol (\geq 99.5%) was purchased from Sigma-Aldrich Co. and used as received. Water was purified in-lab with a Millipore Milli-Q filtration system.

Purification of IL. The preparation and purification of the RTIL has been described somewhere else.³⁰ BMIM⁺BF₄⁻ (Sigma-Aldrich, neat concentration 5.35 M) was stored over activated carbon for 3 days prior to further processing. The mixture was centrifuged to separate the RTIL from the activated carbon. Then the majority of the RTIL (several mL) was removed carefully and heated (ca. 0.5 mL) to 70 °C for 50 min with ultrapure Ar (99.9995%, Linde) purging during the process. The RTIL sample was housed in an electrochemical cell that was in a N₂-purged glovebox during the purification process to minimize exposure to H₂O.



Figure 5.1 Structures of BMIM⁺BF₄⁻ and Cresyl violet (cation).

Electrode and Cell Preparation. FTO substrates (Solaronix, TCO22-7, 7 Ω /sq) were cleaned according to the following procedure. FTO substrates were sonicated in water containing detergent (Fisherbrand, Sparkleen 1), 18 M Ω water (Milli-Q), and isopropanol

(Macron, 99.50%) for 15 min each. The cleaned substrates were removed from isopropanol and washed with ethanol and water, and oven-dried at 200 °C for 30 min in air. After cooldown of the substrates, they were put in a UV/ozone cleaner and cleaned for 20 min. The copper wire connections were attached to the substrates by silver conductive epoxy (MG chemicals, 8331S-15G). The epoxy was baked at 120 °C for 30 min before assembly of the cell. The cell spacer was about 1 mm thick and was cut from a silicone rubber sheet (MSC Direct). The spacer was sonicated in water containing detergent and 18 M Ω water (Milli-Q) for 15 min each. Then the clean spacer was washed with ethanol and water, and dried in flowing N₂ and air for ca. 2 h before assembling the cell.



Figure 5.2 Schematic of the self-designed cell holding $BMIM^+BF_4^-$ with the lower support configured as a resistive device. The conducting coating is either ITO or FTO on a silica support. For this cell, d = 1 mm.

Fluorescence Anisotropy Decay Depth Profiling. The instrument used for acquisition of depth-dependent fluorescence anisotropy decay data has been described in Chapter 2.³¹ Briefly, a Nikon Eclipse Ti-U inverted microscope is equipped with a confocal scanning head (B&H DCS-120) which has two time-resolved, polarized detection channels. Each channel has an avalanche photo diode (ID Quantique ID100). A commercial time-correlated single photon counting signal processing system (B&H SPC-152) is used to acquire and process the time-resolved data. B&H software is used operate the instrument and record the data. A

synchronously pumped dye laser (Coherent 702-2) operating at 563 nm (5 ps pulses, 4 MHz repetition rate) is used as the light source. The dye laser used in this experiment is excited by the second harmonic output of a passively mode-locked Nd: YVO₄ laser (Spectra Physics Vanguard). The source laser produces 13 ps pulses at 80 MHz repetition rate and produces 2.5 W average power at 532 nm.

5.4 RESULTS AND DISCUSSION

In previous chapters, we have demonstrated the existence of an induced charge density gradient with a persistence length of ca. 100 μ m in the RTIL BMIM⁺BF₄⁻. We measured the rotational diffusion time constant of three different chromophores (cationic, anionic and neutral) as a function of distance from the IL|Support interface. The existence of ρ_f brought the implication that control over support surface charge of the substrate could, in principle, provide control over the magnitude and sign of ρ_f . We used the cationic chromophore cresyl violet to probe the rotational diffusion time constant as a function of distance from the support surface because it is a well-characterized chromophore. We used ITO and FTO separately as the electrodes. Both thin film materials are conductive and transparent, which are two primary requirements for the experiments reported here. Current was passed through the conductive film on the lower support to change the steady state surface charge density. The experimental results showed that the sign and magnitude of the induced charge gradient density can be changed in response to changes in surface charge density. As noted above, it is well-known that RTILs absorb water from the atmosphere. It is thought that RTIL organization and physical properties are affected significantly by the presence of water, e.g. the viscosity, conductivity and electrochemical window, even though the water concentration might be low.^{28, 32} The data we present here demonstrate that the effects of water on the induced charge density gradient in

RTILs is not consistent with the predictions of the Guoy-Chapman-Stern model (dilute ionic solution).

The configuration of the surface potential-controlled cell was described in Chapter 4. The cell is a sandwich structure as shown in Fig 5.2. The top and bottom support are both FTO electrodes. Between the two electrodes is the silicone spacer. Current was passed through the bottom FTO electrode. Since I = dQ/dt, and the drift velocity of an electron in the FTO or ITO thin film electrode is on the order of 1 cm/s, the surface charge density of the support will change with current.

We measured the rotational diffusion dynamics of CV^+ from the RTIL|FTO interface through a depth of 100 µm into the RTIL. TCSPC data is of the form of polarized emission transients, $I_{\parallel}(t)$ and $I_{\perp}(t)$, where the subscripts refer to the polarization of the emission relative to that of the excitation. Taking the normalizing difference between polarized emission transients produces the induced anisotropy decay function R(t), of CV⁺ in the RTIL BMIM⁺BF4⁻ (eqn 5.1).

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}$$
[5.1]

The chemical information of importance to this work is contained in the decay functionality of R(t), as has been described thoroughly in the literature. ³³⁻³⁷ In the RTIL BMIM⁺BF₄, CV⁺ can be treated as a prolate rotator and R(t) is fitted using a single exponential decay function (eqn 5.2).

$$R(t) = R_0 exp(-t/\tau_{OR})$$

$$[5.2]$$

In eqn. 5.2, τ_{OR} is the decay time constant of R(t), and this quantity is related to system properties through the modified Debye-Stokes-Einstein (DSE) model (eqn 5.3).³⁴⁻³⁷

$$\tau_{OR} = \frac{\eta V f}{k_B T S}$$
[5.3]

In eqn. 5.3, η is the viscosity of the medium. V is the hydrodynamic volume of the reorienting entity, *f* is a frictional boundary condition term. k_B T is the thermal energy and S is a shape factor to account for the non-spherical shape of the volume swept out by the reorienting entity. We discussed in Chapter 3 that V, the weighted average hydrodynamic volume of the free and complexed form of the chromophore is the quantity we extract from the experimental data. The gradient of τ_{OR} in the data is actually the gradient of V, which is related to the induced charge gradient, ρ_f , as described in Chapter 3.

The water concentration $[C]_{H20}$ of the dry BMIM⁺BF₄⁻ sample used for this work was measured using a Quacounter AQ-2100 Karl-Fischer coulometric analyzer. Using this instrument, the BMIM⁺BF₄⁻ was found to have an ambient water concentration of ca. 500 ppm. A microsyringe was used to add specific amounts of water to the BMIM⁺BF₄⁻ sample, to achieve $[C]_{H20}$ of 1600 ppm, 3000 ppm, 5500 ppm, 7600 ppm, 10100 ppm, 12100 ppm and 24500 ppm. The rotational diffusion dynamics of CV⁺ in these eight samples are shown in Fig 5.3. From Fig 5.3 we can see, for the dry sample ($[C]_{H20} \approx 500$ ppm), the positive surface charge is meditated by electrons in the FTO thin film on the support, resulting in the sign and magnitude of ρ_f being controllable experimentally. This result agrees with results reported in Chapters 3 and 4. When $[C]_{H20}$ increases in the samples, the magnitude of ρ_f decreases. However, the length scale of ρ_f is not affected by $[C]_{H20}$. ρ_f ceases to be observable for currents when the water concentration reaches 24500 ppm.



Figure 5.3 Depth-dependent reorientation time constant, τ_{OR} , of CV⁺ as a function of distance from the lower supporting FTO electrode. Data were acquired with the cell configured as shown in Fig 5.2. Currents applied ranged from 0 mA to 200 mA using FTO as the conducting film on the support plate with a water concentration of ca. (a) 500 ppm, (b) 1,600 ppm, (c) 3,000 ppm, (d) 5,500 ppm, (e) 7,600 ppm, (f) 10,100 ppm (g) 12,100 ppm and (h) 24,500 ppm in the

Figure 5.3 (cont'd) BMIM⁺BF₄⁻ sample.



Figure 5.3 (cont'd)







There is literature that consider how water interacts with RTILs, using experimental and computational (Monte Carlo) methods. Tran *et al.*²⁸ used near-infrared (NIR) spectroscopy to
show that interactions between water and RTILs are strongly dependent on RTIL anion identity, for a given cation. Water appears to interact strongly with RTIL anions, leading to changes in the organization of the water. One consequence of this finding is that the organization of water within the RTIL will vary with RTIL identity. For BMIM⁺BF₄⁻, water interactions with BF₄⁻ lead to stronger hydrogen bonds than are seen between water and

bis(trifluoromethylsulfonyl)imide (Tf₂N⁻) or hexafluorophosphate (PF₆⁻). Gutiérrez et al.³⁸ carried out MD simulations for binary systems of 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM⁺BF₄⁻) and BMIM⁺BF₄⁻ with several molecular solvents. Their computations showed that the molecular solvents interact preferentially with BF₄⁻ whereas the interactions between the cation and the molecular solvent is less important. Zhang *et al.*³⁹ applied two-dimensional (2D) IR spectroscopy to investigate the dilution process of EMIM⁺BF₄⁻ in H₂O. Their data showed that the interactions between RTIL cation and anion become weaker with the addition of H_2O . During the dilution process, the three-dimensional (3D) network structure of EMIM⁺BF₄⁻ is gradually degraded into ion-clusters, with the ion-clusters then becoming predominantly ionpairs surrounded by H₂O for higher H₂O concentrations. Even when $\chi_{H2O} = 0.9$, EMIM⁺BF₄⁻ has not been fully dissociated into ions. Spickermann *et al.*⁴⁰ reported similar results using Molecular Dynamics (MD) simulations. Even for RTIL: $H_2O = 1:60$ for 1-Ethyl-3methylimidazolium chloride (EMIM⁺Cl⁻), contact ion pair still exist. In this Dissertation we have focused on the RTIL BMIM⁺BF₄⁻, where only a small fraction of the compact ion pairs are expected to dissociate. Dissociated BF₄⁻ anions will bind with CV⁺ to from the ion-paired complex CV⁺BF₄⁻. Induced charge density gradient ρ_f in the sample is thus the concentration gradient of free BF_4^- . Based on the data we reported in this chapter, the increase in $[C]_{H2O}$ interferes with the ability of BF_4^- to form the complex with CV^+ , precluding the ability of

rotational diffusion experiments to sense a gradient in the fraction of free and complexed chromophore. This is not to say that the actual free charge density gradient has been affected by the presence of water (indeed, the experimental persistence length of the gradient is not seen to change), but the ability to sense the gradient is compromised. If the increased water concentration in the sample functioned as a simple diluent, the approach to behavior described by the Gouy-Chapman-Stern model would manifest as a decrease in the characteristic length scale of the gradient, and this is not observed experimentally. It is thus important that another way to measure the charge density gradient be devised.

5.5 CONCLUSIONS AND FUTURE DIRECTIONS

We report the effects of water dilution on the induced charge density gradient ρ_f in the RTIL BMIM⁺BF₄⁻ by measuring the rotational diffusion dynamics of CV⁺ in the RTIL. The results showed the magnitude of the induced charge density gradient ρ_f is sensitive to the presence of water, but the characteristic persistence length does not exhibit a water concentrationdependence over the concentration range examined (500 ppm – 25,000 ppm). There are two possible reasons for this finding: Water molecules interact strongly with BF₄⁻ interfering with the anion's ability to form a complex with CV⁺. It is also possible that the addition of water decreases the viscosity of the RTIL, making the solution behaves more like dilute electrolyte solutions. This latter explanation is not consistent with the observed absence of a persistence length-dependence on water concentration.

In order to determine the effects of water on the persistence length of the free charge density gradient, an alternative means of measuring the gradient is thus required. As noted in previous chapters, there is an analogy to be made between the persistence length of the free charge density

gradient seen in RTILs and the existence of piezoelectric behavior in a solid material. While this analogy remains to be explored, one attribute of piezoelectric materials is that the unit cell does not possess a center of inversion and the material thus possesses a second order nonlinear optical response in the bulk. This is a property that can be measured experimentally, either through induced birefringence or the generation of second harmonic light. A possible alternative means for measuring the magnitude and persistence length of the induced charge density gradient in RTILs is to measure the intensity of second harmonic light produced as a function of system properties, such as charge density on the support plate, identity of the RTIL, amount of water present in the RTIL, polarization of the incident electric field and orientation of the (charged) support plane with respect to the direction of the incident electric field. An immediate benefit to this approach, if successful, is that the measurement of second harmonic light would not require the use of a chromophore in the RTIL. Rather, the measurement would sense organization in the RTIL directly. Miller has showed that the second order polarization coefficients that describe the nonlinear interactions of laser beams with piezoelectric crystals vary from one material to another by several orders of magnitude.⁴¹ By performing SHG measurements we can further prove the existence of ρ_f and the effects of water concentration in the RTIL directly.

Another approach to measurement of the free charge density gradient in RTILs is to use the established rotational diffusion experimental method, but with a different RTIL which has a hydrophobic anion (e.g. TfN_2^- or PF_6^-). The idea behind this approach is to reduce water interference with the formation of the CV⁺ chromophore with the RTIL anion. At some level, this approach would be limited by the interactions of water with either CV⁺ or the RTIL constituents, and for this reason the demonstration of second harmonic generation as a means of characterizing ρ_f would be preferable.

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CHAPTER 6: SUMMARY AND FUTURE WORK

6.1 SUMMARY OF THE DISSERTATION WORK

The ultimate goal of this research is to understand dynamics, organization and the response to external forces of room temperature ionic liquids (RTILs). In previous chapters, we have demonstrated that the RTIL BMIM⁺BF₄⁻ in contact with a charged surface can exhibit a free charge density gradient ρ_f over ca. 100 µm. Other experimental and theoretical investigations of RTILs have elucidated organization on ca. 10 nm and ca. 1 µm length scales. While the 10 nm¹⁻³ and 1 µm⁴⁻⁵ organization have precedent in electrochemical and liquid crystal literature, the existence of a free charge density gradient with a spatial extent of ca. 100 µm in an ionic liquid is without precedent and needs to be understood.

On physical grounds, ionic interactions and the spatial extent of the electrostatic forces associated with them cannot account for the longer-range order seen in RTILs. This situation, combined with the knowledge that it can take minutes to hours for dipolar annealing to occur in thin RTIL films⁴, leads to the conclusion that long-range induced order in RTILs bears a mechanistic similarity to field-induced distortions in piezoelectric materials. We focus in this dissertation on what is understood about organization in RTILs over the longest length scale because that is the most difficult to reconcile with the current understanding of RTILs and it also persists over distances that could be deterministic to how this family of materials is used in future applications. The spatial extent and functional form of the observed free charge density gradient $\rho_{\rm f}$ provides insight into possible reasons for its existence. These experiments are presently in progress and the ability to characterize induced $\rho_{\rm f}$ in RTILs will bring with it the development of a variety of novel applications such as electronically tunable ionic liquid optics.

In Chapter 2 of this dissertation, we described the instrumental method to measure the rotational diffusion dynamics of fluorescent probe molecules and thus to examine local organization in RTILs. The fluorescence anisotropy decay depth profiling instrument is introduced as a means to spatially resolve variations in the fluorescence anisotropy decay dynamics of the chromophores in RTILs. This instrument combines a time correlated single photon counting (TCSPC) laser system and an inverted confocal laser scanning microscope (CLSM), and provides ca. 50 ps time resolution, limited by the avalanche diode detectors and the TCSPC detection electronics. The time-resolved data generated from this instrument is related to the local environment of probe chromophore in RTILs.

In Chapter 3, we reported long range charge density gradient $\rho_{\rm f}$ in RTILs over a range of ca. 100 µm that was induced by a (charged) planar silica support.⁶ The fluorescence anisotropy decay of the chromophores resorufin (anion), cresyl violet (cation) and nile red (neutral) was measured in the RTIL BMIM⁺BF₄⁻ as a function of distance from the charged support. The instrument is equipped with an inverted confocal microscope thus depth resolution can be achieved through mechanical control over the microscope stage position. The chromophores exhibit depth-dependent reorientation dynamics that depend on their ionic charge. For resorufin, there is a decreasing gradient of the reorientation time constants (τ_{OR}) vs. the distance from the silica support and the gradient is inverted for cresyl violet. And for nile red, τ_{OR} is independent of the distance from the silica support. τ_{OR} is the decay time constant of the anisotropy decay function R(t), which is related inversely to the rotational diffusion constant, D_{ROT}. The observed distance-dependent dynamics differ according to chromophore charge, implicating charge as a contributing factor. The chromophore dynamics in ethylene glycol (a viscous but non-ionic solvent) supported on the same charged silica surface are also measured as control experiments

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and no depth-dependence in those data is found. To evaluate the role of surface charge, the surface silanol functionalities is capped using dichlorodimethylsilane. Reacting the silica surface in this manner terminates surface silanol functionalities with neutral dimethylsilane groups, resulting in depth-independent anisotropy decay dynamics for all of the chromophores. The occurrence of spatially varying chromophore dynamics is thus unique to RTIL and is induced by the surface charges of silica support.

The quantity in Debye-Stokes-Einstein (DSE) model⁷⁻⁹ responsible for the observed chargeand depth-dependent behavior of τ_{OR} in RTIL is the chromophore hydrodynamic volume (V).⁸ Since the silica surface is negatively charged, there will be an excess of (dissociated) BMIM⁺ in the RTIL near the surface compensating for the surface negative charge. This situation is somewhat analogous to the formation of an electric double layer in dilute solution except that for an RTIL there is no solvent medium and all constituents are either charged or are Bjerrum pairs capable of dissociation. The existence of one charge requires a compensatory opposing charge to maintain bulk electro-neutrality. The presence of a surface charge induces a gradient in RTIL dissociated constituent concentrations, giving rise to a gradient in the concentrations of the free and complexed chromophores (BMIM⁺ Resorufin⁻ and Cresyl violet⁺ BF₄⁻) since the chromophore is present at low concentration (typically ca. 10⁻⁵ M), and this gradient is manifested as a gradient in the anisotropy decay time constant.

With this understanding of the long range induced charge density gradient ρ_f in RTIL, we reported the applicable methods to modulate ρ_f in Chapter 4.¹⁰ In order to gain control over the surface charge density we have constructed a closed cell that confines the RTIL between two transparent conductive surfaces (fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO)). Initial attempts to control surface charge density were through the potential difference

between the two conducting surfaces, based on the relationship Q = CV. However, depthdependence of ρ_f does not change as a function of applied potential difference between the FTOor ITO-coated plates. The reason is that only ca. 1 ppm of the ambient charge is changed with the application of a potential across the plates. Another way to control surface charge density is to use the individual FTO- or ITO-coated plates as resistors (ca. 10 Ω) and to pass current across them (I = Q/t). By controlling the current passed through the FTO or ITO, the charge density can be controlled in a range that is comparable to the native surface charge density of silica. Thus conclusively control over ρ_f in the RTIL can be achieved. An important consideration in controlling ρ_f in this manner is understanding the role that Joule heating plays in the observed effect. By measuring the temperature-dependent rotational diffusion dynamics of cresyl violet (CV⁺) in ethylene glycol (EG) as a function of current applied to the ITO plate, the contribution of heating to the data can be quantitated.¹¹⁻¹² There is no depth-dependence of τ_{OR} for CV⁺ for a given applied current and there is a current-dependence of τ_{OR} for CV^+ which is related directly to the change in temperature of the system through the known temperature-dependence of ethylene glycol viscosity.¹³ The control experiments showed that Joule heating does not induce a thermal gradient and the temperature is constant at a given current across the ca. 1 mm film.

The work described in Chapter 5 investigated the effects of water on the induced charge density gradient ρ_f in the RTIL BMIM⁺BF₄⁻. By measuring the rotational diffusion dynamics of CV⁺ in the RTIL using the resistive device cell schematic (Fig 4.1b), we showed that the magnitude of ρ_f is sensitive to the presence of water. However, the characteristic persistence length does not exhibit a water concentration-dependence over the water concentration range of 500 ppm – 25,000 ppm. The concentration of water in the RTIL sample is measured by Karl-Fisher titration method. The possible explanation for this finding is that water molecules interact

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strongly with BF_4^- interfering with the anion's ability to form a complex with CV^+ . The change of the viscosity of the RTIL is also considered since adding water decreases the viscosity of the RTIL, making the solution behave more like dilute electrolyte solutions. However, this explanation contradicts the observed absence of a persistence length-dependence on water concentration.

As introduced in Chapter 1, four length scales of organization in RTILs have been revealed by experimental and theoretical methods. These are hydrogen bonded network, ca. 10 nm, ca. 1 µm and ca. 100 µm. Unfortunately, the term "organization" is still a vague definition here. For the hydrogen bonded network organization, it is mainly formed between cations and anions of RTILs in the solid state, and it is maintained in the liquid phase to a significant extent and even in the gas phase.¹⁴ For the 10 nm length scale the primary "organization" is thought to be roughly analogous to the electric double layer, present when RTILs are in contact with a charged surface.¹⁻³ For the 1 µm length scale, the "organization" has been characterized as structural,⁴ and for the 100 µm length scale, the "organization" is in the context of a free charge density gradient.^{6, 10} The presence of any organization over such a range of length scales is highly unusual for a fluid medium. While the 10 nm and 1 µm organization have some precedent in electrochemical¹⁵ and liquid crystal¹⁶⁻¹⁷ literature, the existence of a free charge density gradient with a spatial extent of ca. 100 µm in an ionic liquid is without precedent and requires a deeper understanding.

The main focus of this work is necessarily on the longest range organization in RTILs because it is the most difficult to explain in the context of known models. The fact that there is a ca. 100 μ m charge density gradient, however, cannot be accounted for in the framework of current models. The existence of such long-range order implies that the treatment of RTILs as

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"liquids" is not appropriate. The work described in this dissertation provides a new insight and a deeper understanding of RTILs, which is a prerequisite for using this family of materials most effectively and, more importantly, will provide a new way to think about ionic liquids and similar materials in future studies.

6.2 FUTURE WORK

The work we reported in this dissertation shows promise in studying the induced long range charge density gradient in RTILs. Future studies can be carried out in different directions to complement the knowledge we have at this point.

Second-Harmonic Generation (SHG) Measurements of Pure RTILs. As introduced in previous chapters, the creation of ρ_{f} in the RTIL in response to the surface charge density, σ_{s} , on the silica support is reminiscent of the response of piezoelectric materials to the presence of external force. For a material to exhibit piezoelectric behavior, it must be non-centrosymmetric. The application of an electric field across a piezoelectric material induces stress in the material, resulting in strain, which is an induced polarization. Induced polarization can be measured optically, and the lowest order optical response that requires a non-centrosymmetric medium is second order optical nonlinearities. It has already been established that RTILs exhibit a bulk second order nonlinear optical response based on work by the Shaw group.⁴⁻⁵ In analogy, we can measure the intensity of produced second harmonic light of RTILs as a function of system properties, such as the surface charge density etc. If this approach is applicable and successful, then the measurement of second harmonic light can be done without the use of a chromophore in the RTIL, and organization in the RTIL can be sensed directly.

Piezoelectric Response of RTILs. A key assertion of this dissertation is that the ca. 100 μ m order seen in RTILs is not consistent with established models for free charge density gradients or any other type of order in liquid media. The existence of long-range organization that is influenced by the presence of interfacial charge is described in the context of the piezoelectric effect. If an effect analogous to the piezoelectric effect is operative in RTILs, however, it should also exist when the RTIL is in the solid phase. Arguably the most direct means of measuring the piezoelectric effect is with atomic force microscopy, a technique that can measure dimensional changes in (solid) materials as a result of a potential difference applied across the material. Temperature-dependent AFM is well-established and the instrumentation is available in the MSU Composite Materials and Structures Center (CMSC) surface science facility. By performing SHG measurements, the calibration for the piezoelectric response by AFM measurements and how this effect changes in magnitude and spatial extent for temperatures above the RTIL melting point can be connected. The suite of measurements described above provide a direct means of evaluating the relative efficiency of the piezoelectric behavior of RTILs. This property is a direct consequence of the ability to induce a free charge density gradient, ρ_f , in the RTIL.

Dependence of ρ_f **on RTILs Structures.** The dependence of ρ_f on the chemical structure(s) of the RTIL anions and cations will depend on several factors. The magnitude of ρ_f will be determined by the extent of dissociation of the RTIL, while the spatial extent of ρ_f will be determined by the mobility of the ionic species in the RTIL medium.

The manner in which the identities of the RTIL cation and anion will influence ρ_f is through the extent to which each RTIL ion pair dissociates. The extent of dissociation of the RTIL is characterized through the equilibrium constant, K_{eq} for that ion pair. Structure-dependent changes in K_{eq} will alter the free ion concentrations in the RTIL. Thus the amount of free ions that can be complexed with the charged chromophores will be changed.

While the magnitude of ρ_f will depend on RTIL identity, the spatial extent of ρ_f will depend on the mobility of the dissociated ions in solution. We thus expect that the viscosity of the RTIL will mediate the characteristic length scale of the effect. Both the magnitude and length scale of the effect will be seen in the anisotropy decay gradient data.

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