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## TRANSLATIONAL AND ROTATIONAL DIFFUSION IN IONIC LIQUIDS

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Chemistry

by

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## Abstract

In this work, we have investigated both translational and rotational diffusion in neat ionic liquids (ILs) and in IL solutions using nuclear magnetic resonance (NMR) methods. Translational diffusion studies focus on ionic liquid solvents N-alkyl-N-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imides  $[Pr_{n1}][Tf_2N]$ , with n = 3, 4, 5, 6, 8, 10, and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide  $[P_{14,6,6,6}][Tf_2N]$ . Solutes include fused or bridged aromatics, fluorinated and nitrile-substituted benzenes, tetraphenylphosphonium benzoate, and other ionic liquids. Translational diffusion coefficients were measured using the longitudinal-eddy-current delay (LED) stimulated echo NMR pulse sequence with bipolar gradient pulse pairs. Applied field strengths were 400 and 850 MHz for <sup>1</sup>H frequency. Additional data were collected, from various sources in the literature, for both IL solvent and conventional solvent systems. These data were used both as a point of comparison for our own measurements and as a broader sampling of solutes and solvents, allowing for an assessment of the effect of solute-solvent properties on the friction coefficient.

Although the diffusion of solutes has been widely studied in conventional solvents and, to a lesser degree, in ionic liquids, many deviations from hydrodynamic predictions continue to be reported, often accompanied by their own competing models and hypotheses. One common deviation is that of sub-slip diffusion of small solutes in dilute solution. Study of such cases has been difficult because many of the more commonly-used analysis techniques are unable to measure small solutes or are prone to error. By contrast, NMR spectroscopy is ideal for such studies in that it is applicable for nearly all solutes, and provides more reproducible data than do several competing techniques. Despite this fact, NMR has been little used in studying dilute small molecule diffusion in ionic liquids. As a result, our work in this area provides a significant amount of new data and insight.

We find that deviations of translational diffusion coefficients from the Stokes-Einstein (SE) equation in ILs are analogous but more pronounced than those in conventional solvents, in part due to the typically larger size of IL solvents. The ratio of solute-to-solvent size in IL solutions has a significant effect on the friction coefficient for translational diffusion, as it does for conventional solutions. The friction coefficient is also affected, in both conventional solvents and ILs, by the difference in the intermolecular forces of the solute and of the solvent. We find that the effect of solute shape on translational friction coefficient is minimal with respect to other

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sources of deviation from SE behavior. We also consider several SE corrections which were proposed by other researchers for conventional solutions, and assess their accuracy for IL solutions.

Rotational diffusion studies focused on a different set of (deuterated) samples; neat 1ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide  $[Im_{21}][Tf_2N]$ , and a dilute solution of benzene in1-butyl-3-methyl-imidazolium tetrafluoroborate  $[Im_{41}][BF_4]$ . A series of solutions spanning 0 to 1 mole fraction of  $[Im_{21}][Tf_2N]$  in tetrahydrofuran (THF) was also analyzed. Rotational diffusion coefficient measurements utilized a deuterium inversion recovery NMR pulse sequence, with spectrometers ranging in magnetic field strength from 300 to 850 MHz proton frequencies.

The calculation of rotational correlation times,  $\tau_c$ , from NMR longitudinal decay times,  $T_1$ , is so complex that it has often been simplified to the point of inaccuracy. Any given molecule will likely have multiple rotational correlation times, depending on structure, symmetry, and internal rotational dynamics. All correlation times, which may be similar in value, are comprised by a single  $T_1$  for each observed nucleus in a molecule. The fractional contribution of each  $\tau_c$  to an observed value of  $T_1$  depends upon the placement of the observable nucleus within the molecule. These multiple correlation times, combined with such factors as the structure and symmetry of the molecule, result in strikingly disparate correlations between  $\tau_c$  and  $T_1$  for different molecules. Currently, it is common practice to calculate  $\tau_c$  using a single exponential dependence, the simplest of all relations to  $T_1$ , despite the fact that this is only expected to be strictly correct for spherical molecules. In this work, we present a method of interpreting NMR data in conjunction with molecular dynamics (MD) simulations in order to allow for a more accurate calculation of  $\tau_c$ .

The temperature-dependant rotational diffusion data we acquire by this method also contributes to the understanding of sub-slip rotations of small solute molecules in ionic liquids. Although many authors have proposed many different hypotheses in an attempt to explain this behavior, there is still no consensus. A systematic study by NMR has the advantage of accommodating smaller solute molecules than is possible using several of the more commonlyused techniques, while simultaneously providing greater reproducibility than can many other methods.

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In comparing rotational diffusion measurements made over a range of temperatures with three different magnetic field strengths to molecular dynamics simulations, we are able to fit various possible models for rotational correlation functions. Specifically, we generate time correlation functions via variable-temperature MD simulations, fit them to a parameterized functional form, in order to represent the simulated time and temperature dependence. Varying the parameters of such representations enables us to extract more meaningful rotational correlation functions and their temperature dependence from the measured NMR T<sub>1</sub> data. For both benzene and 1-ethyl-3-methyl-imidazolium, we find very fast dynamics that fall within the extreme narrowing regime at laboratory-accessible conditions, as well as slower dynamics. The faster dynamics likely correspond to in-plane rotations, while the slower correspond to tumbling. The slower component may be described with a single exponential or stretched exponential decay, but the faster component requires a bi-exponential. Solutions of [Im<sub>21</sub>][Tf<sub>2</sub>N] and THF display a single-exponential decay with increasing viscosity.

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## **Chapter 1.** Introduction

## 1.1. Ionic Liquids

#### **1.1.1.** Characteristics

Ionic liquids (ILs), bulky salts with melting temperatures at or below 100  $^{\circ}$ C, have been a focus of much research lately because of their many unusual properties, as well as their tunability. Among other attributes, they have extremely low vapor pressures, high thermal stability, wide electrochemical windows, high conductivity, and are generally chemically inert.<sup>1</sup> Additionally, the ease with which cations or anions can be exchanged allows ionic liquids to be designed for specific purposes. Even changing the length of an alkane chain, for example, results in a slight difference in properties. All of these qualities make them attractive options for a wide variety of applications. Low vapor pressure, high chemical and thermal stability, and tunability make them ideal as green solvents for many organic and inorganic reactions.<sup>2</sup> Their wide electrochemical windows and high conductivity are clear assets for electrolytes in solar cells and batteries.<sup>3,4</sup> As chromatographic stationary phases, their tunability itself is very desirable.<sup>5</sup> Many other potential applications are also garnering interest in ionic liquids. To further research into these various applications, a thorough understanding of the properties of ionic liquids is necessary. To this end, we have studied rotational and translational diffusion in ionic liquids, the factors influencing this diffusion, and the strengths and shortcomings of some of the many models for diffusion in ionic liquids.

#### 1.1.2. Microstructure

Ionic liquids, as a family, are ordered liquids. As may also be expected from any highconcentration salt solution, positive and negative charges are attracted to each other, forming a rough lattice of balanced charges.<sup>6</sup> This structuring is clearly demonstrated by center of mass radial distribution functions, g(r), such as those shown in Figure 1. 1. In these diagrams, the probability of occurrence of a given molecule is graphed against the distance from a randomlyappointed central molecule of interest. Probability densities rise and fall according to the size of the molecules, while the disorder inherent to fluids results in an exponential decay in the height of maxima with increasing distance from the central molecule. In a neutral mixture (NM), where the charges of the "cations" and "anions" have been turned off, the cation-to-cation distances (CC) are approximately equivalent to the anion-to-anion distances (AA), as well as to the cationto-anion distances (CA). The charges of the ions, once turned back on, have the effect of cutting in half the minimum distance between cations and anions, as well as shifting the CA radial distribution function to be exactly out of phase with the CC and AA functions. The reduction in the CA minimum distance is the result of opposite charge attraction coupled with like charge repulsion, causing a rough staggering of cations and anions, as may be predicted from solid salt structures. Likewise, the difference in phasing of CA maxima, in comparison to CC and AA maxima, is due to the pervasiveness of this staggering throughout the liquid. These staggered charges also have the effect of regulating the ion-to-ion spacing, so that g(r) in the ionic liquid displays a slower decay with distance.



**Figure 1. 1.** Center of mass radial distribution functions of a simplified model of butyl-methylimidazolium hexafluorophosphate, showing cation-to-cation distance (CC), anion-to-anion distance (AA), and cation-to-anion distance (CA); (a) with charges turned off "neutral mixture", (b) with charges turned on "ionic liquid".<sup>7</sup>

Some ionic liquids are additionally structured by formation of polar and nonpolar domains. Because the nonpolar parts of ionic liquid ions are chemically bound to at least one of the charge centers, these phases are necessarily small, with at least one dimension approximately equal to two molecular widths. The size and shape of the nonpolar domains varies in accordance with various aspects of the ions comprising them, such as the relative amount of polar-to-nonpolar constituents, and the charge placement on each ion (at one end, as in1- methyl-3-tetradecyl-imidazolium ( $Im_{14,1}^+$ ), as opposed to the more central placement in N-methyl-N,N,N-tributyl-ammonium ( $N_{1444}^+$ ) (Figure 1. 2).<sup>8</sup> Ionic liquids with similar overall aliphatic volumes

but significantly different chain lengths, such as N-methyl-N,N,N-tributyl-ammonium  $([N_{1444}][Tf_2N])$  and  $[Im_{14,1}][Tf_2N]$ , are also dissimilar in their nonpolar domain sizes. It is thought that certain types of nanostructures may aid or inhibit the diffusion and reaction of solutes, based on solute polarity and the connectivity of the better-solvating domain.



**Figure 1. 2.** Snapshots of simulation boxes taken from Shimizu, et. al.<sup>8</sup> Nonpolar segments shown in grey, cations in blue, anions in red. Ionic liquids are, from left to right: N-methyl-N,N,N-tributyl-ammonium bis(trifluoromethylsulfonyl)imide ( $[N_{1444}][Tf_2N]$ ), 1-methyl-3-tetradecyl-imidazolium bis(trifluoromethylsulfonyl)imide ( $[Im_{14,1}][Tf_2N]$ ), and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide ( $[P_{14,6,6,6}][Tf_2N]$ ).

Simulation studies have also demonstrated the presence of dynamic heterogeneity in neat ionic liquids. Although potentially related to the nanostructures described above, dynamic heterogeneity is a distinct phenomena, referring to spatial regions of higher and lower ionic mobility. Generally, regions with higher mobilities are also less dense than those with lower mobilities as there is less hindrance to molecular motion from neighboring ions. In other words, solvent ions in denser regions cannot rearrange as quickly as those in less-dense regions.<sup>9</sup> Solvent fluctuations will occasionally remove the obstacles to probe rotation, enabling largeangle "jump" rotations.<sup>10</sup> Dynamic domains are constantly moving and growing or shrinking over time, though much more slowly in ionic liquids than the solvent averaging in conventional solvents at room temperature. This results in non-Gaussian diffusion in ionic liquids, in which solvent averaging is too slow to allow for similar dynamics at different locations over relatively lengthy periods of time (in the case of molecular dynamics; nanoseconds). Solute molecules in ionic liquids experience similar effects, displaying a wide range of diffusional rate constants, as well as non-exponential fluorescence quenching, among other things. Although absent in conventional solvents, dynamic domains are also found in glassy liquids and supercritical fluids.<sup>9</sup>

### 1.2. Motivation

The purpose behind the studies in this thesis is twofold: to help elucidate the relation of IL structure to translational and rotational dynamics in ionic liquids, and to contribute to the usefulness of the models used in studying diffusion in ionic liquids. Linking IL structural trends, viscosities, and other factors to diffusion coefficients will allow future researchers to more readily identify the ionic liquids that are best suited to particular purposes, where diffusion is a limiting factor. Further development of models that may be applied in the study of diffusion in ionic liquids is also needed, as there is no simple model that can provide satisfactory results under a wide variety of conditions.

### 1.3. Analytes

In this study, research considering translational diffusion focuses on a series of N-alkyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquids ( $[Pr_{n1}][Tf_2N]$ , n=3,4,6,8,10) with varying lengths of alkane ligands (Figure 1. 3). By altering the chain length on the cation within one series, we hope to better understand the effects of ion size, shape, charge density, and viscosity on translational diffusion. Solutes have also been chosen so that, as a series, they may represent specific properties. The size/shape series is made of unsubstituted aromatics of increasing size and varying aspect ratio: benzene, naphthalene, biphenyl, anthracene, and pyrene. The intermolecular forces (IMF) series consists of benzene derivatives with nonpolar, dipolar, and ionic interactions: benzene, p-difluorobenzene, o-difluorobenzene, 2-fluorobenzonitrile, tetraphenylphosphonium benzoate [TPP][BA], and the pyrrolidinium cations of the neat ionic liquids. Concentration effects are considered for solutions of dimethylaniline (DMA) ranging from 0.3 M down to 0.01 M. Some other ionic liquids and solutes have also been considered, to a lesser degree, to demonstrate the reliability of our data.

Rotational diffusion studies focus on deuterated 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ( $[Im_{21}][Tf_2N]$ ) and 1-butyl-3-methyl-imidazolium tetrafluoroborate ( $[Im_{41}][BF_4]$ ), respectively. Deuterated imidazoliums are either singly deuterated at the acidic ring position, or are hexa-deuterated at all three ring positions and the three methyl positions. Hexa-deuterated benzene is also used as a solute in these studies. We analyze these samples across a range of temperatures in order to allow identification of more than one rotational correlation time if the times are significantly divergent. We also consider a mixture of ionic liquid ( $[Im_{21}][Tf_2N]$ ) and the conventional solvent tetrahydrofuran (THF) across the full range of compositions, to better understand the source of IL deviations from Stokes-Einstein-Debye predictions by observing the transition from the more accurately-described conventional solvent.



Figure 1. 3. Analytes used in this study.

### 1.4. Thesis Layout

The remainder of this dissertation is divided into six chapters. Chapter 2 discusses the principles behind nuclear magnetic resonance spectroscopy, specifically the translational diffusion experiment and the longitudinal relaxation experiment. In Chapter 3, I detail the experimental methods used in these studies, such as sample preparation, viscosity and NMR measurements, and data analysis techniques. Chapter 4 is dedicated to my translational diffusion project, in which translational diffusion and viscosity data are analyzed across several families of solutes and IL solvents. Various modifications to the Stokes-Einstein equation are considered with respect to conventional solvent data, as well our IL data. The rotational diffusion project is introduced in Chapter 5, which consists of rotational and translational diffusion into the changes in rotational and translational diffusion, and viscosity, as a solution progresses from neat conventional solvent to neat ionic liquid. Chapter 7 summarizes our findings overall. Finally, the Appendix contains detailed instructions for NMR setup and for performing rotational and translational diffusion diffusion and viscosity for several of our group's favorite ionic liquids and solutes.

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## Chapter 2. NMR Background

## 2.1. Basic NMR Spectroscopy

### 2.1.1. Nuclei

Every nucleus has both an intrinsic angular momentum, called spin, and an intrinsic magnetic moment. I will first address the intrinsic magnetism. Although magnetism can arise from the circulation of electric currents, such as the motions of electrons around the nucleus of an atom, this is not its only source. Magnetism is also an innate, unchanging property of both nuclei and electrons, independent of any current loop or rotation. The magnetic moment and the spin angular momentum of a given nucleus are related via the gyromagnetic ratio ( $\gamma$ ), according to;  $\hat{\mu} = \gamma \hat{S}$ , where  $\hat{\mu}$  is the magnetic moment operator and  $\hat{S}$  is the spin angular momentum of nucleus,  $\gamma$  has a specific value and may be either positive (most nuclei) or negative (electrons and a few nuclei). The nuclear magnetic moment is parallel to the spin angular momentum vector in the case of a positive  $\gamma$ , and antiparallel for negative  $\gamma$ .

Unlike macroscale angular momentum, spin angular momentum is not the result of rotation of the particle in question, but is simply an inherent property of the particle. Spin angular momentum can take on the values s = S, S-1, ...-S, where S is the lowest potential energy level (eigenstate) for the spin in a magnetic field. S may be either an integer, for bosons, or a half integer, for fermions. In the absence of a magnetic field, all available spin states are energetically degenerate and the spins of a set of particles will point in all directions, isotropically. The situation changes when an external magnetic field is applied to the system. For this discussion, I will consider only spin  $\frac{1}{2}$  nuclei.<sup>1</sup>

### 2.1.2. Spin States

In nuclear magnetic resonance (NMR) spectroscopy, the external magnetic field  $B_0$ defines the z-direction. For  $S = \frac{1}{2}$  nuclei, this leads to a loss of degeneracy between the  $\frac{+1}{2}$ ( $\alpha$  is aligned parallel with  $B_0$ ) and  $\frac{-1}{2}$  ( $\beta$  is aligned antiparallel to  $B_0$ ) spin states, known as Zeeman splitting. The  $\alpha$  spin state acquires a lower energy than the  $\beta$  state, resulting in a very small excess of  $\alpha$  spins, which creates a net magnetic moment aligned with the external magnetic field (Figure 2. 2). The spin state of a spin  $\frac{1}{2}$  nucleus in an external magnetic field is not, however, the binary function that it is often presented to be. In fact, the  $\alpha$  and  $\beta$  spin states can only be assigned values of +1/2 and -1/2 spin angular momentum along the z-axis. If the xor y-components of spin angular momentum are measured, they will have values of +1/2 or -1/2, with equal probability. What's more, spin  $\frac{1}{2}$  nuclei are not confined to only the  $\alpha$  and  $\beta$ spin states, but may occupy any superposition of the two (Figure 2. 1). In a superposition of states, it is not predictable whether the z-component of spin angular momentum will be +1/2 or -1/2. This distinction in possible spin states is important in understanding the workings of any NMR experiment, as even a simple 90° rotation for a 1D structural analysis by chemical shift and splitting patterns requires the ability of the spin to align itself in the xy-plane. When the spin is aligned neither parallel nor antiparallel with the z-axis, it is important to realize that, despite the arrow diagram depictions, x-, y-, and z-components are still  $\pm 1/2$  when measured.<sup>1</sup>



**Figure 2. 1.** An assortment of possible superposition spin states for spin  $\frac{1}{2}$  nuclei, represented in vector notation and as arrow diagrams. Although the diagrams are useful in considering spin dynamics, they are not completely accurate depictions of spin states; macroscale models for quantum mechanical phenomenon generally have some inaccuracies.<sup>1</sup>

## 2.1.3. Precession of Spins

In the simplest case, observation of the net magnetic moment is accomplished by irradiating the sample with a radio frequency (r. f.) pulse at the resonant Larmor frequency. This irradiation rotates all of the spins in the sample, regardless of their original orientation, and

thereby rotates the net magnetic moment. The length of the pulse (for constant intensity pulses) determines the angle through which the spins are rotated, with the strongest signal resulting from a 90° rotation ( $\pi/2$ ).



**Figure 2. 2.** Spins in an external magnetic field (at left)<sup>1</sup>; and the effect of a radio frequency (r. f.) pulse on the net magnetic moment (at right). In both illustrations, the thick grey arrows symbolize the net magnetic moment, the thick white arrows represent the external magnetic field, and straight black arrows symbolize individual nuclear spins.

Any spins which are not exactly parallel or anti parallel to the external magnetic field will precess at a fixed rate known as the Larmor frequency ( $\omega_0$ ). This rate is determined by the spin nucleus via its gyromagnetic ratio ( $\gamma$ ), and by the external field strength ( $B_0$ ) experienced by the nucleus (Eq. 2. 1).

$$\omega_0 = \gamma B_0 \qquad \qquad 2.1$$

The net magnetic moment for all spins of a given type of nucleus and chemical environment will precess as one. This precessing magnetic moment induces an oscillating voltage in the receptor coil of the spectrometer, the time-dependence of which is Fourier transformed to give the basic one-dimensional NMR spectrum.

## 2.1.4. Spin-Spin Interactions

The different chemical shifts in a spectrum are indicators of the various local chemical environments experienced by nuclei at different positions in a molecule. Classically, in circling a nucleus, electrons create their own magnetic fields, which partially counteract the external magnetic field, shielding the nucleus. If a polar functional group pulls electron density away from an electropositive nucleus (i.e. H), this shielding effect is smaller and the experienced magnetic field stronger than it would be for the same nucleus if it were not near an electronegative group. The stronger or weaker the perceived magnetic field, the higher or lower the Larmor frequency, respectively. This shift in Larmor frequency gives rise to chemical shifts in the spectra, with protons neighboring more electronegative functional groups displaying greater chemical shifts than protons in less polar environments.

When nuclear spins interact with neighboring nuclear spins, either directly by the through space dipolar interaction or indirectly by J coupling that is mediated by electron density, the result is spectral splitting. Because a given nucleus may be either spin up or spin down, its neighbors will experience either an increased local magnetic field or a decreased local magnetic field, respectively. Those with the slightly stronger local field will show a slightly larger chemical shift than those experiencing a weaker local field. As the populations for spin up and spin down are nearly equal, this produces two essentially equivalent peaks only slightly offset from each other; a doublet.

## 2.1.5. Spin Relaxation

There are two categories of relaxation in NMR that are considered in this thesis. Transverse relaxation, with relaxation time  $T_2$ , arises from a loss of coherence in the transverse components of the precessing net magnetic moment. This happens when initially aligned nuclear magnetic moments experience different local magnetic field strengths, causing them to precess at different rates. These magnetic field variations can be the result of inhomogeneities in the instrument's applied magnetic field or natural variations (transient and spatial) in the local microscopic structure of the solute or solvent. As illustrated in Figure 2. 3, the spread of precession frequencies leads to a decay of the transverse magnetization. Longitudinal relaxation, with relaxation time  $T_1$ , describes the fact that the net magnetic moment, when rotated away from its equilibrium alignment with the +z-axis by an r. f. pulse, slowly realigns with the external magnetic field. This relaxation is stimulated by fluctuations in the direction and magnitude of the local magnetic field. This cannot be caused by inhomogeneities in the applied field of the magnet, but is the effect of instantaneous fluctuations in local moments produced by nearby nuclear spins. These mechanisms happen concurrently. Generally,  $T_2$  relaxation is faster than  $T_1$ .

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**Figure 2. 3.** Transverse relaxation (at left); and longitudinal relaxation (at right). In both illustrations, the arrows are assigned as in Figure 2. 2. For clarity, transverse and longitudinal relaxation have been represented separately; they actually occur concurrently.

## 2.2. Translational Diffusion Measurements

### 2.2.1. Competing Techniques: Strengths and Limitations

Among the less intuitive quantities that can be measured using NMR are translational self-diffusion coefficients. How these measurements are conducted is discussed in the following section. As there are many other methods for measurement of self-diffusion, some consideration is due the choice of analysis technique. Besides NMR, there are many electrochemical techniques, fluorescence correlation spectroscopy, and various home-grown methods for the determination of diffusion coefficients.

### 2.2.1.1. Electrochemical Methods

Electrochemical analysis of diffusion coefficients in ionic liquids carries with it a few requirements, regardless of the specific technique. Voltammetric methods involving, for example, disk electrodes, almost invariably use ultramicroelectrodes (UMEs), electrodes with a dimension of 25 µm or less, rather than the macroelectrode alternatives. This is likely due, at least in part, to the much smaller sample size requirements. Many scientists also prefer to work within a Faraday cage. And, as with any diffusion measurement of ionic liquids, the much lower diffusion coefficient must be factored into the experimental design. In the case of electrochemical measurements, that often means accounting for a significant shift in the necessary potential scan rates (or RPMs, in the case of rotating disk electrodes) for steady-state and transient regions, with respect to more conventional solvents. The ionic solvation of charged solutes- inescapable when conducting electrochemical experiments in ionic liquids- particularly

lends itself to convolution of electrochemical data, as is discussed presently. And, of course, all electrochemical measurements are limited to redox active analytes.

One way to measure diffusion coefficients using electrochemical methods is by potential step chronoamperometry. This method has the advantage of measuring analyte concentration, as well as the diffusion coefficients of both the analyte and its redox partner.<sup>2</sup> It is also has the option of not requiring steady-state conditions, which are very slow measurements when using UMEs.<sup>3</sup> There are two methods of extracting the diffusion coefficient by chronoamperometric means. According to the first of these, the current-response is monitored as the potential is stepped from the region of no Faradic current to a region of mass transport-limited reduction or oxidation. Diffusion coefficients can be determined by fitting these data to one of several relations, the most common of which are the Shoup and Szabo equations.<sup>4</sup> The analysis is more complex for a backwards (return) step, in the case of double potential step chronoamperometry. To determine the diffusion coefficient of the redox product of the reaction from the first potential step, the current-response of the second, backwards step must be analyzed by computer simulation, as described by Klymenko, et al.<sup>5</sup> When using this analysis method, simulation results were verified by using the same model to predict cyclic voltammograms in the transient region, and matching them against experimental CV results.<sup>5</sup> Another method of determining diffusion coefficients from chronoamperometric measurements requires both transient and steady-state data, but yields the same information.<sup>2</sup>

Cyclic voltammetry (CV) is another method which has often been used to determine diffusion coefficients in conventional solvents. Some scientists dislike it for use with ionic liquids because reduction-oxidation rates in such high-viscosity solvents fall in-between transient and steady-state behavior, when practical scan rates are used with UMEs, as indicated by equation 2. 2.<sup>6</sup> This makes extraction of a diffusion coefficient at UMEs very difficult, while measurement with larger electrodes requires much larger sample sizes than are easily or cheaply attained.

$$\nu \ll \frac{RTD}{nFr_d^2} \qquad 2.2$$

In the above equation,  $\nu$  is the potential scan rate, R is the universal gas constant, T is temperature, D the diffusion coefficient, n the number of electrons involved in the redox reaction, F is Faraday's constant, and  $r_d$  is the radius of the disk electrode. The often very large

difference in diffusion coefficients of the oxidized and reduced forms of a redox pair are also difficult to detect in CV measurements, thereby causing inaccurate determination of kinetic parameters.<sup>7</sup> It has also been argued, however, that CV has many advantages for measuring diffusion coefficients of ionic liquids, as the shape of the voltammogram indicates the redox potentials, and warns of any complicating reactions or electrode passivation, not indicated by such methods as chronoamperometry.<sup>8</sup> In a recent study<sup>9</sup> comparing the diffusion coefficients calculated by NMR with CV measurements using various types of electrodes, the authors found general agreement among all the methods. Electrodes considered include a macroelectrode (1 mm diameter), Random Assembly of Microdisks (RAM) electrodes (7 µm diameter, each, with non-overlapping diffusion layers), and an intermediately-sized rotating disc electrode (2.9 mm diameter). The authors note that the RAM electrode assembly suffered less from Ohmic effects and charging currents than did the larger diameter electrodes. Although UMEs can suffer from very small and difficult-to-measure currents, especially when measuring steady-state diffusion in high viscosity solvents, this problem is largely addressed by the signal-multiplying effects of the RAM array.

Scanning Electrochemical Microscopy (SECM), whereby current generated at an ultramicroelectrode is recorded as a function of distance from a substrate, has also found favor as a method of detecting translational diffusion. For most electrochemical methods, the "ionic solvation" of charged solvents- the strong solvation of ionic solutes by solvent ions, thereby increasing the hydrodynamic volume of the solute- is particularly problematic. Many electrochemical analyses assume that diffusion coefficients of reduced and oxidized components of a redox pair are comparable. While this assumption is reasonable in conventional solvents, the often substantial increase in hydrodynamic volume of one half of a redox pair in comparison to the other, results in a similarly substantial reduction of the diffusion coefficient in ionic solvents. Whereas most electrochemical methods cannot easily detect this, transient mode SECM draws attention to the difference in diffusion coefficients across a redox pair, even allowing measurement of the two (different) values.<sup>7</sup> Analysis by this method has some pitfalls, however. Preliminary cell measurements must be carried out in a conventional solvent (as opposed to the solvent of interest, as is often the case in SECM), and measurements in steadystate mode with a moved electrode may be easily misinterpreted, are prone to convection effects in the highly-viscous ionic liquids, and are difficult to analyze.<sup>10</sup>

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Two more electrochemical methods of assessing translational diffusion are impedance spectroscopy (at low frequencies) and polarization measurements. Both require the use of thin layer cells, which generally give larger uncertainties than do measurements at UMEs, because of the variation in electrode distance and the difficulty of measuring that distance.<sup>3</sup> These measurements also tend to be even slower than methods involving steady-state conditions at microelectrodes. Of the two, however, polarization measurements are both more accurate and faster than impedance spectroscopy, because of the very low frequencies required by the latter.<sup>8</sup>

#### 2.2.1.2. Other Methods

In the Taylor dispersion method, which has been used to assess diffusion coefficients of alkylimidazolium tetrafluoroborates and hexafluorophosphates<sup>11</sup>, neat solvent is slowly forced through a length of cylindrical capillary by means of a pressure differential. A relatively small amount of solution, made with the same solvent, is injected into the flow line. Eventually, convection and diffusion will carry the solute to the end of the capillary, where its concentration is continuously detected. Laminar flow, combined with radial diffusion of the solute, will result in a Gaussian concentration distribution upon elution. According to Taylor's analysis, the diffusion of the solute may be calculated from the retention time for the solute's concentration maximum ( $\tau_R$ ), and the full width at half-maximum for the concentration profile ( $w_{1/2}$ ) as follows;  $D = 0.2310R^2 t_R / W_{1/2}^2$ , where R is the capillary radius. Diffusion coefficients also depend on the load time; the time required to inject the saturated solution without changing the pressure or flow rate. Samples with a long load time will have a greater difference between actual diffusion coefficients (D(0), assuming delta functions as solution injection profiles) and those calculated above, D(t), such that  $D^{-1}(t) = D^{-1}(0) + bt^2$ . This technique may be used over a wide range of temperatures, including those above the solvent boiling point, so long as pressure is increased enough to avoid boiling. Care must be taken to minimize temperature and pressure changes upon elution from the capillary and detection, as well as the effects of tube coiling.12

The lag-time technique, favored for its ability to measure both diffusivity and solubility of gases simultaneously, uses a dual chamber cell, with feed chamber and permeate chamber separated by a liquid support membrane. The entire apparatus is contained within an insulated box for temperature control. Both chambers are separately connected to a vacuum pump, to

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allow evacuation of the cell after the membrane is in place. Test gases are injected into the feed chamber via a septum port once the cell is fully evacuated, and both diffusion and solubility are calculated from the observed rise in pressure in the permeate chamber as the gas diffuses across the membrane. Convection is essentially eliminated through use of the membrane's glass supports, allowing for a clear determination of diffusion. Daynes' equation<sup>13</sup> relating the diffusion, solubility, and experimental conditions requires some specific circumstances in order to yield accurate results. The membrane volume must be very small in comparison to the chamber volumes to allow for the approximation of infinite chamber volumes. Care must also be taken to ensure steady-state conditions, generally reached after 2.5 - 3 times the "lag" time;  $L^{2}\tau^{2}/6D_{i}$ . To prevent the ionic liquid membrane from being forced into the permeate chamber when the solute gas is injected, a porous film which is not wettable by the membrane liquid, in this case ionic liquids, is applied to the permeate chamber side of the membrane. The small pore size and non-wettability prevent the liquid from being forced through the glass support and into the permeate chamber by the pressure differential upon injection of the gas solute. Although the lag-time method is useful in its determination of both diffusion and solubility, and its small liquid sample size (<1 mL), it is not the most accurate technique for determination of gas diffusivities in liquids and suffers from some membrane tortuosity<sup>14</sup>. It also may not be used for samples with low solubility, as solubility and diffusivity are not separable under these conditions.<sup>15</sup>

A couple other methods observe both diffusion and solubility by measuring the change of pressure of the gaseous analyte. These methods rely on diffusion into a substantial volume of ionic liquid, rather than diffusion into a membrane. Observation of gaseous diffusion in ionic liquids by semi-infinite volume measurements have been made by Camper *et al.*<sup>16</sup>, using a homemade pressure decay-dual transducer solubility apparatus. This instrument measures the diffusion of gaseous analyte into the ionic liquid by observing the gaseous pressure decay in a chamber of known volume as the gas is absorbed by a stagnant volume of ionic liquid. Diffusion is calculated from the pressure drop of the gas over the first 20 minutes after the gas is released into the cell holding the ionic liquid. Because the ionic liquid is un-stirred during this time, the gas will reach its maximum solubility concentration at the ionic liquid surface, and the drop in pressure will be controlled by gradient diffusion, rather than by the rate of absorption. Once the data for the diffusion coefficient has been collected a stirrer is turned on, allowing the solution to

reach its equilibrium concentration more quickly. The overall pressure drop, once maximum dissolution has been achieved, is used to calculate Henry's constants for solubility. A similar technique, the transient thin film method<sup>14</sup>, differs mainly in the amount of ionic liquid used (a thin film rather than a "semi-infinite" volume) the time required for data collection, and the mathematical relation of pressure measurements to diffusion coefficients. The transient thin film method is also able to assess solubility, as well as diffusivity, in a single measurement, with the benefit of greater accuracy, because of the larger quantity of data. Both of these methods, as well as the lag-time technique discussed above, only measure diffusion along a gradient, rather than self-diffusion within a homogeneous solution.

There exist many variations on the above-mentioned techniques, as well as several distinctively different methods. Among these are the Schlieren scanning technique, a.k.a. the Schlieren cylindrical lens method, in which diffusion coefficients are determined from the change in refractive indices as a concentration gradient moves across the observation cell.<sup>17,18</sup> The transient grating method also relies on differences of refractive index (as well as absorbance) for diffusion measurements. In this case, a split beam is used to excite the sample, creating a grating-like pattern of excited and ground-state analytes, distinguishable by their different optical properties. This grating will refract the probe laser beam until it is dispersed by self-diffusion of the solution (so long as the relaxation rate is slower than the diffusion rate).<sup>19</sup> Gravimetric methods have also been used to measure transient diffusion.<sup>20</sup> A gravimetric microbalance is, essentially, a very sensitive balance enclosed in a temperature and pressure controlled atmosphere. The weight of the evacuated ionic liquid sample is monitored as it is exposed to the solute gas. This method also relies on diffusion along gradients, and the uncertainties are increased by the effects of temperature and pressure changes and aerodynamic drag on the instrument sensitivity, buoyancy force, and sample volume.

## 2.2.2. Simple Pulsed Field Gradient (PFG) Technique

In order to measure the self-diffusion of a species by NMR, the individual molecules must somehow be labeled. This is achieved by first creating transverse magnetization (initially equivalent to the net magnetic moment) with a radio frequency pulse. Measurement of the motion of the molecules is accomplished through the use of a magnetic field with varied intensity along the *z*-axis; a gradient field (Figure 2. 4). Because spins precess more quickly in

stronger fields, the spins at regions of weaker field strength fall behind those at locations of stronger field. It is most convenient to consider what happens from the rotating frame, the reference frame spinning at the Larmor frequency, so that the average spin appears stationary. In such a frame of reference, the component spin magnetizations comprising the initial "labeled" magnetization of the spins dephase in the magnetic field gradient, taking on the form of a spiral in the z-direction. This destroys the net magnetization which appears to be zero after gradient induced dephasing. In Figure 2. 4, the arrangement of component spin magnetizations along the z-axis after the first gradient pulse (g) is such that, assuming a system with positive  $\gamma$ , the stronger field must be at high z and the weaker field at low z. After a sufficient amount of time, the gradient field is removed and the system is allowed to evolve in a homogeneous magnetic field, during which time the analytes diffuse. The eventual 180° r. f. ( $\pi$ ) pulse has the effect of rotating every spin around the x-axis, transforming the "spiral" into its mirror image, with faster precessing spins behind their slower counterparts. The gradient pulse is then repeated with the same intensity and duration as earlier, so that faster-precessing spins catch up to their slowerprecessing counterparts, producing a gradient echo. However, the echo intensity is reduced if the nuclei (e.g. molecules) have changed in z position. If all the nuclei are at the same z-position for the second gradient pulse as they were for the first, the echo will have nearly the same magnitude as the original signal, except for relaxation effects. If a significant fraction of the spins have diffused into another z-region, however, the magnitude of the echo will be reduced.<sup>1</sup>



**Figure 2. 4.** Simple Pulsed Field Gradient (PFG) technique with a *z*-gradient magnetic field. Radio frequency pulses (r. f.) can be of a duration to induce 90° ( $\pi/2$ ) or 180° ( $\pi$ ) spin rotation. Gradient fields (*g*) have pulse length  $\delta/2$ , and  $\Delta$  is the time allowed for diffusion of analytes between gradient pulses.

## 2.2.3. Time Coordinate

PFG-NMR is a type of two-dimensional technique known as a DOSY (Diffusion-Ordered Spectroscopy). The 1D measurements described above are repeated several times for a given sample, with different gradient field strengths on each repetition and all other rf pulses and delays of the same duration. In this way, there is no difference in echo intensity due to relaxation. In so doing, an array of data is obtained, in which each peak of a spectrum has a set of intensities associated with the set of measured gradient strengths (Figure 2. 5). By changing the intensity of the gradient field, we are essentially changing the pitch of the magnetization "screw" in Figure 2. 4 and thereby the sensitivity of the measurements to molecular motion in the z direction. A weak gradient field results in a large pitch, i.e. very little change in net magnetic orientation along the *z*-axis, so that a molecule must diffuse a great distance for its signal to be lost to the echo. Conversely, a strong gradient field will ably distinguish between very small distances along the *z*-axis. The echo peak intensities exhibit Laplacian decay with increasing gradient strength. Fitting this decay produces the diffusion coefficient of the analyte.<sup>1</sup>



**Figure 2. 5.** Decay of anthracene signal with increasing gradient strength. Rows in the foreground correspond to low gradient strength measurements, whereas rows in the background correspond to higher gradient strengths. Fitting the decay of the peak areas with changing gradient strength allows calculation of the diffusion coefficient.

## 2.2.4. Parameter Optimization

Some parameter optimization is required in NMR diffusion measurements in order to find diffusion coefficients with precision and accuracy. The wait time between gradient pulses ( $\Delta$ ) may be lengthened to allow slower compounds more time to diffuse, or the gradient pulse duration ( $\delta$ ) may be lengthened for higher sensitivity of lower diffusion coefficients. Increasing  $\delta$  has the effect of winding the "spiral" of magnetic moments tighter. As a result, even small movements of slow-moving molecules will take the analyte out of the region where its signal could be recovered for the echo. The  $\Delta$  and  $\delta$  parameters are set to their optimal values during the experimental setup to ensure the necessary amount of peak area decay over the range of applied gradient strengths. By varying the applied fraction of maximum gradient strength ( $f_{i}$ where the applied gradient intensity is equal to *f* times the maximum gradient strength) over the course of the experiment, the pitch of the magnetization "screw" is changed, inducing the exponential peak area decay which is fit to yield the diffusion coefficient. An experiment could be set up to vary the gradient pulse length ( $\delta$ ), leaving the gradient pulse intensity (g) constant, or to vary the diffusion time ( $\Delta$ ), leaving both  $\delta$  and g unaltered, but these techniques are not as accurate because varying the times allows for slightly different amounts of longitudinal and translational relaxation.
Pulse programs which are currently used in transverse diffusion measurements are more complex than that described above, as is necessary for undistorted, high-resolution data. The method used in our experiments was the bipolar gradient stimulated echo version, which has the advantage that the slower T<sub>1</sub> relaxation is occurring during the fixed  $\Delta$  without signal loss from faster T<sub>2</sub> relaxation.<sup>21</sup> The relation between the diffusion coefficient (*D*) and the variables discussed above for the pulse program employed in these experiments is given in equation 2. 3.<sup>21</sup>

$$I(g) = I(0)exp\left[D(\gamma\delta g)^2\left(\Delta - \frac{\delta}{3} - \frac{\tau}{2}\right)\right]$$
 2.3

In the above equation, I refers to the signal (peak area), g is the gradient strength for any given row of the DOSY,  $\gamma$  is the gyromagnetic ratio, and  $\tau$  is the wait time for gradient recovery before another pulse is applied.

#### 2.2.5. Experimental Pulse Sequence

Our experiments utilize a pulse program designed by Wu, et.al.<sup>21</sup>, which addresses several complications associated with earlier pulse programs for measuring translational diffusion. One major difficulty in PFG-NMR is the eddy currents that are induced in the metal components of the probe and magnet by strong gradient pulses. Actively shielded gradient coils and use of the longitudinal-eddy-current delay (LED) pulse sequence have greatly reduced the effect of eddy currents on diffusion measurements, but do not fully address the problem. The asymmetric arrangement of metal parts, and the prevalence of conducting surfaces within the confined bore magnets limit the effectiveness of active shielding. The LED pulse sequence further reduces the impact of eddy currents by the use of prepulses; gradient pulses identical to those used to label the spins and to produce the echo. The first two gradient pulses may be reasonably assumed to produce different eddy currents, as the second pulse is impacted by the lingering effects of the first, but repetition of the gradient pulses ensures repeatable gradients and eddy currents within the experiment itself. Remaining eddy currents are further removed from the data by introducing a settling time ( $T_e$ ) after the final gradient pulse and before beginning to collect the signal. This technique is not ideal, however: the prepulses heat the sample, resulting in unreliable temperature control and occasionally significant convection currents. Additionally, the remaining effects of the eddy currents are substantial enough that a settling time short enough to avoid signal loss from  $T_2$  relaxation cannot fully outlast the eddy currents. These problems

are effectively eliminated by introduction of Bipolar Pulse Pairs (BPP) into the LED sequence. Because the last 90 pulse converts transverse magnetization into z magnetization before the wait time for diffusion, faster  $T_2$  relaxation is no longer in effect (Figure 2. 6).<sup>21</sup>



**Figure 2. 6.** Bipolar Pulse Pair (BPP) manifestation of the Longitudinal Eddy-Current Delay (LED) pulse sequence. Gradient pulses are shown in grey, with those of opposite polarity shown as negative. 90° and 180° r. f. pulses are shown as vertical lines.  $\tau$  represents the necessary wait time for gradient recovery before the next pulse.<sup>21</sup>

A bipolar pulse pair is characterized by a gradient pulse followed closely by a 180° r. f. pulse, which is immediately followed by another gradient pulse of equal intensity and duration but antiparallel to the first pulse (Figure 2. 6). In this manner, the two gradient pulses of the pair have an additive effect. A bipolar pulse pair with pulse lengths  $\delta/2 \sim 1$  ms, and close pulse spacing (<1 ms) produces the same effect with regard to spin labeling as a monopolar gradient pulse of duration  $\delta$ , but with many times less distortion from eddy currents.<sup>21</sup> This is because eddy currents resulting from gradient pulses of opposite polarity and equivalent area mostly cancel each other out, greatly reducing the eddy current-induced magnetic field distortions to the signal baseline (Figure 2. 7). Eddy currents resulting from these BPPs are so much smaller than those from monopolar gradient pulses that the use of heat-producing prepulses is unnecessary and a much shorter settling time may be used at the end of the sequence, allowing for better signal resolution and the measurement of compounds with shorter relaxation times. The BPP-LED pulse sequence we use is shown in (Figure 2. 6).<sup>21</sup>



Figure 2. 7. Effects of monopolar and bipolar gradient pulse pairs on deuterium lock signal.<sup>21</sup>

#### 2.3. Rotational Diffusion Measurements

#### 2.3.1. Competing Techniques: Strengths and Limitations

In addition to NMR, there are many other methods for measuring rotational diffusion, such as dielectric relaxation measurements, fluorescence anisotropy measurements, and EPR spectroscopy. To measure rotational diffusion by dielectric relaxation, the sample is placed within an oscillating electric field. If the frequency is low enough for molecular rotations to keep up, all the dipoles will rotate to align themselves with the oscillating field. If the frequency is too fast for molecular rotations to keep up, which often occurs in the microwave regime, the sample will absorb energy from the field and this absorption as a function of frequency can be analyzed to deduce the time correlation function of the collective dipole moment of the sample. If dynamical intermolecular reorientation. This is an L = 1 relation, meaning that the rotational diffusion coefficient depends on the observable to the first order of the Legendre polynomial,  $P_L(x) = x$ , as seen in Eq. 2. 4. Some other methods of measuring rotational diffusion at L = 2 functions. This does not affect the reliability of the resulting data, but only the mathematical function needed to interpret the measurements.

$$P_1(x) = x$$

$$P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$$

$$x = \cos(\Delta\theta(t))$$
2.4

In the above equations, x is the observable, and  $P_L(x)$  is the function describing the rotational diffusion. Dielectric relaxation measurements are also limited in that rotation about the molecule's dipole moment cannot be sensed, but on this point NMR and fluorescence have similar limitations with regard to different molecular axes.

In fluorescence anisotropy measurements, polarized light is used to excite a fluorescent analyte. Each such type of molecule has a transition dipole moment; an axis along which the electron density will shift when moving from the ground to the excited state. When polarized light is used to excite the molecules, only those molecules whose transition dipole moments are aligned with the electric field of the light become excited. If the molecules in a sample do not have time to rotate before relaxing back to the ground state, their transition dipole moments will still be anisotropically aligned, as they were when excited, and their fluorescence will have the same polarization as the excitation pulse. Alternatively, if the molecules do have time to rotate, the anisotropy will dissipate, as will the polarization of their fluorescence. By measuring only specific polarizations of fluorescence emission, this relaxation, and the rotational diffusion causing it, can be measured. Fluorescence anisotropy has the great advantage of giving timeresolved data for the entire rotational correlation function. In fact, it is possible to fit the data precisely enough to allow detection of multiple different rotational diffusion constants from a single measurement. This technique does, however, have several major limitations. Measurements are only possible for fluorescent molecules, few of which are small. Only rotation times that are faster than the fluorescence lifetime of the analyte (generally a few nanoseconds) are measurable. Finally, it is only sensitive to rotation that reorients the transition dipole moment; any rotation about the transition dipole axis is essentially invisible. The rotational correlation time has a second order dependence on the anisotropy decay seen in fluorescence measurements, making this an L=2 relation.<sup>22</sup>

Electron paramagnetic resonance spectroscopy (EPR), also known as ESR or EMR, is very similar to NMR, with the distinction that it measures electron spins, rather than nuclear spins. In order for a compound to be detectable by EPR, it must have a magnetic moment in its electronic ground state which is capable of weak interactions with neighboring magnetic moments. This limits potential analytes to paramagnetic materials. Although the principles of EPR closely resemble those of NMR, the techniques are very different in practice, owing to the larger linewidths, higher frequencies, and faster relaxation experienced in EPR. The much more limited applications of EPR prevent it being as widespread a technique for rotational diffusion measurements as those previously mentioned.<sup>1</sup>

As for its relative advantages and disadvantages over the above-mentioned alternative methods, inversion recovery measurements of quadrupolar nuclei are not limited by the size, shape, or fluorescence of an analyte, but can measure any molecule that has even one NMRactive quadrupolar nucleus, so long as its signal is strong enough. Given the possibilities of isotopic labeling (deuterium, for example), the rotational diffusion constants of most molecules are measurable by NMR. Although it is possible to extract the rotation tensor from NMR measurements, thereby yielding time-resolved relaxation and all anisotropic rotational modes, this is an extremely time-intensive and complicated method which has not been deemed necessary for this study. In most liquids, it is possible to assume isotropic rotational relaxation that corresponds to a single rotational diffusion coefficient and rotational correlation time. The analysis required to extract this time is relatively straight-forward, without many overlycomplicating factors. Although this version of T<sub>1</sub> relaxation, and EPR, lack time-resolved capabilities, producing instead an averaged value for all rotational modes, it may still be able to provide qualitative data on multiple rotational diffusion constants for a given molecule, so long as that molecule has more than one quadrupolar NMR-active nucleus. Overall, NMR allows for reliable data over the widest range of analytes.

Longitudinal relaxation of quadrupolar nuclei will be discussed at length in the following sections. There are, however, several other spin-lattice interactions that may contribute to spin relaxation and must, therefore, be considered. For non-quadrupolar nuclei, those with  $I = \frac{1}{2}$ , the most common mechanisms of longitudinal relaxation are magnetic dipole-dipole interactions, chemical shift relaxation, and spin-rotation interactions. In magnetic dipole-dipole interactions, movements of neighboring nuclei (and the magnetic moments of those nuclei) cause fluctuations in the local magnetic field of the observed nucleus. These subtle fluctuations in the local magnetic field allow small amounts of energy transfer between the observed nucleus and its surroundings, contributing to longitudinal relaxation. The strength of this coupling drops off with distance at r<sup>-6</sup>, so that dipole-dipole relaxation is most effective for intramolecular

25

interactions. Spin-rotation interactions do not concern neighboring nuclei, but instead deal with the electrons in the rotating molecule. Cycling charges, electrons for example, produce their own magnetic fields. The fluctuating magnetic fields caused by rotations of electrons in a tumbling molecule produce the same energy exchange between nucleus and lattice as described for dipole-dipole interactions. These interactions are strongest for small molecules undergoing fast molecular tumbling, usually in nonviscous solutions. Chemical shift anisotropy is a dominant source of fluctuating magnetic fields (in the absence of protons, which are dominated by dipole-dipole interactions). Although the chemical shift appears to be an isotropic constant in non-viscous liquids and solutions, under conditions of slow enough molecule reorientations, the inherently-anisotropic components of the screening tensors are not averaged. This orientationdependent screening rotates with slow-enough molecular motion, producing fluctuating magnetic fields. Other less common sources of magnetic field fluctuations include the paramagnetic (or electron-nuclear) interaction, involving the magnetic moments of unpaired electrons (orders of magnitude larger than that of paired electrons); and the scalar interaction, involving fluctuations of the coupling constant (J) or of the spin state of a covalently-bound nucleus. Any of the above spin-lattice relaxation mechanisms may play a part in longitudinal relaxation, but if the observed nuclei are quadrupolar, the quadrupolar interaction will so dominate over the others that they may reasonably be ignored.<sup>23,24</sup>

## 2.3.2. Nuclear Quadrupolar Moment

In order to explain the mechanism of rotational diffusion measurements using NMR, several other concepts must first be explored: quadrupolar nuclei, electric field gradient (EFG), and quadrupolar coupling. Nuclei are often thought of as point charges but, of course, this is not the case. Because they are made up of both charged and uncharged particles, there is a charge distribution within the nucleus of an atom. This electric charge distribution, C(r), can be mathematically represented by a sum of the various multipole contributions. In Figure 2. 8, the symmetry of the multipole moments is represented schematically;  $C^{(0)}$  is the charge,  $C^{(1)}$  the dipole moment, and  $C^{(2)}$  the quadrupole moment of the nucleus. Depending on the value of the ground state nuclear spin quantum number (I), symmetry dictates that  $C^{(n)} = 0$  for n > 2I. It has also been shown that the dipolar contribution is always zero to within experimental uncertainties.

As a result, only nuclei with  $I > \frac{1}{2}$  have non-spherical symmetry. Such nuclei are referred to as quadrupolar.<sup>1</sup>



**Figure 2. 8.** Multipole contributions to the electric charge distribution C(r), where  $C^{(0)}(r)$  is monopolar,  $C^{(1)}(r)$  the dipolar, and  $C^{(2)}(r)$  the quadrupolar contribution.<sup>1</sup>

# 2.3.3. Molecular Electric Field Gradient (EFG)

The electric charge of a nucleus interacts with the electric potential, V(r), and its derivatives at the nuclear position. Similarly to the nuclear electric charge distribution, the spatial variation of V(r) can be decomposed into a superposition of many terms of different order (Eq. 2. 5).

$$V(r) = V^{(0)}(r) + V^{(1)}(r) + V^{(2)}(r) + \cdots$$
 2.5

The zeroth order of electric charge is the electric potential,  $V^{(2)}(r)$ , which interacts with the net charge,  $C^{(0)}(r)$ . This interaction determines the position of the nucleus within the atom, which lies at the minimum electric potential energy, but is independent of the orientation of the nucleus. The interaction between the first-derivative of electric potential (the electric field at the nucleus:  $V^{(1)}(r)$ ), and the electric charge distribution,  $C^{(1)}(r)$ , can be ignored because of the lack of nuclear electric dipolar moment. In quadrupolar nuclei, the quadrupolar moment,  $C^{(2)}(r)$ , interacts with the second-derivative of the electrical potential,  $V^{(2)}(r)$ . The electric field gradient (EFG), or  $V^{(2)}(r)$ , can also be thought of as the curvature of the electric potential, or the gradient of the electric field. The EFG takes the form of a tensor (matrix), thereby continuing the progression of point charge for electric potential, vector for electric field, and rank two tensor for EFG. It can be shown by diagonalizing the EFG that the curvature along one of its axes,  $V_{zz}$  is larger than that along the others. In the case of deuterium, of interest here, this axis lies along the D-X bond. In addition, because the electron distribution is close to cylindrically symmetric about such a bond ( $V_{xx} = V_{yy}$ ). As far as treating the effect of molecular rotation on deuterium

relaxation is concerned, it is the orientation of the bond lying along  $V_{zz}$  which is of central importance.<sup>1</sup>

# 2.3.4. Rotational Time Correlation Functions

## 2.3.4.1. General

There are many different types of molecular rotation including, among others, twisting of a ligand and tumbling of an entire rigid molecule.<sup>23</sup> To simplify our analysis, we have limited our measurements to rigid molecules, like benzene, and partially-rigid molecules, where the observable nuclei of interest are in a rigid section of the molecule. In so doing, we confine our rotational measurements to tumbling motions of relatively small analytes.

The connection between molecular rotations and the longitudinal relaxation time (T<sub>1</sub>) is not immediately obvious. Molecular rotation produces a relative reorientation of the main axis of the electric field gradient,  $V_{zz}$ , as seen from the frame of reference of the spin, which does not reorient with molecular rotation (Figure 2. 9). The resulting change in angle between  $V_{zz}$  and the nuclear quadrupolar moment constitutes a change in energy, transferred either from the surroundings to the nucleus or vise versa<sup>23</sup>, much as the movement of a ball over a potential energy surface requires an input or a release of energy from the ball. If the frequency of reorientation of the  $V_{zz}$  is comparable to the Larmor frequency or twice the Larmor frequency, the reorientation most efficiently stimulates  $T_I$  relaxation. The strength of the coupling between the nuclear quadrupolar moment and the EFG is indicated by the quadrupolar coupling constant (QCC).<sup>1</sup>



Figure 2. 9. The effect of molecular rotation on the electric field gradient and the spin.

These reorientations are not coherent, instead resembling more of a random walk, the general trend of which may be represented by a rotational time correlation function,  $C_r(t)$  (Eq 2. 6).

$$C_r(t) = \left\langle \frac{3}{2} \left[ \hat{V}_{zz}(0) \cdot \hat{V}_{zz}(t) \right]^2 - \frac{1}{2} \right\rangle = \left\langle \frac{3}{2} \cos^2 \theta(t) - \frac{1}{2} \right\rangle$$
 2.6

In a time correlation function, some observable, in this case the orientation of  $V_{zz}$  at an initial time,  $\hat{V}_{zz}(0)$ , is compared to its condition at later times,  $\hat{V}_{zz}(t)$ . The angle through which  $V_{zz}$  rotates is referred to as  $\theta$ . If conditions are identical, the value of the correlation function is 1. Once the conditions have changed enough so as to appear completely unrelated to the initial conditions, the value of the time correlation function is reduced to 0. This means that a molecule that rotates very slowly will show a much slower decrease from 1 than would a molecule that rotates quickly.<sup>25</sup> The form taken by this correlation function identifies it as a second rank Legendre (L = 2) correlation function, because the observable,  $\cos \theta$ , appears to the second power.

Most molecules cannot be considered spherically symmetric, but may instead be modeled as non-symmetric ellipsoids. A non-symmetric ellipsoid will rotate at different speeds about its different axes. Because  $V_{zz}$  reorientation affects the longitudinal decay rate, the orientation of  $V_{zz}$  relative to the ellipsoidal axes is extremely influential. If, for example, we consider a prolate ellipsoid,  $V_{zz}$  could be aligned along the major axis, along one of the minor axes, or anywhere inbetween. If  $V_{zz}$  lies along a symmetry axis, it will not reorient in space with molecular rotation about that axis, rendering the longitudinal decay rate blind to one of the molecule's rates of rotation. If  $V_{zz}$  is not aligned with any symmetry axis, such that its orientation in the laboratory frame changes with rotation about any symmetry axis, then the inversion recovery will be at least somewhat sensitive to all the molecule's rotations. The degree to which rotation about any given axis effects the orientation of  $V_{zz}$  is the degree to which rotation about that axis will affect the time correlation function  $C_r(t)$  and, therefore, the longitudinal decay rate. If measurements are made of only one nucleus in a molecule (thereby involving only the  $V_{zz}$  vector at that nucleus), the various contributing rotational diffusion rates are not generally distinguishable without the aid of simulations. If, however, the molecule includes more than one NMR active quadrupolar nucleus, different orientations of  $V_{zz}$  at these different nuclei within the molecule may form different angles relative to the molecule's rotational axes. If so, they will be affected by the

various rotational rates of the molecule to different degrees, producing different rotational correlation functions. Comparisons of two or more rotational correlation times resulting from such different functions, when considered in light of the molecular structure that produced them, may give a better idea of the range of rotation rates experienced by the molecule.

## 2.3.4.2. Shape Concerns

For the simplest case of a single exponential time correlation function, relating to a spherically symmetric molecule,  $C_r(t) = e^{-t/\tau_c}$ . Things become more complicated for non-spherical molecules. Ellipsoidal molecules, with substantially different lengths of semi-axes, will have different diffusion coefficients for rotations of the various semi-axes. The simplest rotational correlation function of a symmetric ellipsoidal molecule (an ellipsoid with two degenerate axes) is one in which the main axis of the EFG ( $V_{zz}$ ) lies along the unique, "symmetry," axis of rotation. In this case, the correlation function cannot see the rotation about the symmetry axis, but only rotations about the degenerate axes, producing the following time correlation function (Eq 2. 7).<sup>26</sup>

$$C_r(t) = exp(-6D_{\perp}t)$$
 2.7

In the above representation, (-6D<sub> $\perp$ </sub>) is equal to  $\tau_c^{-1}$ . Likewise, in the following equations,  $\tau_{c,i}^{-1}$  is equal to the multiple of t.<sup>26</sup>

If  $V_{zz}$  lies along one of the degenerate axes, the relation becomes more complex (Eq 2. 8).

$$C_r(t) = 0.25 \exp(-6D_{\perp}t) + 0.75 \exp[-(2D_{\perp} + 4D_{\parallel})t]$$
 2.8

For  $V_{zz}$  lying off-axis, the relation does not gain a diffusion coefficient, as there are still only two different lengths of axes, but the way the components are related will change.<sup>26</sup>

In the case of an ellipsoidal solute with three unique sub-axes, the correlation function incorporates three different diffusion coefficients and between two and five exponentials, depending on the orientation of  $V_{zz}$  with respect to these axes (Eq 2. 9).<sup>26</sup>

$$C_{r,i}(t) = \left(\frac{1}{2} + \frac{3(D_r - D_i)}{4\Delta}\right) exp[-(6D_r + 2\Delta)t] + \left(\frac{1}{2} - \frac{3(D_r - D_i)}{4\Delta}\right) exp[-(6D_r - 2\Delta)t]$$
  
where  $D_r = \frac{1}{3}(D_x + D_y + D_z)$   
and  $\Delta = \sqrt{D_x^2 + D_y^2 + D_z^2 - D_x D_y - D_x D_z - D_y D_z}$  2.9

# 2.3.5. Spectral Density Function

Taking the Fourier transform of the rotational time correlation function  $C_r(t)$  produces the spectral density function,  $J(\omega)$  (Figure 2. 10). The spectral density function for a single exponential correlation function, i.e. a spherically-symmetric object, is as follows.

$$J(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} C_r(t) e^{-i\omega t} dt = \frac{\tau_c}{1 + (\omega \tau_c)^2}$$
 2.10

In the above, the rotational correlation time,  $\tau_c$ , characterizes the rate of decay of a given time correlation function.

Larger values of  $J(\omega)$  at a given frequency,  $\omega$ , indicate a greater contribution of motions at that frequency to the correlation function. This implies that slower-rotating molecules have spectral densities with greater intensity at low  $\omega$  than do faster-rotating molecules. Because the half-intensity of  $J(\omega)$  occurs at  $\omega = \tau_c^{-1}$  for exponential correlation functions, the spectral density of slower-rotating molecules drops off at much lower  $\omega$  than does that of faster-rotating molecules. The rotational correlation time, which indicates the rate of longitudinal relaxation, may be defined in several ways. It is equal to the inverse of  $\omega$  at the half-intensity of  $J(\omega)$ .<sup>23,27</sup> It is also equal to  $J(\omega_0)$ , which may be calculated as the time integral of the rotational time correlation function.<sup>28,29</sup>



**Figure 2. 10.** Spectral density functions for various rotation rates. Both graphs show the same functions, with a linear x-axis at the left and a logarithmic x-axis at the right. Drop-lines on the logarithmic plot show the half-intensity points, at which  $\omega = \tau_c^{-1}$  (for exponential correlation functions, only). The y-axes for both graphs are linear.

#### 2.3.6. Extreme Narrowing Regime

Only rotations of  $V_{zz}$  that are at the Larmor frequency ( $\omega_0$ ) or at twice the Larmor frequency ( $2\omega_0$ ) can stimulate energy transfer between a spin and its surroundings, resulting in a change in the angle of precession, and thereby shortening  $T_1$  relaxation.<sup>23</sup> As a result, rotations with correlation times  $\tau_c$  that are close to the Larmor frequency  $\omega_0$  or twice the Larmor frequency result in the shortest  $T_1$  relaxation times (Figure 2. 11). Because Brownian motion covers a range of diffusion rates, even when an average rotational frequency is above or below  $\omega_0$ , some component of the diffusion is at the Larmor frequency. When  $\omega_0\tau_c \ll 1$ , the effect of  $\omega_0$  on  $T_1$  becomes vanishingly small and the external field strength becomes irrelevant in determining the longitudinal relaxation time (Eq 2. 11). This is called the "extreme narrowing" or "motional narrowing" region.

Under extreme narrowing conditions for a single exponential time correlation function, the relation between  $T_1$  and  $\tau_c$  is shown in equation 2. 11.<sup>30</sup>

$$\frac{1}{T_1} = \frac{3\pi^2}{10} \left(\frac{e^2 Q q}{h}\right)^2 \left\{\frac{1}{1 + (\tau_c \omega_0)^2} + \frac{4}{1 + 4(\tau_c \omega_0)^2}\right\} \tau_c$$
 2.11

In the above equation, the  $(e^2Qq/h)$  term is the quadrupolar coupling constant (QCC). In extreme narrowing conditions, the relation simplifies to  $1/T_1 = (3\pi^2/2)(e^2Qq/h)^2\tau_c$ . This equation is often used in analyzing inversion recovery data, sometimes for solutes that are unlikely to display single exponential time correlation functions, and without first demonstrating extreme narrowing conditions. There is not currently a generally-accepted formalism for determining the form of  $\tau_c$  from T<sub>1</sub>, outside of single exponential decay and extreme narrowing conditions.

The benefit of measuring within the motional narrowing region is that the field strength of any spectrometer may be used for the measurement without impacting the data. Measurements made outside this region may also be useful, however, as several measurements at different field strengths will demonstrate the dependence of  $T_1$  on the correlation time. The temperature may be altered in order to control whether a system is within the extreme narrowing region or outside it. For example; lowering the temperature will result in slower rotation (larger correlation times) and, as  $\omega_0$  is independent of temperature,  $\omega_0 \tau_c$  will increase. Increasing the applied field strength will result in higher Larmor frequencies, according to  $\omega_0 = -\gamma B_0$ , and lead to a corresponding shift of the minimum  $T_1$  to smaller correlation times, where  $\tau_c^{-1}$  is equal to the new  $\omega_0$ . (Figure 2. 11) Systems may also be chosen for measurements within or without the motional narrowing region by considering the likely rotation times of smaller or larger, compact or bulky analytes in solvents of high or low viscosity. Rotational diffusion also affects the rate of transverse relaxation, as demonstrated in Figure 2. 11.



**Figure 2. 11.** Dependence of  $T_1$  and  $T_2$  relaxation on rotational correlation time ( $\tau_c$ ) and relative field strength (dotted vs. solid lines), with minimum  $T_1$  at inverse Larmor frequency ( $\omega_0^{-1}$ ).

## 2.3.7. Inversion-Recovery Pulse Sequence

The inversion-recovery pulse sequence is the most accurate experimental method used to measure longitudinal relaxation and, from it, rotational diffusion of quadrupolar nuclei (Figure 2. 12). The net magnetization of an equilibrated sample in the presence of an external magnetic field ( $B_0$ ) is rotated 180° by a  $\pi$  r.f. pulse, so that the net magnetic moment of the sample is antiparallel to the external field. The system is then allowed to evolve for a variable time  $\tau$ , so that the net magnetic moment relaxes back towards equilibrium. When the  $\pi/2$  r.f. pulse is applied, interrupting the relaxation, the net magnetic moment at that instant is rotated into the *xy* plan and its strength is detected as the (positive or negative) area of the detected peak; for a molecule with only one measureable peak, this is also conveyed by the initial intensity of the resulting free induction decay (fid). With longer  $\tau$  values, the intensity of the observed signal increases back to its original (positive) magnitude. The change in signal intensity with  $\tau$  can be fit to reveal the  $T_I$  value.



**Figure 2. 12.** A simplified diagram of an inversion-recovery experiment. The pulse sequence is boxed in at top left, where blue rectangles signify r. f. pulses of sufficient length to rotate spins by  $\pi$  and  $\pi/2$ , respectively. The next line down represents the progression through the  $\tau$  delay of the net magnetization (thick grey arrow), as well as some of the more populous individual spin orientations which contribute to it (cones), under the influence of an external magnetic field (thick white arrow "B"). Blue arrows down represent the effect of the second ( $\pi/2$ ) r. f. pulse at different  $\tau$  delay times. Precession is symbolized by curved arrows, and the conclusion of the experiment is indicated by the cartoon of a free induction decay curve (fid)

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# Chapter 3. Experimental

## 3.1. Ionic Liquid (IL) Sources and Drying

Ionic liquid samples were obtained from several different sources. Dr. Gary Baker, at the University of Missouri, provided spectroscopically-pure N-alkyl-N-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide  $[Pr_{n1}][Tf_2N]$  with alkyl lengths of n = 3, 4, 5, 6, 8, 10. Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide [P<sub>14,6,6,6</sub>][Tf<sub>2</sub>N] was synthesized by Xiang Li<sup>1</sup>. 1-Butyl-3-methyl-imidazolium hexafluorophosphate [Im<sub>41</sub>][PF<sub>6</sub>] was obtained from EMD-Millipore (high purity). Both 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [Im<sub>21</sub>][Tf<sub>2</sub>N], and [Im<sub>41</sub>][BF<sub>4</sub>] came from Ioletic at 99% purity. All samples were used as provided unless otherwise stated. Tetraphenylphosphonium benzoate was prepared from silver benzoate (Sigma-Aldrich, 99% purity) and tetraphenylphosphonium chloride (TCI, 98% purity). The tetraphenylphosphonium chloride was dissolved in methanol at 0.65 M. After full dissolution, excess silver benzoate was added to the solution, which was stirred for several hours. The insoluble AgCl was filtered out. The filtrate was evaporated to form a brownish resin which tested negative for chloride with application of silver nitrate. Singly-deuterated [Im<sub>21</sub>][Tf<sub>2</sub>N] was prepared from 6.9 mL [Im<sub>21</sub>][Tf<sub>2</sub>N] (Ioletic, 99%) and 3.6 mL D<sub>2</sub>O (99 atom % D, Sigma-Aldrich), resulting in an IL mole fraction of 0.117. The mixture was heated to approximately 75 °C and stirred overnight, but no significant exchange occurred until transfer to an Erlenmeyer flask with a large stir bar, to allow for optimal mixing. Over 90% deuteration of the acidic peak was achieved this way. Further heating and stirring failed to exchange any of the non-acidic ring protons.

Before mixing solutions or sealing NMR samples, all ILs were dried on a vacuum line for several hours or overnight to a pressure of less than  $10^{-2}$  Torr. Samples were dried in 5-25 mL round bottom flasks with a ground glass elbow adapter attachment to the vacuum line. All samples were stirred while under vacuum and most were heated to 60 °C in a sand bath to speed the drying process. Once dry, ILs were transferred to a positive pressure nitrogen glove box, maintained at 0.8 LPM nitrogen flow rate, while checking water content and mixing or otherwise preparing samples.

Water content was determined by use of a Karl-Fischer apparatus. Sample sizes suggested by the manual increase significantly for smaller water content samples, with 1000 ppm samples requiring 1 g for accurate measurement, and 10 ppm samples requiring 8 g for the same level of accuracy.<sup>2</sup> Test measurements were therefore performed to determine the increase in error with decreasing sample size at two different water contents in order to minimize sample use without increasing error too much (Figure 3. 1). Three measurements were averaged for each graphed value, with uncertainty reported as twice the greatest deviation between the average and one of the data points. Two samples were used for these measurements: a water content standard at 1,002 ppm, and a mixture of leftover ionic liquids which was dried in the regular manner so as to approximate the usual water content of an IL sample. Ionic liquids making up the mixture included  $\leq 5.5$  mL each of: [Pr<sub>61</sub>][Tf<sub>2</sub>N], [Im<sub>A1</sub>][Tf<sub>2</sub>N] (1-allyl-3-methylimidazolium<sup>+</sup>),  $[Im_{41}]$  [Tf2N],  $[Pr_{41}]$  [Tf<sub>2</sub>N],  $[Pip_{31}]$  [Tf<sub>2</sub>N] (1-methyl-1-propylpiperidinium<sup>+</sup>), and  $[Pip_{41}]$  [Tf<sub>2</sub>N]. As indicated by the manual, the accuracy of the lower water content IL mix (Figure 3. 1(b)) begins falling off at much higher sample sizes than does that of the higher water content standard (Figure 3. 1(a)). As the water content of our typical IL samples is more closely represented by that of the IL mix, this curve is referred to in determining a minimum sample size for our ionic liquids. We chose 0.8 g (~0.6 mL) as the smallest sample size with acceptably small error, despite the fact that this error is not negligible. As a result, our reported ionic liquid water contents are an underestimation of the actual values, but as our largest measured water content was 60 ppm, with most ionic liquids much lower, we considered it reasonable to report water contents of less than 100 ppm.



**Figure 3. 1.** Effect of sample size on Karl-Fischer water content measurements at: (left) 1,002 ppm standard, and (right) dried ionic liquid mixture. A sample size of 0.8 g ionic liquid corresponds to approximately 0.6 mL. Although water contents in ionic liquids reported here are negative at <1.5 g sample sizes, comparable measurements of IL water content have not been. We remain confident of our measurements, however, because the Karl-Fischer apparatus was giving unreasonably-low values in general when these mass-water content relations were made. Such behavior has not been seen since.

## 3.2. Sample Preparation

For sample mixtures, non-ionic liquid solutes were weighed outside the glove box and added to a pre-weighed and labeled scintillation vial with cap and stir bar. Small quantities of liquid solutes were measured by dipping a microspatula into the solute and touching the tip to the inside of a vial. The excess liquid was then allowed to evaporate in order to achieve the desired weight. Because the liquid solutes used in these studies evaporated slowly, only about 0.0005 g per minute, it was not difficult to catch the solute at the desired weight and quickly add the solvent, essentially stopping the evaporation. Vials were opened upon introduction to the glove box to allow the air to diffuse away so that additional water vapor would not be dissolved in the ionic liquid. Ionic liquid solvents were measured out by volume and added to the solute vial while within the glovebox. The capped vial was then re-weighed outside the box so that a more accurate value for the added solvent could be calculated by difference. Low-concentration mixtures prepared from pure components were stirred for a minimum of four hours or overnight. Concentration series were prepared by serial dilution of the most concentrated sample. All reported solute concentrations were calculated from 1D NMR spectra, by comparing solute peak areas to solvent peak areas. Ionic liquid densities were measured by a previous group member, except for that of  $[Pr_{81}][Tf_2N]$ , which I measured using the same method as was previously employed.<sup>3</sup> A 1 mL volumetric flask was filled with the ionic liquid in question and, after several hours of evacuation on our vacuum line, the mass of the 1 mL of fluid was calculated by difference, yielding a value of 1.28 g/mL.

In order to prevent samples from dissolving atmospheric water with time, NMR samples of dried solutions were vacuum-sealed in thin walled, 5mm economy 8" 200 MHz NMR tubes. Before sealing an IL sample, NMR tubes and long-stem disposable glass pipettes were baked at a minimum of ~66 °C to remove adsorbed water vapor. Samples were added slowly to NMR tubes, at an angle. The more viscous liquids have a tendency to stop flowing part way down the tube, trapping a bubble of air at the bottom. It is time-consuming to shake the ionic liquid down to the bottom when this happens. Adding the ionic liquid very slowly, while holding the NMR tube and pipette at ~40 degree angle helped prevent this problem. The long-stem pipettes also sped things up by shortening the distance the viscous liquids had to flow. Care was taken when removing the pipette from the NMR tube to avoid leaving droplets on the side, as the liquid in these droplets had a tendency to decompose when vacuum-sealing the tubes. It seems likely that the flame-sealing process may have facilitated the degradation of the sample in the droplets near the flame.

Sample preparation for rotation measurements on the AV-III-850 was slightly different than that described above. Although the ionic liquid drying and solution preparation was the same, the NMR tubes had to be scored and broken off at approximately 2.8 cm length. These were too short to flame-seal, especially as they were filled with ionic liquid to only about 3 mm shy of the top. Instead, sealing was accomplished by first making a plug of slightly larger diameter than the NMR tube out of Parafilm<sup>®</sup>. This plug was then shoved into the NMR tube in order to provide a support for the Loctite<sup>®</sup> Weld<sup>TM</sup> epoxy, which was applied to cap the tube. This cap had to be kept very small in order to fit into the sample holder of the probe, so the Parafilm<sup>®</sup> plug could not be allowed to protrude from the NMR tube before the epoxy was applied. Although small enough to not protrude, the plug also needed to be substantial enough to stop the liquid epoxy from making contact with the ionic liquid, as it had a tendency to form a fine precipitate that collected on the bottom of the tube and likely contaminated the sample. Getting the samples capped by this method was not easy to do and could not be accomplished in the glove box, so each sample was exposed to air for the duration of the sealing process. Most of the caps were no longer secure by the time the measurements were complete- samples lie on their side during measurement, and the ionic liquids and the methanol calibration standard seem to disrupt the adhesion of the small epoxy cap to the glass. Although the plugs stayed in placepreventing any significant amount of leakage- by the time measurements were complete, leaks allowed air and water to diffuse into the samples.

#### 3.3. Infinite Dilution

In order to determine the upper concentration limits of infinite dilution behavior, we measured the effect of solute concentration on translational diffusion coefficients of dimethylaniline (DMA) across the  $[Pr_{n1}][Tf_2N]$  series. Concentrations were varied from 0.01 M to 0.3 M using five or six different samples, and fit by linear regression. Although increasing solute concentration did produce a systematic increase in translational diffusion coefficients and a decrease in viscosity, the changes were small. The percent difference between extrapolated diffusion of DMA at infinite dilution and diffusion at 0.05 M is within experimental uncertainties.

	D at [0] / m <sup>2</sup> s <sup>-1</sup>	D at [0.05] / m <sup>2</sup> s <sup>-1</sup>	D % Change	uncertainty / m²s⁻¹
[Pr <sub>31</sub> ][Tf <sub>2</sub> N]	3.69E-11	3.81E-11	3.32	5.72E-12
[Pr <sub>41</sub> ][Tf <sub>2</sub> N]	3.63E-11	3.75E-11	3.37	5.63E-12
[Pr <sub>61</sub> ][Tf <sub>2</sub> N]	3.36E-11	3.48E-11	3.65	5.22E-12
[Pr <sub>81</sub> ][Tf <sub>2</sub> N]	2.57E-11	2.69E-11	4.77	4.04E-12
[Pr <sub>10,1</sub> ][Tf <sub>2</sub> N]	2.43E-11	2.55E-11	5.04	3.83E-12

**Table 3. 1.** Translational diffusion of DMA in  $[Pr_{n1}][Tf_2N]$ , calculated from regression fits of NMR measurements. Each regression is specific to the solvent ionic liquid across varying concentrations. Diffusion percent change is with respect to values at 0 M. Uncertainties are with respect to the larger 0.05 M diffusion values.

We have also measured viscosities of both neat and 0.05 M pyrene  $[Pr_{10,1}][Tf_2N]$  and found the differences to be within experimental uncertainties (Figure 3. 2). Uncertainties for viscosity measurements are based on differences in viscosities of the same type of ionic liquids

when measured by different individuals in order to account for variations in sample and measurement technique. We have therefore accepted measurements at 0.05 M as representing behavior at infinite dilution. Pyrene was chosen for this comparison as the largest nonpolar solute used in this study and therefore the most likely to disrupt the structure of the ionic liquid and alter the viscosity. The similarity of the temperature-dependent viscosities further confirms our approximation of 0.05 M solute as infinite dilution, as well as our use of neat viscosity values in 0.05 M solute calculations.



**Figure 3. 2.** Vogel-Fulcher-Tammann (VFT) viscosities fits of neat  $[Pr_{10,1}][Tf_2N]$  with and without 0.05 M pyrene.

# 3.4. Viscosity Measurements

#### 3.4.1. Rheometer

Viscosity measurements for high-viscosity fluids were taken on a Brookfield Programmable DV-III + Rheometer with a CPE 40 spindle. The spindle was washed and dried immediately prior to use and after washing, only touched with gloves and light-weight tissues. Sample volume was precisely measured to 0.50 mL, as measurements showed significant changes in viscosity for small changes in sample size (Figure 3. 3). The electronic gap was adjusted immediately prior to each measurement to ensure the correct spacing between the spindle and the base of the sample cup. Sample temperatures were controlled using a VWR circulating bath and standard controller. Data was recorded in increments of 5 °C, beginning at 25 °C and continuing up to 65 °C, and then from 20 °C down to 5 °C. This method was adopted after unreliable data was obtained when starting at 5 °C and working up to 65 °C. The problem was likely due to contamination of the sample by condensation of water vapor at lower temperatures. The sample area was purged with N<sub>2</sub> for at least 20 minutes before beginning measurements. A minimum of eight minutes were allowed for the ramp and equilibration of each 5 °C change. When cooling from 65 °C to 20 °C, the sample was allowed to sit at 20 °C for ten minutes upon completion of the ramp before measuring, to insure equilibration.



**Figure 3. 3.** Measured viscosity of the Cannon RT100 standard at various sample sizes, 25 °C, and 250 RPM.

Viscosity data were fit to the Vogel-Fulcher-Tammann (VFT) equation, as shown below;

$$Ln(\eta) = A + \frac{B}{T - T_0}$$
 3.1

where  $\eta$  is viscosity, and *A*, *B*, and *T*<sub>o</sub> are constants which are determined by fitting the data in SigmaPlot. The rheometer was calibrated using Cannon calibration standard RT100 and the correction value (*k*) was added to *A*. Comparisons of current data to measurements of the same ionic liquids made by previous group members resulted in an overall assignment of 10% uncertainty for Rheometer viscosity data.

## 3.4.2. Glass Viscometers

Low viscosity fluids could not be measured on our Rheometer with the spindles available to us. These fluids were instead measured with Cannon-Fenske Routine Glass Viscometers, numbers 50 and 100. Measurements were taken under nitrogen purge, to keep the samples dry. Temperature was regulated by immersion in a >8 inch tall bath which was connected to a VWR circulating bath and standard controller. The bath was filled with ethylene glycol in order to avoid the introduction of water vapor. After the addition of each new sample, the system was closed and allowed to purge and thermally equilibrate for a minimum of 20 minutes before measurement. A stopwatch with a precision of hundredths of seconds was used to time the dropping liquid. Although Cannon instructions specify a 7 mL sample size, we have opted to use 5 mL volumes for all measurements, including calibration standards, in order to conserve ionic liquid while retaining reproducibility. Calibration standards used for the number 50 viscometer were acetonitrile, water, and 1-pentanol. The number 100 viscometer was calibrated with 1pentanol and ethylene glycol. All calibrant measurements were repeated to reach an agreement of  $\leq 1\%$  for at least three measurements, with half of the calibrant measurements being repeated six or more times. Three of the lowest viscosity samples measured on the number 50 viscometer took less than 200 seconds to time, putting them under the minimum viscosity Cannon recommends for that viscometer. This was done because of an unavailability of a number 25 viscometer. To minimize the effect of the error, the lowest-viscosity calibrant run on the number 50- acetonitrile- had a lower viscosity than any of the analyte solutions. The measured time is related to the viscosity by the following equation.

$$\frac{\eta}{\rho} = Bt \qquad 3.2$$

In the above,  $\eta$  is the solution viscosity,  $\rho$  is the solution density, *B* is a constant specific to the viscometer which must be determined by calibration, and t is the time required for the liquid's meniscus to drop from the higher mark on the viscometer to the lower mark.<sup>4</sup>

To determine viscosities, densities were also measured and fit against the ionic liquid concentration of the solutions. We use densities from this fit in our calculations, rather than the

measured densities. Uncertainties for these measurements were assessed by calculating the average percent error between observed densities and the calculated values. Average percent errors were also calculated for the repeat measurements of the dropping times for each mixture. Together, these assessments suggest an uncertainty of 4% for the glass viscometry, although the standard error of estimate for viscosity vs. concentration gave a 6% error. Given the liberties taken with Cannon's recommendations for the viscometers' use, an uncertainty of 10% seems wisest.

# 3.5. NMR Temperature Calibration

We calibrated the AV-III-850 (850.23 MHz, 20.0 T), the DRX-400 (400.13 MHz, 9.4 T), and the DPX-300 (300.13 MHz, 7.0 T) using 100% methanol temperature standards. After allowing the sample to equilibrate for approximately 30 minutes at the temperature of choice, the shims were re-adjusted and a 1D spectrum acquired. At warmer temperatures, O-H bond lengths increase, with the result that oxygen shielding of the acidic hydrogen is reduced, moving the OH peak upfield.<sup>5</sup> The chemical shift between the hydroxyl and methyl peaks is therefore directly correlated to the temperature at which the measurement was taken. Raiford, et. al. <sup>6</sup> have repeated earlier works in measuring this relation for a higher field strength (220 MHz) than was previously used. We used Raiford's relation to calibrate our own spectrometers. We use our chemical shift measurements to calculate the temperature, according to Raiford's equations, for several different temperature points. We then find the relation between these calculated temperatures (T<sub>R</sub>) and the apparent temperatures reported by our instrument (T<sub>app</sub>). The resulting relations are as follows, with equation 3. 3 corresponding to the DPX-300 with R<sup>2</sup>=0.9993, and equation 3. 4 to the DRX-400 with R<sup>2</sup>= 0.9969.

$$T_R = 1.033 T_{app} - 9.6366 \qquad 3.3$$

$$T_R = 2.691 \times 10^{-3} T_{app}^2 - 0.4083 T_{app} + 180.4$$
 3.4

Unfortunately, a temperature dependent calibration was not conducted for the AV-III-850, although the calibration conducted at room temperature demonstrated a temperature offset from the expected value of only 0.4 °C.

#### 3.6. Translational Diffusion Measurements

Translational diffusion measurements employed a DRX-400 Bruker NMR spectrometer with a 5 mm inverse broadband probe (BBI) with triple axis gradients, as well as a Bruker AV-III-850 NMR spectrometer with a Diff-30 probe with triple axis gradients. Measurements were made using the longitudinal-eddy-current delay (LED) stimulated echo pulse sequence with bipolar gradient pulse pairs as developed by Wu *et al.*<sup>7</sup> All translational diffusion measurements have been from <sup>1</sup>H-NMR spectra

## 3.6.1. DRX-400 Spectrometer

#### 3.6.1.1. Measurement Setup

Because no lock solvent was added to the neat ionic liquids or the IL solutions, NMR measurements were run unlocked after tuning and shimming for each new sample. The necessary radio frequency pulse duration for a  $\pi/2$  rotation may be determined by setting a constant phasing ("pk") for the signal from an approximately  $\pi/2$  rotation, and then changing the P1 variable until a rotation of  $2\pi$  is achieved. As the radio pulse length is increased, the signal decreases from near maximum intensity ( $\pi/2$ ) down to zero ( $\pi$ ), to maximum negative intensity ( $3\pi/2$ ), and then back to zero ( $2\pi$ ). The  $\pi/2$  rotation can be easily found by dividing P1 for the  $2\pi$  rotation by four.

Once the radio pulse duration has been determined, two other parameters must be optimized;  $\Delta$ , the delay for diffusion between gradient pulse pairs, and  $\delta$ , the gradient pulse duration (see Fig. 2.6). The relation of these variables to the peak attenuation is effected by the gradient pulse intensity and the translational diffusion coefficient of interest, as given in equation 3. 5.

$$S(g) = S(0)exp\left[D(\gamma\delta g)^2\left(\Delta - \frac{\delta}{3} - \frac{\tau}{2}\right)\right]$$
 3.5

In this expression, S is the peak area, g is the strength of the applied gradient (gradient amplitude), D is the translational diffusion coefficient,  $\gamma$  is the gyromagnetic ratio of the observed nucleus, and  $\tau$  is the time allowed for gradient recovery before the next pulse. S(g) is acquired from the raw data; S(0) may be ignored as a mere coefficient of the exponential decay. D is calculated from the fit to the data.  $\gamma$  is known for a given nucleus. g can be measured

using calibrants, as explained below.  $\tau$  is set to  $2x10^{-4}$  s for all measurements, since this is the shortest time allowed by DRX-400 electronics.  $\Delta$  and  $\delta$  are adjusted to accommodate the diffusion coefficient of interest in a parameter optimization step during the experimental setup. A larger diffusion coefficient requires a larger  $\Delta$ ,  $\delta$ , or both. For each sample,  $\Delta$  and  $\delta$  were optimized simultaneously for solute diffusion. (Early testing showed that optimization of  $\Delta$  and  $\delta$  for dimethylaniline, rather than for the ionic liquid cation, did not significantly impact results of the cation diffusion measurements.)

The parameter optimization for  $\Delta$  and  $\delta$  is conducted by assigning values and then testing the degree of peak amplitude decay as the gradient strength is varied from low to high. During optimization, the gradient strength starts at five percent of the maximum and increases by ten percent with each of ten steps. In order to optimize the precision of the eventual data, the peak amplitude should decrease by approximately ninety percent over the range of gradient strengths measured. Decays of much more than ninety percent result in many unusable data points as the signal decays into noise. A decay of much less than ninety percent will only measure the beginning of the decay, and so a fit would have to extrapolate within the measurable range. If a given combination of  $\Delta$  and  $\delta$  does not result in the necessary amount of peak decay, one or both of the values is altered and the paropt is repeated. Only when a combination of parameters is found which results in approximately ninety percent peak intensity decay, will the actual two-dimensional experiment be run. For further detail, please see Appendix A.

#### 3.6.1.2. Data Analysis

Evaluation of NMR peak areas is carried out in SpinWorks  $3.1.7^8$ . Prior to exporting the data from the NMR spectrometer, it is Fourier transformed, phased, and baseline corrected with the Bruker software. In SpinWorks, the free induction decay (fid) is again Fourier transformed ("Process Array"), with processing parameters for Phasing "Constants", Window Function "Lorentz (Exponential)", and an F1 (Evolution) Size slightly larger than the number of rows (1D scans; 16). The baseline is again corrected, using the least squares method. If the solute and solvent peaks have very different chemical shifts from each other, the baseline around each is corrected separately in order to achieve the best baseline possible around the very small solute peaks. When integrating, the domain for each peak in the first row (the spectrum corresponding to g = 2%) is chosen separately and the areas for the entire array are acquired by processing with

"Integrate Stacked Array". The decaying areas of each peak can then be graphed against  $f^2$  (Figure 3. 4), where f is the fraction of  $g_{max}$  applied for a given row, 2% to 95%, and fit to a two parameter, single exponential decay in SigmaPlot, which corresponds to equation 3. 5 as follows.

$$S(f^2) = S(0) \exp(-\alpha f^2)$$
 3.6

In order to avoid introducing artifacts into the data, peak areas of less than 10% their initial area are not included in the fit.



**Figure 3. 4.** Biphenyl (0.05 M) in  $[Pr_{10,1}][Tf_2N]$ . The exponential decay of the peak area for each chemical shift can be fit against the square of the fraction of maximum gradient strength applied to find the translational diffusion coefficient. The stronger dependence of solute peak area on applied gradient strength signifies a faster diffusion coefficient.

Each of the observed molecules yielded several peaks at different chemical shifts, all of which are fit to exponential decays of  $\log[S(f^2)]$  vs.  $f^2$ . The  $\alpha$  values for each fit are then averaged to obtain a final value  $\alpha_{avg}$ . The translational diffusion coefficient is calculated from  $\alpha_{avg}$  by setting it equal to  $D(\delta\gamma g_{max})^2(\Delta - \delta/3 - \tau/2)$ . The  $\Delta$  (D20) and  $\delta$  (P16) values can be found in the "acqus" file of the relevant experiment (which is in the same folder as the "ser" data file), listed by letter with the numbers incrementing from zero. In the following example, the sixteenth value of P, counting from zero, is 2000 µs. For a proton, the gyromagnetic ratio,  $\gamma$ , is 2.67522x10<sup>8</sup> rad/s T.

##\$P= (0..31) 6.45 10.05 20.1 114 16.35 23.034 34.9 69.8 13.4 100 0 0 0 5 5 250000 2000 2500 2000000 2000 34.9 3 3 0 5 0 250000 0 2000 200 0 0

**Figure 3.5.** List of parameter values in "acqus" file.  $\Delta$  (D20) and  $\delta$  (P16) values can be found by counting up to the correct numerical increment, starting with zero.

The maximum gradient was calibrated by measuring several liquids with known diffusion coefficients (DMSO, hexadecane, and BmimPF6) and solving  $\alpha_{avg} = D(\delta \gamma g_{max})^2 (\Delta - \delta/3 - \tau/2)$  for  $g_{max}$ . The gradient strength was found to have a maximum value of 0.38 T/m rad  $\pm 0.04$  T/m rad.

#### 3.6.1.3. Uncertainty Assessment

We have compared our diffusion measurements with those in the literature (Table 3. 2) in order to verify the reliability of our method. Several different sources report cation diffusion coefficients for neat  $[Pr_{31}][Tf_2N]$  and  $[Pr_{41}][Tf_2N]$ . Those measured at other temperatures have been adjusted to 25 °C according to the Stokes-Einstein equation, with the use of our temperature-dependent VFT viscosity fits.

$$D_{298} = D_T \left( \frac{k_B (298 \, K) / 6\pi r \eta_{298}}{k_B T / 6\pi r \eta_T} \right) = D_T \left( \frac{298 \, K / \eta_{298}}{T / \eta_T} \right)$$
3.7

In the above equation,  $D_T$  is the diffusion coefficient at temperature *T*,  $k_B$  is the Boltzmann constant, *r* is the solute radius calculated using van der Waals increments<sup>9,10</sup>, and  $\eta$  is the solution viscosity. As can be seen in Table 3. 2, our data fits in nicely with the assorted literature values, especially the data measured on the 850 spectrometer.

Literature	Measured	Raw Diffusion		Diffusion adjusted to 25 °C	
References	Temp	$Pr_{31}^{+}$	$Pr_{41}^{+}$	$Pr_{31}^{+}$	$Pr_{41}^{+}$
	/ °C	$/ 10^{-10} \text{ m}^2 \text{s}^{-1}$	/ 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup>	/ 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup>	/ 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup>
<b>PSU 400</b>	24.7	0.219	0.170	0.222	0.172
PSU 850	25	0.238	0.174	0.238	0.174
11	20	0.181	0.139	0.230	0.177
12	20	0.221		0.281	
13	32		0.251		0.183
14	25		0.178		0.178
15	24.47	0.255		0.261	
16	20	0.195		0.248	
17	25	0.260	0.177	0.260	0.177
Literature A	verage at 2	0.256	0.179		

**Table 3. 2.** Translational diffusion coefficients of IL cations from literature sources, adjusted to 25 °C, in comparison to our measurements at on our Bruker DRX-400 and AV-III-850.

In order to incorporate the effects of differences in tuning, shimming, parameter optimizations for different measurements, or any inconsistencies in sample preparation into an uncertainty assessment, we compare repeat measurements of equivalent samples. We have 23 equivalent measurements, only seven of which are repeats of the same sample. All other equivalent measurements resulted from sample pairs which were prepared and measured on different days. This assessment yielded a maximum percent difference of 12 %, from among the different sets of diffusion coefficients of equivalent samples. The average percent change was found to be 3 %, suggesting that most percent differences are significantly less than the 12% maximum value. Equivalent measurements taken both of the two spectrometers, the DRX-400 and the AV-III-850, showed a maximum 17% difference in resulting diffusion coefficient, with an average of 6% difference. As a result, we have chosen to apply an overall uncertainty of 15 % for NMR-measured translational diffusion coefficients.

To test the validity of comparisons between measurements taken by this group and those taken by other groups using different methods, we have measured some samples that have been cited by authors using a variety of techniques. We found no significant discrepancy in the small set of data we considered (Table 3. 3). Although comparisons of our measurements with these data gave a 12% average difference overall, comparisons with NMR literature data alone showed a much better 6% average difference (Table 3. 2). For discussions of transient grating and cyclic voltammetry measurements of translational diffusion coefficients, see Section 2.2.1.1.

			<b>Benzophenone</b>
<b>Reference</b>	<u>Ionic liquid</u>	<u>Technique</u>	Diffusion /m <sup>2</sup> s <sup>-1</sup>
18	[Im <sub>41</sub> ][BF <sub>4</sub> ]	transient grating	1.80E-11
18	$[Im_{41}][Tf_2N]$	transient grating	3.40E-11
19	$[Im_{41}][Tf_2N]$	cyclic voltammetry	1.10E-11
19	$[Pr_{41}][Tf_2N]$	cyclic voltammetry	2.50E-11
Our data	[Im <sub>41</sub> ][BF <sub>4</sub> ]	NMR	1.33E-11
Our data	$[Im_{41}][Tf_2N]$	NMR	2.77E-11
Our data	[Pr <sub>41</sub> ][Tf <sub>2</sub> N]	NMR	2.27E-11

**Table 3. 3.** Diffusion of benzophenone in three different ionic liquids is measured by three different techniques as a gauge of consistency between the methods.

#### 3.6.2. AV-III-850 Spectrometer

Translational diffusion measurements on the 850 MHz spectrometer were much more automated than were those on the 400 MHz spectrometer. Tuning and sometimes shimming is required before running each sample. Measurement of the radio frequency pulse length for a  $\pi/2$  rotation is as described in Section 3.6.1., but parameter optimization for  $\Delta$  and  $\delta$  is fully automated, based on the user's estimation of the diffusion coefficient. Calculation of the diffusion coefficients from the spectra is incorporated into the automated software.

Uncertainty values calculated from DRX-400 data were applied to 850 MHz data as well. Data measured on the 850 MHz spectrometer is generally better fit by the exponential decay than is data from the DRX-400, reducing this source of uncertainty relative to the DRX-400 value. With the greater automation of the software for the 850 MHz spectrometer, variations in the quality of parameterization or set-up procedures are presumed to be less than for the DRX-400. The general agreement of values measured on both the 850 MHz and the DRX-400 spectrometers suggests systematic errors are minimal. As a result, we assume uncertainties for measurements on this spectrometer are no more than those assessed for the DRX-400, above.

## 3.7. Rotational Diffusion Measurements

#### 3.7.1. Data Acquisition

Rotational diffusion measurements were conducted on the AV-III-850 spectrometer using a wideline broadband solids probe, the DRX-400 spectrometer using a BBI triple axis gradient

high-resolution probe, and the DPX-300 spectrometer using a broadband multinuclear probe. Care must be taken to remove any deuterium filters from the X channels, and to disconnect the deuterium lock cable. Inversion recovery measurements require tuning, shimming, and optimization of  $\pi$  and  $\pi/2$ . Measurements utilized a deuterium inversion-recovery pulse sequence with 50 rows on the DRX-400 and 62 rows on the DPX-300, spanning six orders of magnitude or more of  $\tau$  (see Section 2.3.7) in order to be sure of accurate  $T_1$  calculations. The longitudinal relaxation may then be fit using nonlinear least squares methods available on Bruker software. Line-by-line instructions for data collection and analysis are included in Appendix A for the DRX-400 and DPX-300. The user-interface on the AV-III-850 makes the measurements so simple, that these instructions have been omitted from this work.

#### 3.7.2. Uncertainty Assessment

Repeat measurements gave average uncertainties of 3% for the DRX-400 and 13% for the DPX-300. Repeat data on the AV-III-850 is not currently available, but variations in the application of the automated analysis program suggested a 3% uncertainty. Although we ran temperature calibrations for all three spectrometers, it is possible that some temperature inconsistencies remain, from one to the next. The VFT viscosity fit for  $[Im_{41}][BF_4]$  showed that an error of 1 K causes about a 5% error in viscosity (when at higher points in the temperature range), and as much as 13% difference (at the lowest applied temperature of 240 K). To account for differences between temperature sensors of the different spectrometers, as well as reproducibility of measurement on a single spectrometer, we have assigned uncertainties of 8% for the AV-III-850, 8% for the DRX-400, and 15% for the DPX-300.

# Ch 3 References

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# Chapter 4. Translational Diffusion in Ionic Liquids

#### 4.1. Introduction

In this study, we attempt to assess the reliability of the Stokes-Einstein (SE) equation for predicting the diffusion coefficients of a variety of solutes in a series of ionic liquids, and determine the effects of solute size, shape, and intermolecular forces on deviation from the equation. Results of these measurements are applied to test several diffusion models previously developed for conventional solvents, and some conclusions are drawn about the relative applicability of the models to ionic liquids.

#### 4.1.1. Traditional Stokes-Einstein Model

Ionic liquids have shown potential for a wide variety of uses, as green solvents for organic and inorganic reactions,<sup>1</sup> electrolytes in solar cells and batteries,<sup>2,3</sup> and chromatographic stationary phases,<sup>4</sup> to name a few. To aid further progress in these various potential applications, a thorough understanding of the properties of ionic liquids (ILs) is necessary. The high viscosities characteristic of ionic liquids, and the correspondingly low diffusion coefficients, may limit both reaction rates and charge transport, making these dynamical properties especially important targets for study. If diffusion is slow enough, it may be the limiting step in chemical reactions and is therefore of interest when considering ionic liquids as green solvents. In electrochemical applications, high viscosity may likewise result in low charge transfer and transport rates. Understanding the relationship between translational diffusion coefficients in a given ionic liquid and the structures of component cations and anions would allow for design and investigation of solvents better suited to the intended purpose. The Stokes-Einstein (SE) equation, which models a solute/solvent system in terms of a smooth spherical solute moving through a continuous fluid, is shown below.

$$D = \frac{k_{\rm B}T}{\zeta} \qquad \zeta_{\rm SE} = 6\pi\eta r \qquad 4.1$$

In these expressions, *D* is the translational diffusion coefficient,  $k_B$  is the Boltzmann constant, *T* is temperature,  $\zeta$  is the translational friction coefficient,  $\zeta_{SE}$  its approximation in terms of the

Stokes friction,  $\eta$  is viscosity, and *r* is the solute radius. Molecular volumes are determined from van der Waals increments and used to calculate radii as if the molecules were spherical.

The Stokes-Einstein equation combines the Einstein equation connecting transport and thermal equilibrium with Stokes' relation for the frictional coefficient of a macroscopic sphere,  $\zeta = 6\pi \eta r$ .<sup>5</sup> Stokes' law assumes stick boundary conditions, meaning that the drag of the spherical solute on the surrounding solvent is strong enough to result in solvent immediately adjacent to the solute having the same velocity as the solute. Although the original SE equation applied stick boundary conditions, slip boundary conditions, which assume zero drag velocity of the solvent tangential to the solute motion, can also be considered. Slip boundary conditions result in a coefficient of  $4\pi$  rather than  $6\pi$  in Eq. 4. 1. Neither the slip nor the stick variants of the SE equation has proven to be completely reliable in predicting observed translational diffusion coefficients. Slip predictions tend to be more accurate for self-diffusion of a molecule in a neat liquid (Figure 4.1), but stick boundary conditions are generally more accurate when solutes are much larger than solvent molecules. Self-diffusion coefficients of uncharged molecules in conventional solvents are generally within a factor of two of SE predictions, but divergences are greater in ionic liquids. Because of its relative accuracy, we consider the translational diffusion and viscosity of ionic liquids in terms of the Stokes-Einstein equation, and apply stick boundary conditions in accordance with the majority of published calculations.


**Figure 4. 1.** Observed self-diffusion values for neat conventional solvents, reported by Marcus<sup>6</sup>, compared to SE-calculated values with stick boundary conditions. The ratio  $D_{obs}/D_{SE}$  is equivalent to  $\zeta_{SE}/\zeta_{obs}$  (discussed in Section 4.3.2.)

## 4.1.2. SE Adjustments and Alternate Models

While the SE equation is fairly accurate, it does have a few shortcomings. It is generally accepted that its reliability decreases as the solute-to-solvent size ratio is reduced. This is a result of assumptions made in Stokes' derivation of the frictional coefficient for spherical particles. Stokes's hydrodynamic predictions assume a macroscopic sphere in a continuous fluid, but in most solutions, solute and solvent molecules are much too close in size to be approximated this way, and this representation worsens as the volume ratio shrinks.

It is also, of course, inaccurate to present solutes as smooth spheres, as most molecules are nonspherical in shape. In addition, solutes often have many sites of partial charge and may occasionally hydrogen bond with the solvent. Such solute-solvent intermolecular interactions cannot be addressed by the traditional SE equation.

There have been a variety of approaches to improving on the Stokes-Einstein equation in conventional solvents, including empirical power law adjustments, alterations to the frictional coefficient, computational modeling fits, and models that disregard the SE equation altogether.

We examine the utility of several of these adjusted SE models to the IL data later in the chapter. A brief review of these models is presented below.

The Gierer-Wirtz model <sup>7</sup>, published in 1953, is a theoretical description, motivated by the 1953 empirical results of Spernol and Wirtz<sup>8</sup>. The Gierer-Wirtz model adjusts the SE frictional coefficient in order to account for solute-solvent volume differences. The derivation is based on a thought experiment in which two planes, separated by only a few molecular layers of solution, are moved anti-parallel to each other at a constant rate. Radii were calculated from molar volumes of the pure components and adjusted for packing fraction assuming spherical molecules. The difference in solute and solvent sizes is included in the model in terms of their radii;  $r_u$  and  $r_v$ , respectively (Eq 4. 2).<sup>7</sup>

$$D_{GW} = \frac{k_B T}{6\pi \eta r_u f_{GW}} \quad where \ f_{GW}^{-1} = \left(\frac{3r_v}{2r_u} + \frac{1}{1 + \frac{r_v}{r_u}}\right)$$
 4.2

The Wilke-Chang model<sup>9</sup>, published in 1955, is favored for its simplicity and relative accuracy. This is an entirely empirical model. The authors assumed  $D \propto T/\eta$ , and fit a set of experimental data to several relevant variables. First, a dependence on solute size was ascertained by plotting  $T/D\eta$  against solute molal volume ( $V_u$ ). They found a linear relation between the solute diffusion coefficient (D) and  $V_u^{0.6}$ , similar to the SE linear dependence on  $V^{0.\overline{3}}$ . Several other solvent properties were considered for possible correlation to the diffusion coefficient, using similar methods. The strongest correlation was found for the solvent molecular weight ( $M_v$ ), for which they found a proportionality to  $M_v^{1/2}$ . The proportionality constant, however, was found to vary among different solvents. This variability was interpreted in terms of the degree of solute-solvent association and was accounted for by a multiplicative constant x as shown in equation 4. 3. The association parameter (x) is reported as x = 1 for unassociated solvents, x = 1.5 for ethanol, x = 1.9 for methanol, and x = 2.6 for water.

$$D_{WC} = 7.4 \times 10^{-8} \frac{(xM_v)^{1/2}T}{\eta V_u^{0.6}}$$
 4.3

The Kooijman model, published in 2002,<sup>10</sup> also corrects for solute-solvent size differences but, unlike those mentioned above, it includes an empirical correction to account for the non-spherical shapes of the molecules. The asphericity ( $\phi$ ) of a given molecule is zero for spheres, positive for any non-spherical shape, and is calculated using the following equation:

$$\phi = \left| 1 - \frac{R/Q}{(R/Q)_{ref}} \right|$$
 4.4

where R is the volume, Q is the surface area, and the reference unit,  $(R/Q_{ref}) = 1.249$ , modeled on methylene, is used to normalize the correction. All R and Q values are calculated from UNIQUAC or UNIFAC group contributions (used in the models for prediction of activity coefficients). The correction for volume ratio ( $\theta$ ) is given by:  $\theta = \frac{R_u^{1/3} + R_v^{1/3}}{R_u^{1/3}}$ . These ideas are combined to produce the translational diffusion coefficient according to Kooijman ( $D_K$ ) as follows.

$$D_{K} = A_{0} (1 - \phi_{u})^{A_{u}} (1 - \phi_{v})^{A_{v}} \theta^{A_{v}} D_{SE}$$
4.5

In the above, "A" values are various fitting parameters;  $A_0$  is between 1 and 4, while the others take some combination of the values 0, 1/3, or 1. The subscripts u and v refer to solutes and solvents, respectively, and  $D_{SE}$  is the diffusion coefficient according to the un-altered SE equation. <sup>10</sup>

In the Chen-Wei model,<sup>11</sup> published in 2011, discrepancies in translational diffusion coefficients ( $D_{CW}$ ) due to differences in solute-solvent interactions are addressed, in addition to solute-solvent size ratio. This is a semi-empirical model and, like the Geirer-Wirtz model, it is applied through alterations to the SE frictional coefficient.

$$D_{CW} = \frac{k_B T}{6\pi \eta r_u f_{CW}} \quad where \ f_{CW}^{-1} = 1 + 0.695 \left(\frac{r'_u}{n_v^{1/3} r_v}\right)^{-2.234}$$
 4.6

In the above equation,  $n_v$  is the solvent molecular association number,  $r_v$  is the solvent radius,  $r'_u$  is the effective radius of the solute molecule, which depends upon the solute molecule's solvation number  $(N_s)$  via the following relation:

$$r'_{u}{}^{3} = r_{u}{}^{3} + N_{s}r_{v}{}^{3}$$
 4.7

The solvent molecular association number reflects the number of strong solvent-solvent associations, such as hydrogen bonds, that persist during solvent flow. It has been calculated independently from X-ray diffraction data,<sup>12</sup> as well as from the ratio of the energy of activation of viscous flow vs. the energy of vaporization.<sup>13</sup> In contrast, the solvation number corresponds to the number of strong solute-solvent bonds per solute molecule. For unassociated solute-solvent systems,  $r'_u = r_u$  and  $n_v = 1$ , so that equation 4. 6 simplifies to  $f_{CW}^{-1} = 1 + 0.695(r_u/r_v)^{-2.234}$ . The authors calculated van der Waals radii using Bondi's method,<sup>14,15</sup> the

solvation number was taken from literature sources,<sup>16</sup> and the solvent molecular association number ( $n_v$ ) was determined from shear viscosity data.<sup>11</sup>

The Stokes-Einstein equation, variations on the SE equation, and hydrodynamic representations in general are by no means the only models of translational diffusion in liquids. Some researchers argue that the SE equation is not the best basis for a diffusional model. Stokes-Einstein deviations are even more frequent in glass-forming mixtures such as ionic liquids than in conventional solvents. These models also have little capacity for accounting for solute-solute interactions, resulting in inaccuracies when the equation is applied to concentrated solutions.<sup>17</sup> Simulations by Affouard *et al.* suggest that the SE equation cannot accurately represent diffusion in ionic liquids or other glass-forming solutions, instead supporting the idea of jump-like diffusional motion between vacancies, in accordance with hole theory.<sup>18</sup>

Hole theory is one of several types of vacancy models, falling in between the rigid Schottky-vacancy model and the low density gas-oriented model. According to the Schottkyvacancy model, fluids adhere to a loose lattice with vacancy sizes and placements determined by component ions. In gas-oriented models, ions are assumed to be surrounded by free volume. Hole theory describes vacancies with random size and location, both in constant flux, determined by thermally-driven local density fluctuations. The average radius of these vacancies, or "holes"  $\langle r_H \rangle$ , is related to the surface tension ( $\gamma$ ) and temperature (T) via equation 4. 8. Although derived for use in molten salts, hole theory has also been applied to a wide range of conventional solvents.<sup>19</sup>

$$4\pi \langle r_H^2 \rangle = \frac{3.5k_BT}{\gamma}$$
 4.8

In hole theory, viscosity and diffusion are presented as related to the probability of forming holes of sufficient size to accommodate a molecule. The model assumes that when adjacent to a vacancy of larger volume than itself, a molecule will move into the hole in the same manner as a gas, with the only significant difference between gasses and liquids being the relative probability of vacancies. Since large vacancies are considered to be at infinite dilution in ionic liquids, Taylor, *et al.*<sup>17</sup> have calculated the diffusion of the hole using the SE equation. In this application of Stokes-Einstein (Eq 4. 1), the "*r*" value refers to the radius of the hole, not of the diffusing compound, and is calculated from the relation to surface tension, above. Because a hole must be larger than the molecule, for a diffusing compound to fit inside, hole theory predicts

that a solute radius calculated by the SE equation should be larger than that of the diffusing molecule.<sup>17</sup>

Hole theory attempts to address an anomaly reported by several researchers; that of temperature-dependent hydrodynamic radii. Taylor *et al.* found that the temperature dependence of the SE-calculated hole radius correlated well with the calculations from surface tension values. Plots of surface tension-calculated radii vs. SE-calculated radii for an ionic solute in several different ionic liquids yielded linear relations for a range of temperature data. Although the SE-calculated hole radii were as much as 4.3 times the surface tension values, recent positron annihilation lifetime spectroscopy measurements<sup>20</sup> indicate that the missing proportionality factor is likely in the surface tension calculations and that the SE-calculated radii are almost exactly equal to measured hole radii.<sup>17</sup>

# 4.2. Experimental

## 4.2.1. Analytes

Our research focuses on a series of N-alkyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquids ( $[Pr_{n1}][Tf_2N]$ , n=3,4,6,8,10) with varying lengths of alkane substituents, but also includes work with trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide  $[P_{14,6,6,6}][Tf_2N]$  and several imidazolium ionic liquids as solvents. The solutes used in this study have been chosen to form several series displaying variation of some property of interest. The size/shape series is made of unsubstituted aromatic molecules of increasing size and varying aspect ratio: benzene, naphthalene, biphenyl, anthracene, and pyrene. The intermolecular forces (IMF) series consists of benzene derivatives with nonpolar, dipolar, and ionic character: benzene, p-difluorobenzene, o-difluorobenzene, 2fluorobenzonitrile, tetraphenylphosphonium benzoate (TPP<sup>+</sup> BA<sup>-</sup>), and the pyrrolidinium cations of the neat ionic liquids.

Pyrrolidinium ionic liquids were synthesized by Gary Baker, at the University of Missouri. The phosphonium ionic liquid was synthesized by Xiang Li.<sup>21</sup> Both 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Im<sub>21</sub>][Tf<sub>2</sub>N], [Im<sub>41</sub>][Tf<sub>2</sub>N], and [Im<sub>41</sub>][BF<sub>4</sub>] came from Ioletic, at 99% purity, and were used without further cleaning. They were dried under vacuum, usually at  $10^{-2}$  Torr, for several hours until the water content was found to be significantly less than 100 ppm by the Karl-Fischer method. All transfer, addition, and stirring of the solutes and dried ionic liquids took place inside a nitrogen glove box. NMR samples were sealed under vacuum in sample tubes prior to measurement and, unless otherwise specified, all measurements were made at 25 °C.

Most of our solutes were obtained commercially and used without further purification. Properties of solutes and ionic liquid solvents used in this study are presented in Table 4. 1. Tetraphenylphosphonium benzoate was prepared from silver benzoate (Sigma-Aldrich, 99% purity) and tetraphenylphosphonium chloride (TCI, 98% purity). The tetraphenylphosphonium chloride was dissolved in methanol at 0.65 M. After full dissolution, excess silver benzoate was added to the solution, which was stirred for several hours. The insoluble AgCl was filtered out. The filtrate was evaporated to form a brownish resin which tested negative for chloride with application of silver nitrate.

Compound	Volume /Å <sup>3</sup>	Radius /Å	Dipole moment /D	Charge
benzene	80.4	2.6775	0	0
naphthalene	123.4	3.0885	0	0
biphenyl	150.2	3.2975	0	0
anthracene	166.4	3.4120	0	0
pyrene	182.6	3.5194	0	0
p-difluorobenzene	89.6	2.7759	0	0
o-difluorobenzene	89.6	2.7759	2.4 22	0
2-fluorobenzonitrile	104.1	2.9182	5.6 22	0
benzophenone	169.6	3.4338	3.11 23	0
ferrocene	139	3.2134	0	0
cobaltocenium <sup>+</sup>	139	3.2134		+1
1-butyl-3-methylimidazolium <sup>+</sup>	150.5	3.2997		+1
hexafluorophosphate <sup>-</sup>	74.2	2.6067		-1
tetraphenylphosphonium <sup>+</sup>	315.2	4.2218		+1
benzoate -	104.6	2.9229		-1

**Table 4. 1.** Properties of solutes used in this study. Volumes and radii are calculated according to van der Waals increments. <sup>14,15</sup>

## 4.2.2. Diffusion Setup

Diffusion measurements employed a DRX 400 Bruker NMR spectrometer with a 5 mm inverse broadband probe (BBI) with triple axis gradients, as well as a Bruker AV-III-850 MHz NMR spectrometer with a Diff-30 probe with triple axis gradients. Measurements were made using the longitudinal-eddy-current delay (LED) stimulated echo pulse sequence with bipolar gradient pulse pairs as developed by Wu *et al.*<sup>24</sup> Temperature calibrations were conducted for the DRX-400 as described in Section 3.5.

Diffusion data were analyzed according to equation 4.9, in which S is the peak area, S(0) is the peak area at zero gradient strength, g is the applied gradient strength, D is the diffusion coefficient,  $\gamma$  is the gyromagnetic ratio of the observed nucleus,  $\delta$  is the gradient pulse duration,  $\Delta$  is the delay between gradient pulse pairs, and  $\tau$  is the time allowed for gradient recovery before the next pulse.

$$S(g) = S(0)exp\left[D(\gamma\delta g)^2\left(\Delta - \frac{\delta}{3} - \frac{\tau}{2}\right)\right]$$
4.9

S(g) is acquired from the raw data. S(0) may be disregarded, as a coefficient will not affect the exponential constant of an exponential fit. D is calculated from a fit of S(g) vs  $g^2$  to an exponential function. Gradient strengths were calibrated using standard samples, as mentioned in the Appendix.  $\tau$  is generally set to  $2x10^{-4}$  s, as this is the shortest time allowed by our electronics.  $\Delta$  and  $\delta$  are adjusted with respect to the diffusion coefficient of interest in a parameter optimization step during the experimental setup. A larger diffusion coefficient requires a larger  $\Delta$ ,  $\delta$ , or both. For each sample,  $\Delta$  and  $\delta$  were optimized with respect to the solute diffusion coefficient. (Early testing showed that optimization of  $\Delta$  and  $\delta$  for dimethylaniline, rather than for the ionic liquid cation, did not significantly impact results of the cation diffusion measurements.) Evaluation of NMR peak areas was carried out in SpinWorks 3.1.7<sup>25</sup> and data analysis was performed in SigmaPlot. For more detail, please see Appendix B.

In an effort to conduct a comprehensive uncertainty assessment of translational diffusion coefficients, 23 repeat measurements of equivalent samples were compared. Seven of these are repeats of the same sample, and 16 are equivalent samples that were prepared and measured on different days. This assessment yielded a maximum difference of 12 %, with an average difference of 3.5 %. Equivalent measurements taken on both of the two spectrometers, the DRX-400 and the AV-III-850, showed a maximum 17% difference in resulting diffusion coefficients,

with an average of 6% difference. Comparisons of our measurements with published data gave a 12% average difference overall, while comparisons with NMR literature data alone showed a much better 7% average difference. We have chosen to apply an overall uncertainty of 15 % for NMR-measured translational diffusion coefficients for both spectrometers. These assessments are discussed in greater depth in Section 3.6.1.3.

#### 4.2.3. Viscosity Setup

Viscosities were measured on a Brookfield Programmable DV-III + Rheometer with a CPE 40 spindle. Sample temperatures were controlled using a VWR Circulating Bath and standard controller. Data was recorded in increments of 5 °C, from 5 °C to 65 °C. The sample area was purged with  $N_2$  for at least 20 minutes before beginning measurements. For each 5 °C change, the temperature was allowed to equilibrate for 10 minutes. The rheometer was calibrated using Cannon calibration standard RT100 and the resulting correction value was added to parameter A in the Vogel-Fulcher-Tammann (VFT) equation.

$$Ln(\eta) = A - \frac{B}{T - T_0}$$
 4.10

In equation 4. 10,  $\eta$  is viscosity, and A, B, and T<sub>o</sub> are constants which are determined by fitting the data in SigmaPlot. The VFT equation, along with viscosity measurements, are both discussed in greater depth in Section 3.4.1.

## 4.3. Results and Discussion

#### 4.3.1. Viscosity at Infinite Dilution

In order to be sure of measuring solutes at infinite dilution, we first collected diffusion coefficients of the  $[Pr_{n1}][Tf_2N]$  ionic liquids with the solute dimethylaniline (DMA) over a range of concentrations (0 – 0.3 M). Viscosities of these solutions were also measured at the endpoints of this range. Dimethylaniline was chosen as the solute because it was used as a probe in some of our fluorescence quenching studies, which would benefit from a comparison to NMR measurements.<sup>26</sup> The size and aromaticity of DMA also recommends it for comparison with

other solutes in the present study. Although increasing solute concentration did produce a systematic increase in diffusion and a decrease in viscosity, the changes were small.

The variation, in both diffusion and viscosity, between the neat samples and 0.05 M DMA samples (the lowest concentration we reproducibly measured by NMR) was within experimental uncertainties. This was also the case for samples of 0.05 M pyrene in  $[Pr_{10,1}][Tf_2N]$  and neat  $[Pr_{10,1}][Tf_2N]$  (see Fig. 3. 2). For a complete listing of data for solutions of DMA, see Appendix D. The infinite dilution of these 0.05 M solutions was further confirmed by the agreement of the diffusion coefficients of cations in neat and 0.05 M samples to within uncertainties. We have therefore used neat viscosities in all our calculations for solutions at 0.05 M. Viscosity data were analyzed using the VFT equation (Eq 4. 10).

VFT fitting parameters for neat ionic liquids used in this work and representative IL solutions are presented in Table 4. 2. Comparison of our neat viscosity measurements with comparable measurements made earlier by another researcher showed an approximately 10% difference. We have reason to believe that the technique used for our current measurements was more correct than that used for previous measurements, and so have applied a 10% uncertainty to our Rheometer-measured viscosity data overall.

Ionic liquid	Α	В	T <sub>0</sub>
[Pr <sub>31</sub> ][Tf <sub>2</sub> N]	-1.901	839	158
[Pr <sub>41</sub> ][Tf <sub>2</sub> N]	-3.143	1266	128
[Pr <sub>41</sub> ][Tf <sub>2</sub> N], 0.3 M DMA	-0.722	516	192
[Pr <sub>61</sub> ][Tf <sub>2</sub> N]	-1.918	875	166
$[Pr_{81}][Tf_2N]$	-1.906	887	168
[Pr <sub>10,1</sub> ][Tf <sub>2</sub> N]	-2.336	1028	162
[Pr <sub>10,1</sub> ][Tf <sub>2</sub> N], 0.05 M pyrene	-3.536	1400	137
[Pr <sub>14,6,6,6</sub> ][Tf <sub>2</sub> N]	-3.472	1495	137
[Im <sub>21</sub> ][Tf <sub>2</sub> N]	-1.789	814	146
[Im <sub>21</sub> ][Tf <sub>2</sub> N], with T <sub>g</sub>	-1.248	650	163

**Table 4. 2.** Viscosity parameters for various ionic liquids, both neat and solutions, fit between 5 °C and 65 °C to the Vogel-Fulcher-Tammann (VFT) equation. Imidazolium fits are based on literature data<sup>27-31</sup> as well as on our measurements.

# 4.3.2. Temperature Dependence of Diffusion

The top two graphs of Figure 4. illustrate the fact that, for a given solute-solvent combination, solute diffusion coefficients are approximately proportional to  $T/\eta$ , as predicted by

hydrodynamic models. The lower two graphs of Figure 4. make direct comparison of diffusion measurements to the SE predictions by plotting the ratio of observed friction over SE-calculated friction where the frictional coefficient is defined by  $\zeta = k_B T/D$ . Radii in the SE equation are calculated using solute van der Waals volumes  $r_u = (3V_u/4\pi)^{1/3}$ , with V<sub>u</sub> obtained from atomic volume increments.<sup>14</sup>



**Figure 4. 2.** Solute diffusion coefficients (above) and friction ratios (below) plotted as a function of  $T/\eta$  for a temperature range of 2 - 43 °C. Friction ratios ( $\zeta_{obs}/\zeta_{SE} = D_{SE}/D_{obs}$ ) are the ratio of the observed friction coefficient over the SE-calculated friction coefficient. Panels on the left represent solutions in  $[Pr_{41}][Tf_2N]$ , while those on the right represent  $[Pr_{10,1}][Tf_2N]$ .

In contrast to the increase of hydrodynamic radius ( $r_h$ , where  $r_h/r = \zeta_{obs}/\zeta_{SE}$ ) with increasing temperature reported by some other authors<sup>17</sup>, our data shows a general decrease of  $\zeta_{obs}/\zeta_{SE}$  with T/ $\eta$  in [Pr<sub>41</sub>][Tf<sub>2</sub>N]. This trend is far less marked in [Pr<sub>10,1</sub>][Tf<sub>2</sub>N], with some solutes even displaying a slight positive slope. In a repeat measurement of pyrene in [Pr<sub>41</sub>][Tf<sub>2</sub>N], the decrease of  $\zeta_{obs}/\zeta_{SE}$  with T/ $\eta$  was less steep than that shown in Figure 4. 2. Overall, our data are inconclusive concerning any general temperature dependence of  $\zeta_{obs}/\zeta_{SE}$ . Motivated by these observations, we interpret diffusion data by comparison to the simplest hydrodynamic approach which is embodied in the Stokes-Einstein equation (Eq 4. 1). All other measurements in this study were conducted at 25 °C.

# 4.3.3. Departures from the Stokes-Einstein Equation: Relative Volume

#### 4.3.3.1. Ionic Liquid Solvents

Departures from Stokes-Einstein predictions are strongly correlated to the relative sizes of the solute and solvent molecules in conventional solvents.<sup>7</sup> This trend is also found in ionic liquids. The improved accuracy of the SE equation with increasing solute size can be seen in the lower half of Figure 4. 2. Further measurements support the idea that Stokes-Einstein accuracy is not specifically dependent upon solute size, but on the solute-solvent size ratio, as illustrated in Figure 4. 3. It can be seen that the frictional ratio approaches unity not only for larger solutes in a given ionic liquid, but also for smaller ionic liquids with a given solute. This is to be expected because the SE model, in which a sphere moves through a fluid, is most realistic when the solvent molecules are significantly smaller than the solute molecules. In order to better illustrate other variables affecting the SE frictional coefficient without convolution by volume ratio, much of our data will be presented in the format of  $V_{solute}/V_{IL}$ , where the ionic liquid volume is an average of the cation and anion van der Waals increments.



**Figure 4. 3.** The friction ratio  $\zeta_{obs}/\zeta_{SE}$  is graphed as a function of solute/solvent molecular size ratio. Ionic liquid solvents span the  $[Pr_{n1}][Tf_2N]$  series from n=10 at the far left, to n=3 at the far right for a given solute. Stacked values correspond to measurements taken at different temperatures, with  $\zeta_{obs}/\zeta_{SE}$  mostly decreasing with increasing temperature.

## 4.3.3.2. IL Solvents in the Literature

To better understand the factors effecting SE accuracy, we have compiled two sets of data from the literature. Both are comprised of diffusion coefficients of many different solutes in many different solvents for purposes of discerning trends as a function of polarity, intermolecular forces, and other effects. Because there has not been as much measurement of ionic liquid solutions, our set of literature data with ionic liquid solvents (Figure 4. 4) is limited to gaseous solutes. Ionic liquids included in this data set include those having imidazolium, pyrrolidinium, phosphonium, and ammonium cations with varying lengths of alkyl chains ( $1 \le C \le 14$ ) paired with; TfO<sup>-</sup>, PF6<sup>-</sup>, TFA<sup>-</sup>, Tf2N<sup>-</sup>, BETI<sup>-</sup>, DBS<sup>-</sup>, Cl<sup>-</sup>, DCA<sup>-</sup>, and DEP<sup>-</sup> anions. The solutes include

small alkanes and alkenes,  $CO_2$ ,  $O_2$ , and  $N_2$ . Despite this variety, the only trend identified was a dependence on the relative size of the solutes which, as noted above, has already been well documented.



**Figure 4. 4.** Dependence of frictional coefficient on solute-solvent size ratio in ionic liquids. Literature cations include imidazoliums<sup>+</sup>, pyrrolidiniums<sup>+</sup>, phosphoniums<sup>+</sup>, and ammoniums<sup>+</sup> with varying lengths of alkyl chains ( $1 \le C \le 14$ ). Anions used include TfO<sup>-</sup>, PF6<sup>-</sup>, TFA<sup>-</sup>, Tf2N<sup>-</sup>, BETI<sup>-</sup>, DBS<sup>-</sup>, Cl<sup>-</sup>, DCA<sup>-</sup>, and DEP<sup>-</sup>. Solutes include alkanes, alkenes, dienes, CO2, O2, and N2.<sup>32-36</sup>

#### 4.3.3.3. Relative Volume Adjustments in the Literature

As discussed earlier, several improvements on the Stokes-Einstein equation have been proposed in the context of diffusion in conventional solvents. We have considered some of these with regard to ionic liquids. Three that take into account the difference in size between solute and solvent molecules, those due to; Kooijman <sup>10</sup>, Gierer-Wirtz <sup>7</sup>, and Chen-Wei <sup>11</sup> were most applicable. The equations associated with these models were applied with re-adjusted fitting parameters, and the results are shown in Figure 4. 5. Each of these models bases the relative sizes of the fits on  $1 + (V_u/V_v)^c$  or something very similar. All of these ionic liquid-adjusted models have R<sup>2</sup> values of more than 0.84, but only the volume ratio-dependent Kooijman and Chen-Wei level off at high  $V_u/V_v$ , and only Chen-Wei shows a trend of approaching  $\zeta_{obs}/\zeta_{SE} = 1$ at  $V_u >> V_v$ , as would be expected in a real system, where large  $V_u/V_v$  conditions approach SE behavior. It is of interest that, of the three, Chen-Wei is the only model to allow the power c to vary.



**Figure 4. 5.** Attempts to fit IL diffusion data using model functions previously proposed in conventional solvents. Data is comprised of non-ionic solutes in ionic solvents, measured by our groups and some others. Fitting coefficients are:  $a_{kooij} = 2.5703$ ,  $b_{kooij} = -2.9223$ ,  $a_{CW} = 1.9649$ ,  $b_{CW} = 2.1489$ ,  $a_{GW} = 6.0240$ ,  $b_{GW} = -5.9305$ .<sup>32-36</sup>

A few other well-known models were also considered with respect to ionic liquids. Attempts to apply the empirically-derived Wilke-Chang equation resulted in poor fits, even with the addition of an exponential fitting variable.<sup>9</sup> The model put forth by Gordon, *et al.* gives the frictional coefficient as a complex function of solute aspect ratio, and does not concern the relative sizes of solute and solvent molecules.<sup>37</sup> We consider the effect of solute shape presently. From the perspective of hole theory, one model corrects for deviations in the SE equation by setting r proportional to hole radius, a function of temperature and surface area. Although we have not considered our data with respect to solution surface tension, our temperature measurements do not support this approach.

#### 4.3.4. Departures from the Stokes-Einstein Equation: Shape Dependence

The shape of diffusing solutes is another factor which may be expected to have a significant effect on the accuracy of the SE equation. It is clear that diffusion is affected by solute shape, as can be seen in our data (Figure 4. 3) from the position of biphenyl which, despite being slightly larger than naphthalene, is shown to diffuse somewhat faster and to diverge more than naphthalene from SE predictions. This deviation from the overall trend can be understood because it is the only solute in the series which is not entirely comprised of fused aromatic rings. Biphenyl's ability to twist give it more degrees of freedom, allowing for quicker reduce of solvation energy, less steric hindrance, faster diffusion, and a consequently lower SE friction coefficient. Biphenyl is also the only one of the series that is not planar. The SE model does not account for shape, as the Stokes friction coefficient used in the SE equation was derived specifically for spherical solutes, and may therefore be expected to be less accurate for less-spherical molecules.<sup>37</sup> Hydrodynamic friction coefficients for other shapes have also been derived, with Perrin first calculating the coefficients for prolate and oblate ellipsoids.<sup>38</sup> More recently, Hubbard and Douglas expanded these calculations to include asymmetric ellipsoids, which reduce to Perrin's values for the simpler cases of prolate and oblate (Eq 4. 11).<sup>39</sup>

$$\zeta = \frac{12\pi\eta}{\int_0^\infty [(a^2 + x)(b^2 + x)(c^2 + x)]^{-1/2} dx}$$
 4.11

In the above equation, *a*, *b*, and *c* refer to the lengths of the ellipsoidal semi-axes. We have used these friction coefficients, with stick boundary conditions, in place of the Stokes coefficient for several of our solutes. Translating molecular shape into axial lengths was accomplished by first illustrating the solutes as space-filling models and presenting them from two different angles; head-on and from the side (Figure 4. 6). Ellipses were then superimposed over the space-filling models and stretched and re-oriented until the ellipses traced the general perimeter. The axis corresponding to (on-edge) molecular width was set equal to the maximum atomic width and other axes were calculated relative to this in order to provide the correct molecular volume.



**Figure 4.6.** Assigned ellipsoidal axes to anthracene for use in calculating the hydrodynamic friction coefficients, according to Hubbard and Douglas.<sup>39</sup>

Surprisingly enough, the translational diffusion calculated using these friction coefficients resulted in very little difference from those calculated using the spherical Stokes friction coefficient (Table 4. 3). When friction coefficients are calculated this way over a range of symmetric ellipsoids, the friction ratio ( $\zeta_{obs}/\zeta_{SE}$ ) is less than 1.6, even for aspect ratios as extreme as 0.1 and 10. We have therefore concluded that, at least for these types of shapes and systems, solute shape is not a major influence on Stokes-Einstein accuracy.

Ellipsoidal Approximations					
	V /Å <sup>3</sup>	a /Å	b/Å	c /Å	Sellipsoid' Sphere
benzene	80.4	1.75	3.31	3.31	1.036
naphthalene	123.4	1.75	3.60	4.68	1.068
anthracene	166.4	1.75	3.91	5.81	1.099
pyrene	182.6	1.75	4.99	4.99	1.095
biphenyl	150.2	2.24	2.77	5.77	1.068

**Table 4. 3.** Adjustments of SE diffusion predictions with hydrodynamic friction coefficients for asymmetric ellipsoidal shapes. a, b, and c are ellipsoidal semi-axis lengths. Ellipsoidal friction coefficients are calculated from Eq. 4. 11.

# 4.3.5. Departures from SE Predictions: Intermolecular Force (IMF) Effects

#### 4.3.5.1. Conventional Solvents

We also examined trends in a wide variety of conventional (non-ionic) solvents. This set of data included solvents such as n-alcohols ( $1 \le n_c \le 8$ ), cyclohexane derivatives and larger cycloalkanes, water, acetonitrile, acetone, benzene, n-alkanes ( $6 \le n_c \le 16$ ), CCl<sub>4</sub>, and tetrabutyltin. Solutes in the data set included; CCl<sub>4</sub>, tetraalkyltin, noble gases, O<sub>2</sub>, methane, 3,3diethylpentane, benzene, benzene derivatives (fused, bridged, and substituted; Cl, OH, CH<sub>3</sub>, NH<sub>2</sub>, etc.), phenyl-substituted conjugated alkenes, and pyridine derivatives.<sup>40-51</sup> In addition to the expected solute/solvent size dependence, this data set demonstrated another interesting trend. Regardless of the solute/solvent size ratio, one set of diffusion coefficients showed a significantly larger friction ratio than the rest of the data. The distinguishing factor between data in the two groups involved their intermolecular forces (Figure 4. 7).



**Figure 4. 7.** SE accuracy for solute (U) diffusion in non-ionic solvents (V), according to solute-solute and solvent-solvent intermolecular forces. Data sets are grouped (A, B, C) by the similarity or dissimilarity of solute/solvent intermolecular forces. All "H-bond solvents" are n-alcohols except for those labeled "branched". All presented data was gathered from the literature <sup>40-51</sup> except for the data set "nonpolar solute, branched H-bond solvent", which we measured.

In Figure 4. 7, the group of data with smaller values of  $\zeta_{obs}/\zeta_{SE}$  than the rest (group C) is comprised of nonpolar or dipolar solutes in hydrogen bonding solvents. The groups of data with  $\zeta_{obs}/\zeta_{SE}$  closer to unity, A and B, are made up of nonpolar solutes in nonpolar or dipolar solvents (A), and hydrogen bonding solutes in hydrogen bonding solvents (B). The only published diffusion coefficient data we could find for hydrogen bonding solvents were for n-alcohols of one to eight carbons in length, which are known to form microstructures. The data from group C which stray into group A all have either water or methanol as solvents, neither of which is large enough to form significant microstructures, and group B was entirely comprised of methanol, ethanol, and propanol solvents. In order to ascertain whether group C was offset as a result of a difference in strength of solute/solvent intermolecular forces (IMFs) or if it was offset as a result of solvent microstructures, we also measured some diffusion values for benzene and anthracene dissolved in the branched alcohols ethylene glycol and t-butanol (purple hexagons). These values overlapped group C, suggesting that it is the difference in solute and solvent IMFs that causes the reduced SE frictional coefficient, and not the microstructures of n-alcohols. Where the solute IMFs are very similar to the solvent IMFs (groups A and B), the SE equation more accurately predicts the solute diffusion than in the case where the solute IMFs are weaker than the solvent IMFs (group C). This may be because solutes that cannot interact with the surrounding solvent molecules as strongly as the solvent molecules interact with each other are free to move at a faster rate than the more inter-connected solvent molecules. Because the SE equation uses solvent viscosity, a product of these intermolecular interactions, in calculating the solute diffusion coefficient, the SE equation under-predicts solute diffusion in these cases. It appears that the distinction between dipole-dipole forces and London dispersion forces is not large enough to have a marked effect with regards to SE diffusion predictions in relatively smallmolecule conventional solvents such as these (group A circles vs. triangles, and group B diamonds vs. triangles). By contrast, the presence or absence of hydrogen bonding does have a marked effect.

#### 4.3.5.2. Alcohol Solvents

In order to compare ionic liquid solvents and alcohol solvents more directly, we measured the unsubstituted aromatic solutes discussed previously in several alcohols (methanol, n-butanol, n-heptanol, and n-decanol). As can be seen in Figure 4. 8, we get good agreement between our measurements of un-substituted aromatics in n-alcohols and the literature values of non-hydrogen bonding solutes in alcohols. This reaffirms the reliability of our measurements, as well as providing a more direct analogy between the conventional solvent data and our IL solvent data.



**Figure 4. 8.** Observed frictional coefficient of unsubstituted aromatic solutes (U) in n-alcohol solvents (V), compared to literature values for conventional solutions<sup>40-51</sup>, and to our ionic liquid measurements. Those described as IL solutions with "different IMFs" include our fluorinated or unsubstituted aromatic solutes in the pyrrolidinium or phosphonium ionic liquids mentioned above.

The three data points for aromatics in alcohols which fell inside group A, rather than group C, all correspond to anthracene in the three longer-chained alcohols. The data point for anthracene in methanol has the highest  $\zeta_{obs}/\zeta_{SE}$  of all the aromatics in alcohols, forming a clear trend with the other three anthracene points. This odd behavior of anthracene in alcohols is all the more surprising because it does not correspond to what we observe in ionic liquids (Figure 4. 8), where  $\zeta_{obs}/\zeta_{SE}$  increases with increasing solute-to-solvent size ratio. In the n-alcohols,  $\zeta_{obs}/\zeta_{SE}$  increases with increasing size from benzene to anthracene, but decreases from anthracene to the larger pyrene Figure 4. 9. We have repeated these measurements three times and so are sure of the accuracy of the data, but cannot currently offer any explanation.



**Figure 4. 9.** Friction ratio for specific aromatic solutes in n-alcohols, from left to right: decanol, heptanol, butanol, and methanol. Compare with the same solutes in ionic liquids (Figure 4. 2).

#### 4.3.5.3. Ionic Liquid Solvents

The diffusion of solutes in ionic liquids does not follow any of the trends observed in conventional solvents, but forms a third group of data with a steeper slope than either group A or C (Figure 4. 7). In contrast to the conventional solvent data, the IL solvent data does not fall into different groupings based on the polarity, capacity for forming hydrogen bonds, or simple ionicity of the solutes. Many ionic solutes fall into the same trend as non-ionic solutes, when measured in ionic liquids. The distinction, instead, appears to come from the charge density of the solute (Figure 4. 10). Although neutral solutes and larger monovalent solutes follow the same trend, smaller ionic solutes, i.e. those with higher charge density, deviate sharply, producing a non-monotonic relation for charged solutes. This deviation at high charge density is great enough that diffusion of the highest charge density ions fall into the super-stick regime, whereas the friction for neutral solutes and lower charge density ions is typically slip or even sub-slip. Similar behavior has been previously observed for neutral solutes and monovalent ions in aqueous solutions.



**Figure 4. 10.** Friction coefficients of various charged and uncharged solutes in ionic liquid solutions (top left) and aqueous solutions (top right), considered by the electrostatic interactions of the solutes, as well as by solute-solvent volume ratio. Stokes-Einstein stick predictions fall along  $\zeta_{obs}/\zeta_{SE}=1$ . The range of dipole moments studied in ionic liquids is shown (bottom) with the structures of dipolar solutes studied. Structures of some ionic solutes of various charge density are displayed, and identified by abbreviation. Points labeled thusly identify ionic solutes in solution with a non-equivalent ionic liquid, while unlabeled cation and anion solutes in ionic liquids relate to neat ionic liquids. Our measurements for IL solution data were supplemented with data published by Watanabe and coworkers <sup>29,52,53</sup>. Aqueous solution data was entirely obtained from published sources<sup>54,55</sup>

## 4.4. Conclusions

Based on our own measurements as well as those reported by other researchers, we find that diffusion of non-ionic solutes in ionic liquids is primarily dependent upon the ratio of solute to solvent molecule size to solvent molecule size. Analogous behavior has been previously reported in conventional solvents, but in ionic liquids the dependence is much stronger. Dependences on solute shape and on different types of solute-solvent intermolecular forces are minimal for nonionic solutes in ionic liquids. However, for charged solutes the steric effects of size are convoluted with the effects of solvent attachment at high charge densities and produce a non-monotonic variation of  $\zeta/\zeta_{SE}$  with ion size, similar to what is observed for monovalent ions in water.

In considering several models of SE frictional coefficients, proposed for conventional solvent systems by other authors, we have found that both the Kooijman model, and especially the Chen-Wei model, could be easily applied to ionic liquids. Both of these friction coefficients are functions of power-law dependencies on solute-solvent volume ratios.

We also found that in conventional solvents, the accuracy of the SE equation is significantly affected by the difference in intermolecular forces of the solute as opposed to those of the solvent. Predictions are more accurate for systems in which solute IMFs resemble solvent IMFs, whereas the SE equation more greatly under-predicts diffusion for systems with substantially stronger solvent IMFs in comparison to solute IMFs. This is likely due to the dependence of the SE model on the solvent-dominated viscosity. Solute-solvent interactions will be weaker than solvent-solvent interactions in such systems, freeing the solutes to move more quickly than their solvent neighbors.

## Ch 4 References

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# Chapter 5. Rotational Diffusion in Ionic Liquids

## 5.1. Motivation

## 5.1.1 IL Rotation in the Literature

Rotational diffusion is a good indicator of molecular dynamics, and so is a source of much interest in the development of ionic liquids as reaction media and electrolytes, among other things. It also indicates the strength of intermolecular interactions, like hydrogen bonding and, as such, provides insight into solute-solvent interactions in ionic liquids. The Stokes-Einstein-Debye (SED) equation (Eq 5. 1) is fairly reliable in relating viscosity to the rotational correlation times ( $\tau_c$ ) of large solutes in conventional solvents. (For a more thorough discussion of rotational correlation and spectral density functions, refer to Section 2.3.4.

$$\tau_c = \frac{\eta V}{k_B T}$$
 5.1

In the above equation,  $\eta$  is viscosity, V is the solute molecular volume,  $k_B$  the Boltzmann constant, and T the temperature. We calculate volumes using van der Waals increments<sup>1,2</sup>. The Stokes-Einstein-Debye equation is a hydrodynamic model, assuming a hard spherical solute in continuum fluid. It represents rotational diffusion as a series of infinitesimal steps, a random walk, thereby approximating Brownian behavior in an isotropic environment.<sup>3</sup>

The SED equation assumes stick boundary conditions because these are more accurate in the large solute-to-solvent size ratio limit it was designed for. For small solutes rotating in a solvent composed of larger molecules, slip boundary conditions are often preferable, since very small solutes can rotate freely in the chinks between large molecules, sometimes resulting in even faster, "subslip" behavior. When intermolecular interactions are strong, however, as with hydrogen bonding or ionic interactions, the solute-solvent interactions may be enough to drag solvent molecules along with the solute, leading occasionally to "superstick" behavior.<sup>4</sup>

Within the field of molecular motion in ionic liquids, there is no consensus about the most accurate boundary conditions or even the most applicable version of the SED equation. In the past few years, many authors have published data which conform well to the traditional SED equation.<sup>5-11</sup> Many others have found the SED equation required some alteration, such as a

power law dependence on viscosity and inverse temperature,<sup>12-15</sup> as well as a variety of other modifications,<sup>16-18</sup> in order to accurately represent their results. Researchers report a similarly wide array of hydrodynamic boundary conditions.

Subslip behavior is seen in a variety of probe molecules in ionic liquids: neutral, polar, hydrogen-bonding, ionic, and radical. It is often found to set in at higher  $\eta/T$  for a given solvent,<sup>11,14,15</sup> and higher viscosity for otherwise similar IL solvents in a series. A common trend is the appearance of subslip behavior only for those IL solvents with the longest alkyl chains or hardest anions in the series. For example; of the IL solvent series  $Im_{21}^+$  alkylsulfate<sup>-</sup> (alkyl=ethyl, butyl, hexyl, octyl), only the octlysulfate<sup>-</sup> ionic liquid was found to produce subslip rotation of the solute coumarin 153.<sup>11</sup> A similar example demonstrates subslip conditions for the radical probe peroxylamine disulfonate (PADS) in  $[Im_{41}][BF_4]$  and  $[Im_{41}][PF_6]$ , but not in ionic liquids with shorter alkyl chains ( $N_{3111}^+$ ,  $Im_{21}^+$ , etc) or softer anions ( $Tf_2N'$ ,  $CH_3OSO_3^-$ , etc). Also included in the group of non-subslip solvents were ionic liquids with equal length alkyl chains (butyl, in this case) that are directly attached to a charged or highly polar atom, such as  $[Pr_{41}][Tf_2N]$ , which does not have an imidazolium-like resonance structure to allow the charge to delocalize further away from the alkyl chain.<sup>14</sup> Several other groups have found similar trends with regards to ion hardness and alkyl contribution of the IL solvent.<sup>10,17,18</sup>

A variety of different ideas about the cause of this subslip behavior are being considered by these groups and others like them. Some authors attribute the subslip hydrodynamics to molecular shape. Mladenova *et a.l*<sup>8,17</sup> point out the effect of probe shape on the hydrodynamic equations, as the SED equation assumption of spherical probes is not always appropriate. They conclude that, while shape is not a major factor in causing subslip rotation times, microviscosity is. Subslip behavior, combined with an observed power law dependence on viscosity, led these researchers to propose a modified Gierer-Wirtz model, assigning  $\tau$  a fractional dependence on  $\eta$ .

The Spernol-Gierer-Wirtz (SGW) model<sup>19,20</sup> is only quasi-hydrodynamic, employing the stick boundary condition to describe a spherical probe molecule surrounded by concentric shells of spherical solvent molecules.<sup>8</sup> In this model, rotation of the probe molecule is communicated through the solvent, outward from the probe through the concentric shells, much like laminar flow. Because the solvating molecules have a discrete size and shape, solvent molecule size has a significant effect on solute mobility. Larger solvents will allow for more void space around a smaller probe molecule, allowing for free-rotation.<sup>11</sup> The lack of friction in these voids is

thought to be the cause of subslip behavior, and is represented by the fractional viscosity dependence,  $\tau_c \propto \eta^x$ , where x represents the fraction of rotation determined by macroscopic viscous flow, as opposed to the fraction participating in void space free-rotations.<sup>9</sup>

Although many authors are attracted to the microviscosity element of the SGW model, most find that it is not sufficient, by itself, to describe their observations.<sup>10,11</sup> One author attributes this to the uncertainty of how best to represent solvent radii for a liquid comprised of cations and anions.<sup>8</sup> Das *et al.* assessed their data using the Dote-Kivelson-Schwartz (DKS) model,<sup>21</sup> another quasi-hydrodynamic free-space model which also factors in the solute-to-solvent volume ratio. These authors found in the DKS model a satisfactory description of their data.<sup>11</sup> The SGW theory is supported, to some degree, by a computational paper from the Maroncelli group,<sup>13</sup> in which it was found that rotational diffusion coefficients of the cation of the model ionic liquid model "ILM2", are more than 20 times faster than SED slip predictions. Essentially all of this subslip motion derives from rotations about the z-axis (Figure 5. 1), which appear to be mainly comprised of libration in slower dynamics regions, and 180° jumps upon relocation of the cation to faster dynamic regions.<sup>13</sup>



**Figure 5. 1.** An all-atom representation of  $[Im_{41}][PF_6]$  (above) and the coarse-grained model "ILM2" (below) used in MD simulations of cationic rotation.<sup>13</sup>

A related branch of thought involves the structuring of the alkyl substituents of ionic liquids. Fruchey *et al.*<sup>10</sup> explained the increasingly subslip rotation of the neutral fluorophore perylene in ionic liquids of increasing alkyl chain length by interpreting the biexponential rotational time correlation function into two parts, the two out-of-plane rotations, assumed to be equivalent, and a unique in-plane component. The authors found that, while the in-plane rotation became increasingly subslip with increasing chain length, the out-of-plane component became less subslip, approaching the slip boundary condition with increasing alkyl content of the ionic

liquid. Both component values, and the overall rotational diffusion rate, converge upon the rotation of perylene in paraffin oil. These results were explained by referencing prior work on the rotation of perylene in alkanes of varying length, where it was found that the longer hydrocarbon chains would lie more in-line with the main axis of the probe. In lying along the plane of the solute, the alkyl chains fill the void spaces the molecule could otherwise rotate into, reducing the amount of out-of-plane rotations, while allowing the molecule to slide past in the course of in-plane rotations. The similar behavior of perylene in ionic liquids with increasingly long alkyl substituents was taken by Fruchey, *et al.*<sup>10</sup> as evidence of a partitioning of perylene into hydrophobic alkyl pockets of the ionic liquid, which become larger with longer alkyl components.

Strehmel et al. have recently used ESR spectroscopy to measure rotation of a series of derivatives of piperidine-1-yloxyl (TEMPO) in several ionic liquids. For a range of ionic- and hydroxyl-substituted (TEMPOL) derivatives of TEMPO in [Im<sub>41</sub>][Tf<sub>2</sub>N], they found that the hydrodynamic volume of the ionic derivatives is approximately twice that of the nonionic TEMPOL, and that the activation energy of rotation for TEMPO is significantly lower than that of either TEMPOL or the various ionic derivatives. These results were interpreted as demonstrating a stronger interaction between ionic probe molecules and the ionic liquid, requiring rotation of, not simply the isolated probe, but a complex of the probe and interacting solvent ions. Although hydrogen bonding solutes do not demonstrate as strong a solute-solvent interaction as ionic probes, these interactions are still stronger than the unsubstituted TEMPO. Strehmel, et al. also find evidence of anion exchange for solutes and non-SED behavior of TEMPO, which was instead found to follow Gierer-Wirtz predictions.<sup>9</sup> In another work by the same group, a similar set of probes is assessed in the series of imidazolium ionic liquids  $[Im_{n1}]$ [Tf<sub>2</sub>N], where n = 1, 2, 3, 4, 6, 8, 10. In the octyl and decyl imidazolium solvents, cationic TEMPO derivatives were found to exhibit subslip behavior, whereas TEMPOL did not.<sup>18</sup> The authors explained that the longer alkyl chains resulted in larger nonpolar domains with which the ionic solutes cannot interact. This complete lack of interaction between the ionic solute and the solvent within the nonionic domains produces subslip rotation. In contrast, the nonionic TEMPOL can interact, to some degree, with these nonpolar regions, and so does not experience subslip behavior.

Despite these many studies, there is a dearth of NMR-based measurements of rotational diffusion in ionic liquids. As a technique, NMR spectroscopy has the particular advantage of sensitivity to a wide variety of probe molecules. Whereas EPR requires a radical and fluorescence anisotropy measurements require a fluorophore, NMR can be applied to any protonated molecule (as well as many others if multinuclear NMR is applied.) This is particularly useful with regard to very small solute molecules, which more often exhibit subslip rotation than their larger counterparts. Although dielectric measurements are also sensitive to small molecules, NMR spectroscopy is the preferable technique for quadrupolar nuclei, as the resulting data is far less convoluted by additional mechanisms than is dielectric data. NMR spectroscopy is also capable, unlike dielectric measurements, of studying completely nonpolar probes.

In the majority of studies in which sub-slip rotational behavior was observed, imidazolium ionic liquids were used. We therefore base our studies on two imidazolium systems; neat  $[Im_{21}][Tf_2N]$ , and 0.05 M benzene in  $[Im_{41}][BF_4]$ . In choosing these systems, we aim to address both subslip dynamics of a neat ionic liquid and that of an infinitely-dilute solute in an ionic liquid. Because the SED equation assumes small-step Brownian diffusion, it seems likely to us that these sub-slip rotation rates in ionic liquids (IL) are the result of free rotations, where an absence of potential energy barriers frequently allows fast rotation over large angles. Benzene is, therefore, an ideal solute for this line of study; its disk-like shape lends itself to free rotation around its six-fold axis. In addition, it is similar in size and shape to the imidazolium cation  $Im_{21}^+$  which is inclined to show sub-slip rotations, and its six equivalent protons amplify its NMR signal, allowing for less noisy data even at very low concentrations. We hope that our NMR studies in imidazolium-based ionic liquids, in conjunction with computational assessment of the same, will help bring some clarity to this somewhat confused field.

#### 5.1.2. Determination of Rotational Time Correlation Function by NMR

Even in the case of Brownian rotation, common interpretations of rotational diffusion data are a problem. Many researchers relate the longitudinal decay time,  $T_1$ , to  $\tau_c$  by assuming a single exponential rotational time correlation function. In order for this to be an accurate representation of rotational motions, the solute geometry would need to be such that there was only a single diffusion coefficient, which is only strictly true for molecules of extremely high

symmetry. In general one expects three distinct diffusion coefficients to be present. Disc-shaped or elongated molecules might be expected to have at least two rather different diffusion coefficients. For purposes of hydrodynamic predictions molecules are often approximated by ellipsoids. The simplest rotational correlation function of a symmetric ellipsoids (an ellipsoid with two degenerate axes) is one in which the vector of interest (main axis of the EFG,  $V_{zz}$ , for NMR measurements) lies along the unique, "symmetry," axis of rotation. In this case, the correlation function is unaffected by rotation about the symmetry axis, characterized by diffusion coefficient  $D_{\parallel}$ , but only rotations about the degenerate axes ( $D_{\perp}$ ), producing an exponential decay.<sup>22</sup>

$$C_r(t) = exp(-6D_{\perp}t)$$
 5.2

In the above representation,  $\tau_c$  is equal to  $(6D_{\perp})^{-1}$ . If the observed vector lies along one of the degenerate axes, the decay is bi-exponential (Eq 5. 3).

$$C_r(t) = 0.25 \exp(-6D_{\perp}t) + 0.75 \exp[-(2D_{\perp} + 4D_{\parallel})t]$$
 5.3

For  $V_{zz}$  lying off-axis, no new rate constants are introduced, as there are still only two distinct diffusion coefficients, but the amplitudes of the two components will change.<sup>22</sup>

In the case of an ellipsoidal solute with three unique sub-axes, the correlation function incorporates three different diffusion coefficients and between two and five exponentials can appear in the rotational correlation function. If the vector of interest lies along one of the principal axes, i, one has the following.<sup>22</sup>

$$C_{r}(t) = \left(\frac{1}{2} + \frac{3(D_{r} - D_{i})}{4\Delta}\right) exp[-(6D_{r} + 2\Delta)t] + \left(\frac{1}{2} - \frac{3(D_{r} - D_{i})}{4\Delta}\right) exp[-(6D_{r} - 2\Delta)t]$$
  
where  $D_{r} = \frac{1}{3}(D_{x} + D_{y} + D_{z})$  and  $\Delta = \sqrt{D_{x}^{2} + D_{y}^{2} + D_{z}^{2} - D_{x}D_{y} - D_{x}D_{z} - D_{y}D_{z}}$  5.4

Although assumption of single exponential decay is unwarranted, use of other relaxation models in ionic liquids has been little explored. Yasaka, *et al.*<sup>23</sup> have considered this problem via MD simulations, finding a bimodal relaxation of benzene (and of water) in ionic liquid. The slower relaxation component was found to have a single exponential character, but the faster component of the relaxation was found to have a much more complex nature. Due to its very fast nature, Yasaka *et al.* modeled the faster component as a pre-exponential constant the Lipari-Szabo factor "*a*". As a result, the rotational diffusion model presented by this group was not very different from the typical single-exponential  $T_1$ - $\tau_c$  relation,

$$\frac{1}{T_1} = \frac{3\pi^2}{10} a \left(\frac{e^2 Q q}{h}\right)^2 \left\{\frac{1}{1 + (\tau_c \omega_0)^2} + \frac{4}{1 + 4(\tau_c \omega_0)^2}\right\} \tau_c$$
 5.5

the only difference being an overall scaling of the equation for  $T_1$  in the presence of a singleexponential rotational decay by a factor of *a*.

In the present study, we hope to gain a better understanding of how to represent these rotational relaxations, keeping the model as simple as possible in order to facilitate usage.

## 5.2. Samples

#### 5.2.1. Analytes

In order to distinguish between Brownian diffusion and free rotation about different axes for a single molecule, we chose benzene- $d_6$  for one of our solutes. Benzene has the advantage of possessing two very different expected diffusion rates corresponding to a unique in-plane rotation, and two nearly degenerate rotations out of the plane of the molecule. Rotations of the six-fold axis (our-of-plane rotations) are expected to be Brownian, as they require the molecule to sweep out a path through surrounding solvent and must therefore be strongly hindered in dense media. In-plane rotation about the six-fold axis (rotations of the two-fold axes), however, will not require solvent re-ordering, as the hexagonal molecule can be thought of as roughly oblate. The lack of impediment to reorientations about this axis produces large-amplitude inplane rotations. The  $d_6$ -benzene was dissolved in  $[Im_{41}][BF_4]$  to make a 0.05 M solution.  $[Im_{41}][BF_4]$  was chosen as the solvent ionic liquid because it is known to remain liquid at low temperatures and to form a nice glass when it does solidify. The concentration was chosen to keep benzene at infinite-dilution (Section 3.3.) while remaining concentrated enough to provide a usable signal.

Benzene may reasonably be expected to interact weakly with an ionic solvent. In order to consider how solute rotations are effected by strong solute-solvent interactions, we also consider the 1-ethyl-3-methyl-imidazolium cation of the neat  $[Im_{21}][Tf_2N]$  ionic liquid. This molecule has a similar size and shape to that of benzene, although its ethyl and methyl groups likely result in more Brownian character for its in-plane rotations. From among organic ionic liquid components,  $Im_{21}^+$  is one of the closest in shape to an oblate ellipsoid, like benzene. It is also

one of the more thoroughly-studied IL cations, and has proven likely to display subslip dynamics, which we find particularly interesting.

We use inversion recovery with <sup>2</sup>H NMR for our measurements, and so have deuterated the  $Im_{21}^{+}$  cation. Data on  $Im_{21}^{+}$  here come from two samples,  $Im_{21}$ - $d_1^{+}$  with only the acidic (C2) hydrogen exchanged for deuterium, and  $Im_{21}$ - $d_6^{+}$  in which the methyl group and all three ring protons have been exchanged for deuterium. The  $Im_{21}$ - $d_6^{+}$  sample was kindly provided by Dr. Gary Baker, of the University of Missouri. The  $Im_{21}$ - $d_1^{+}$  sample was prepared from  $[Im_{21}][Tf_2N]$ (Iolitec, 99%), as described by Wulf, et. al.<sup>24</sup> A mixture of 6.9 mL of  $[Im_{21}][Tf_2N]$  was combined with 3.6 mL of D<sub>2</sub>O (99.9 atom % D, Sigma-Aldrich), so that the mole ratio was 7.4  $IL/D_2O$ . The mixture was stirred and heated to approximately 60 °C overnight, but no significant exchange occurred until transfer of the mix to an Erlenmeyer flask with a large stir bar, to allow for optimal mixing. Over 90% deuteration of the acidic peak was achieved this way. Further heating and stirring failed to exchange any of the non-acidic ring protons. The ionic liquid was then dried and used without additional purification.

# 5.2.2. Sample Preparation

Before mixing solutions or sealing NMR samples,  $[Im_{41}][BF_4]$  and  $[Im_{21}][Tf_2N]$  were dried on a vacuum line, with stirring and heating to 60 °C, for several hours or overnight to a pressure of approximately  $10^{-2}$  Torr. After drying, both ionic liquids had water contents of below 60 ppm, as measured by Karl-Fischer titration. Solutions to be run on the DRX-400 or DPX-300 were mixed and transferred to 5 mm economy 8" 200 MHz NMR tubes in a nitrogen glove box, maintained at 0.8 LPM nitrogen flow rate. These samples were vacuum sealed to prevent absorption of water vapor. Samples to be measured on the AV-III-850 were sealed in a very different manner. NMR tubes were shortened to 2.8 cm, and capped by inserting a Parafilm® plug into the top of the tube and covering the open end of the tube with epoxy, as described in Section 3.2.

## 5.3. Measurement Setup

#### 5.3.1. Viscosity

The temperature-dependent viscosity of the neat  $[Im_{21}][Tf_2N]$  was measured with a Brookfield Programmable DV-III + Rheometer and CPE 40 spindle, maintained within a N<sub>2</sub>-purged area, as described in Section 3.4.1. We have determined a 10% uncertainty for measurements made on the Rheometer, based on comparisons of current and prior data for the same ionic liquids.

## 5.3.2. Diffusion

Rotational diffusion measurements were conducted on the DRX-400 spectrometer using a BBI triple axis gradient high-resolution probe, on the DPX-300 spectrometer using a broadband multinuclear probe, and on the AV-III-850 spectrometer using a wideline broadband solids probe as described in Section 3.7. Measurements on both instruments utilized a deuterium inversion-recovery pulse sequence, spanning six orders of magnitude or more of  $\tau$  (Section 2.3.7) in order to be sure of accurate  $T_1$  calculations.  $T_1$  was then fit using nonlinear least squares methods available on Bruker software.

Rotation times and thus  $T_1$  times are expected to vary significantly with temperature in ionic liquids. It is therefore important to accurately know the temperatures in these experiments. We calibrated the DPX-300 and DRX-400 using 100% methanol temperature standards, and deuterated methanol for the AV-III-850. The principle behind methanol (and ethylene glycol) as temperature calibrants is as follows. At warmer temperatures, the strength of hydrogen bonding decreases, with the result that oxygen deshielding of the hydroxyl proton is reduced, so that the OH peak moves upfield.<sup>25</sup> Hydrogen bonding has a much smaller effect on methyl protons so that the difference in chemical shift between the hydroxyl and methyl peaks provides a selfcontained indicator of the temperature at which the measurement was taken. We use the correlation between this shift difference and temperature, developed by Raiford, et. al.<sup>26</sup> to calibrate the NMR spectrometers. We use measured chemical shifts to calculate the temperature according to Raiford's equations for several different temperature points. We then find the relation between these calculated temperatures (T<sub>MHz</sub>) and the apparent temperatures reported by

our instrument ( $T_{app}$ ). The resulting relations are as follows for the DPX-300 (Eq 5. 6; N=9,  $R^2$ =0.9996), and the DRX-400 (Eq 5. 7; N=10,  $R^2$ =0.9969).

$$T_{300MHz} = 9.55 \times 10^{-4} (T_{app})^2 + 0.497 (T_{app}) + 65.1$$
 5.6

$$T_{400MHz} = 2.691 \times 10^{-3} (T_{app})^2 - 0.4083 (T_{app}) + 180.4$$
 5.7

We calibrated the AV-III-850 with two different temperature relations, one for measurements taken with a gas flow rate of 670 L/hr at the sample holder (Eq 5. 8), and the other with a gas flow rate of 2000 L/hr (Eq 5. 9). This was made necessary because measurements were taken before it was understood that the gas flow rate has a significant impact on the temperature equilibration of the sample. Unfortunately, gas flow rates were also varied over a similarly broad range for data taken on the DPX-300 and DRX-400, in both translational and rotational measurements. As the gas flow rate was rarely recorded at the time of these measurements, these variations cannot be retroactively corrected, as in the case of the 850 MHz data. However, the lengthy equilibration time, a minimum of 20 minutes for 300 MHz and 400 MHz measurements, and 30 minutes for 850 MHz measurements, as well as the similarity of the temperature calibration relations for the two flow rates on the 850 spectrometer, will hopefully render this difference negligible.

$$T_{670L/hr} = 0.9684(T_{app}) + 11.975$$
 (N = 6, R<sup>2</sup> = 0.9996) 5.8

$$T_{670L/hr} = 0.9684(T_{app}) + 11.975 \quad (N = 6, R^2 = 0.9996)$$

$$T_{2000L/hr} = 0.90238(T_{app}) + 30.620 \quad (N = 5, R^2 = 0.99998)$$
5.9

## 5.4. Results

# 5.4.1. Benzene in [Im<sub>41</sub>][BF<sub>4</sub>]

#### 5.4.1.1. NMR Measurements

Measurements of benzene-d<sub>6</sub> in [Im<sub>21</sub>][BF<sub>4</sub>] gave overall good signal-to-noise ratio, with significant broadening at lower temperatures (Figure 5. 2). Temperatures below -30°C were not measured, as the broadening was considered to be too substantial. The signal-to-noise ratio of data taken on the AV-III-850, DRX-400, and DPX-300 spectrometers were found to be comparable. Peak intensities were used in calculating  $T_1$  values, rather than peak areas, as this was the analysis program default.


**Figure 5. 2**. <sup>2</sup>H NMR spectra of benzene- $d_6$  measured: (A) at various temperatures on the DRX-400 (with arbitrary intensities), and (B) at 41 °C on the AV-III-850, the DRX-400, and the DPX-300 spectrometers.

The temperature series for the 0.05 M d<sub>6</sub>-benzene in [Im<sub>41</sub>][BF<sub>4</sub>] (Figure 5. 3) displays the expected T<sub>1</sub> minima and Larmor frequency ( $\omega_0$ ) dependence at lower temperatures. Repeat measurements showed average scatter of ±3% for the DRX-400 and ±13% for the DPX-300. Repeat data on the AV-III-850 is not currently available, but variations in the application of the automated analysis program suggested a ±3% variation. Variation in repeat measurements is a good basis for assigning uncertainty within a data set from a single instrument; data from multiple instruments must include more variables in uncertainty assessments. Although we ran temperature calibrations for all three spectrometers, it is possible that some temperature inconsistencies remain, from one spectrometer to another. The VFT viscosity fit for [Im<sub>41</sub>][BF<sub>4</sub>] showed that an error of 1 K causes about a 5% error in viscosity at higher points in the temperature range, and as much as a 13% difference at the lowest temperature of 240 K. To account for differences between temperature sensors of the different spectrometers, as well as reproducibility of measurement on a single spectrometer, we have assigned uncertainties of ±8% for the AV-III-850, ±8% for the DRX-400, and ±15% for the DPX-300, for the purpose of overall assessments.



Figure 5. 3. Inversion recovery data for 0.05 M d<sub>6</sub>-benzene in [Im<sub>41</sub>][BF<sub>4</sub>].

## 5.4.1.2. Molecular Dynamics Simulations

In order to better understand the time dependence of the rotational time correlation function (tcf), an appropriate form for the function first had to be identified. Molecular dynamics (MD) simulations of benzene in the model ionic liquid "ILM2" were therefore carried out by Chris Rumble of the Maroncelli group (Figure 5. 4), using simulation procedures very similar to those used in previous work.<sup>30</sup> The ILM2 model represents a generic ionic liquid, chosen to mimic the properties of  $[Im_{41}][PF_6]$ . Although ILM2 is not a precise match for the  $[Im_{41}][BF_4]$  used in NMR measurements, their properties are similar enough that the same qualitative behavior is expected in both. Similar rotational time correlation functions were obtained in the simulations of Yasaka, *et al.* in simulations of  $[Im_{41}][Cl]$ .<sup>23</sup>



**Figure 5. 4.** Reorientational time correlation functions of benzene in ILM2 at 350 K. Degenerate reorientations of the y-axis (red) and z- axis (green) are distinguished from that of the x-axis (black).

It is clear from the functions in Figure 5. 4 that there are two distinct parts to the rotational time correlation functions of benzene. The fast component dominates the relaxation, accounting for around 90% of the y- and z- axis rotations. This is to be expected if the fast component derives from relatively unhindered spinning motions, and the slow component from Brownian diffusion, as we have suggested. Reorientation of the y and z axes is effected by rotation of the molecule about its six-fold axis, which should experience very little frictional resistance. As the x-axis is coincident with the six-fold axis, and therefore unaffected by rotation about the six-fold axis, the tcf of the x-axis will relax solely through the much slower Brownian diffusion, which accounts for about 70% of its relaxation. Both  $P_1$  and  $P_2$  Legendre polynomials are used in studies of rotational diffusion, with  $P_1$  (L=1) describing the rotation-to-observed relation for dielectric measurements, among others, and  $P_2$  (L=2) describing the relation for NMR measurements.

#### 5.4.1.3. Fit of Rotational tcf

The rotational time correlation functions in Figure 5. 4 were fit to several different types of functions using least squares minimization in MATLAB. Of those considered; single exponential, biexponential, triexponential, and lognormal+exponential, the most accurate fits were found with the triexponential and lognormal+exponential functions. As the lognormal+exponential was by far the simpler function (Eq 5. 10), this was the form chosen to represent the rotational time correlation function,  $C_r(t)$ . The agreement of the lognormal+exponential function to the averaged y/z, L=2 tcf can be seen in Figure 5. 5.



**Figure 5. 5.** L=2 reorientational time correlation functions of the in-plane (y/z) vectors of benzene in ILM2 as a function of temperature. The solid curves are the MD data and the symbols on lowest and highest temperature data are lognormal + exponential fits of the NMR results.

$$C_r(t) = f_{LN}C_{LN}(t;\sigma,\gamma) + (1 - f_{LN})exp(-t/\tau_{ex})$$
 5.10

$$C_{LN}(t;\sigma,\gamma) = exp\left\{\frac{-ln(2)}{\gamma^2}\left(ln\left[1+\frac{2\gamma t}{\sigma}\right]\right)^2\right\}$$
5.11

In the above,  $f_{LN}$  is the fraction of the normalized function represented by the lognormal fit,  $\sigma$  is the width parameter,  $\gamma$  is the asymmetry parameter, and  $\tau_{ex}$  is the correlation time of the exponential. The lognormal portion of the rotational tcf is represented by  $C_{LN}(t;\sigma,\gamma)$  (Eq5. 11). The correlation time of the lognormal function is as follows (Eq 5. 12).

$$\langle \tau_{LN} \rangle \equiv \int_0^\infty exp\{-\alpha [ln(1+\beta t)]^2\} dt = \left(\frac{\pi}{4\alpha}\right)^{1/2} \frac{e^{1/4\alpha}}{\beta} \left[1 + erf\left(\frac{1}{2\sqrt{\alpha}}\right)\right]$$
$$\alpha = \frac{ln(2)}{\gamma^2} \qquad \beta = \frac{2\gamma}{\sigma} \qquad 5.12$$

The fit to simulations was continued by optimizing all the variables with respect to the L=2 averaged rotational time correlation function of the in-plane axes,  $C_{y,z}(t)$ . The comparative ease of rotation of the in-plane axis, as well as their degeneracy, means that the majority of the relaxation- and all relaxation observable by NMR- will come from reorientations of these axes. As a result, we have fit only to the tcfs of the y and z axes. The resulting values are given in Table 5. 1.

T /K	η /cP	$f_{LN}$	σ /ps	γ	τ <sub>ex</sub> /ps	$ au_{LN}$ /ps	$\langle \tau_c \rangle$ /ps
300	321	0.89	0.41	2.45	1530	3.71	167
325	70	0.91	0.41	2.16	190	2.27	18
350	26	0.92	0.40	1.81	58	1.29	6.0
375	12.7	0.93	0.40	1.79	45	1.27	4.3
400	7.5	0.92	0.40	1.60	18	0.99	2.3

**Table 5.1.** Temperature dependence of optimized fit parameters for the rotational tcf of the in-plane axes of benzene. The values for  $\langle \tau_c \rangle$  represent the overall rotational tcf.

Table 5. 1 shows that  $f_{LN}$  and  $\sigma$  are nearly temperature-independent but  $\gamma$ , and therefore  $\tau_{LN}$ , do depend on temperature, and  $\tau_{ex}$  has a strong dependence on temperature. The latter dependences can be fit to the functional form  $Y(T) \propto \eta(T)^p/T$ , with powers p = 0.28 and 1.0 for  $\tau_{LN}$  and  $\tau_{ex}$ , respectively. In the model described below, we chose to focus on  $\tau_{LN}$ , rather than  $\gamma$ , in representing the temperature dependence of the fast component of  $C_r(t)$  because the former is the more readily interpretable variable and more comparable to  $\tau_{ex}$ .

$$\tau_{LN}(T) = \left(\frac{T_{ref}}{T}\right) \left(\frac{\eta}{\eta_{ref}}\right)^{p_{LN}} \tau_{LN}^{ref}$$
 5.13

$$\tau_{ex}(T) = \left(\frac{T_{ref}}{T}\right) \left(\frac{\eta}{\eta_{ref}}\right)^{p_{ex}} \tau_{ex}^{ref}$$
 5.14

In the above,  $T_{ref}$  is set to 25 °C,  $\eta_{ref}$  is the viscosity at 25 °C,  $\tau_{LN}^{ref}$  is the lognormal correlation time at 25 °C and  $\tau_{ex}^{ref}$  is the exponential correlation time at 25 °C. The variables  $p_{LN}$  and  $p_{ex}$  simply control the degree of influence of viscosity on the correlation times. The viscosities used for our 0.05 M benzene/[Im<sub>41</sub>][BF<sub>4</sub>] solutions at various temperatures were determined by fitting the data of several groups to the VFT equation (Figure 5. 6). The temperature and viscosity dependence of  $\tau_{LN}$  is factored into the overall correlation function  $C_r(t)$  by setting Eq 5. 13 equal to Eq 5. 12, so that the asymmetry parameter in Eq 5. 11 may be related to the viscosity and temperature. The calculation of  $\gamma$  requires the fixed assignment of  $\sigma$ .



**Figure 5. 6.** VFT fit  $[Ln(\eta) = A + B/(T - T_0)]$  of experimental viscosity data of neat  $[Im_{41}][BF_4]$ .<sup>31-38</sup>

Comparison of tcfs of the system at different temperatures demonstrated that contributions of the fast and slow components of diffusion to the overall reorientational relaxation are not temperature-invariant. This behavior is included in the model by the following equation (Eq 5. 15), in which  $d_{LN}$  controls the temperature dependence of  $f_{NL}$ .

$$f_{LN}(T) = f_{LN}(T_{ref}) + d_{LN}(T - T_{ref})$$
 5.15

#### 5.4.1.4. Fit of NMR Benzene Data

The seven parameters included in the model ( $\sigma$ ,  $f_{LN}$ ,  $d_{LN}$ ,  $\tau_{LN}^{ref}$ ,  $p_{LN}$ ,  $\tau_{ex}^{ref}$ , and  $p_{ex}$ ) were set or varied by turns, to find the best fit of both the simulated rotational time correlation functions and the observed  $T_1$  values (Table 5. 2), with a quadrupolar coupling constant of  $1.90 \times 10^5$  Hz. The overall "goodness of fit" was quantified as  $\chi_v^2$ , where a value of 1 indicates deviations equal to experimental uncertainties, and less than one is smaller than uncertainties. We began with the simplest fit, setting  $f_{LN} = 0$  for a single exponential, after which point parameters were changed to produce a decrease in  $\chi_v^2$ . Several fits of greater interest are illustrated in Figure 5. 7.

Fit #	$\chi^2$	$f_{LN} \\$	σ	$ au_{LN}^{ref}$	$p_{LN}$	$ au_{ex}^{ref}$	p <sub>ex</sub>	d <sub>LN</sub>	Fit Type
1	42	0				38*	1	0	single exponential (p=1)
2	24	0				49*	0.18*	0	single exponential (p varied)
3	17	0.92	0.41	2.28	0.28	633*	0.40*	0	lognormal(fixed) + exp
4	3.4	0.92	0.41	35*	0.28	306*	0.98*	0	$lognormal(\tau varied) + exp$
5	1.4	0.87*	0.41	2.28	0.28	346*	0.73*	0	lognormal(f varied) + exp
6	0.8	0.90*	0.41	2.28	0.28	469*	0.69*	1.0x10 <sup>-3</sup> *	lognormal(f, d varied) + exp

**Table 5. 2.** Proposed model fits to NMR  $T_1$  decay data. An asterisk, \*, denotes a parameter that was optimized in fitting, rather than assigned and fixed. Bold parameters indicate the final values accepted as the best model representation.

Attempts to fit the data with a single exponential or stretched single exponential function (Figure 5. 7, upper left) only demonstrated the necessity that  $C_r(t)$  be bimodal. Only when the lognormal function was added to the fit (fit #3) did T<sub>1</sub>(T) begin to approach the form shown by the experimental data. From the simulated tcfs and NMR data, it is apparent that the faster of the two motions is in the extreme narrowing limit, making the form of its rotational time correlation function indiscernible by NMR. Only the actual rotational correlation time,  $\tau_{LN}$ , can be determined by subtracting the integral of the slow time,  $\tau_{ex}$ , from the overall integral,  $\langle \tau_c \rangle$ . Because experiment is blind to the form of the fast reorientational tcf, many forms could work, including a simple exponential decay. We choose to use a lognormal simply because the simulations suggested it to be a more realistic representation. The lognormal parameters used in fit #3 were set to the values determined from fitting the simulation results. Although this choice

does result in  $T_1$  minima near their experimental values, the fit can be improved by allowing optimization of some variables.



**Figure 5. 7.** Reproduction of  $T_1$  NMR data by different fits of the simulation model. Fits are numbered according to Table 5. 2. Red  $\Delta$ , green  $\nabla$ , and blue O correspond to data taken at 850 MHz, 400 MHz, and 300 MHz, respectively.

Further improvement of the fit was achieved by varying  $f_{LN}$  in addition to the exponential parameters  $\tau_{ex}^{ref}$  and  $p_{ex}$  (fit #5). Although this resulted in a  $\chi_{v^2}$  of 1.4, very near to experimental uncertainties, we have chosen instead to use fit #6, which differs from #5 by also optimizing  $d_{LN}$ . This was decided because it allowed the model to represent the increase in exponential fraction of the simulated tcfs at higher temperature (Figure 5. 5). The adjustment also results in a slightly improved  $\chi_{v^2}$ , so that the goodness of fit is less than assigned uncertainties.



**Figure 5. 4.** Comparison of reorientational time correlation functions derived from the best model fit (#6) of the NMR data (upper curves) to correlation functions simulated for benzene in ILM2 ("MD", lower curves). The NMR data are vertically offset by 0.25 for clarity. Superimposed on the MD data are two fits of the NMR data ("x") having values of  $\eta/T$  equal to those of the simulations at 300 K and 350 K.

The rotational time correlation function produced by the final form of the model, fit #6, to the NMR measurements compares well to the simulated tcfs (Figure 5. 4), despite having altered several of the parameters from their fit-to-simulations values. This agreement not only demonstrates the self-consistency of the model for determining tcfs from NMR data, but also reinforces the reliability of the coarse-grained ILM2 simulations.



**Figure 5. 9.** Comparison of the model fits to the NMR data (curves) against the MD simulations of benzene in ILM2 (points) in terms of the viscosity/temperature dependence of the component times  $\tau_{LN}$  and  $\tau_{ex}$  as well as the overall correlation time  $\langle \tau_c \rangle$ .

The comparison of NMR fits to simulated tcf is broken down into component parts in Figure 5. 9. Of course, the agreement for  $\tau_{LN}$  is the best, as the model for  $\tau_{LN}$  is an unaltered fit to the MD simulation; NMR measurements being unable to assess the tcfs of such fast rotations. By contrast, the agreement for  $\tau_{ex}$  is less ideal, with the model exhibiting a weaker dependence on  $\eta/T$  ( $p_{ex} = 0.69$ ) than is seen in the simulations ( $p_{ex} = 1.0$ ). However, this disagreement may be due merely to the choice to use a single exponential function to represent the fast component, rather than a stretched exponential. Use of a stretched exponential, with  $\beta \approx 0.75$  would result in essentially the same fit, but with  $p_{ex} = 1$ , as in the simulation data.

# 5.4.2. $Im_{21}^{+}$ in Neat $[Im_{21}][Tf_2N]$

## 5.4.2.1. Inversion Recovery Results

Signal-to-noise ratios for the  $Im_{21}$ -d<sub>6</sub><sup>+</sup> cation are very good, overall. The only exception to this is at the acidic ring position (C(2) in Figure 5. 5). Proton exchange during purification resulted in significant loss of deuteration at this position, reducing the peak area significantly. The substantial amount of peak broadening at lower temperatures, combined with the small peak area of the acidic deuterium led to loss of the C(2) signal in the shoulder of the C(4), C(5) peak,

limiting the temperature range at which  $T_1$  can be calculated for C(2) in  $Im_{21}-d_6^+$ . The signals from the two non-acidic ring positions are indistinguishable in these measurements.



**Figure 5. 5.** <sup>2</sup>H NMR spectra at 300.13 MHz; (A) broadening of  $Im_{21}$ -d<sub>6</sub><sup>+</sup> at various temperatures, (B) spectra for  $Im_{21}$ -d<sub>1</sub><sup>+</sup> compared to  $Im_{21}$ -d<sub>6</sub><sup>+</sup> at 41 °C, and (C) spectra of  $Im_{21}$ -d<sub>1</sub><sup>+</sup> and  $Im_{21}$ -d<sub>6</sub><sup>+</sup> at -29 °C. Intensities for all graphs are arbitrary. Behavior is representative of that seen at 400.13 MHz and, with regards to  $Im_{21}$ -d<sub>6</sub>, 850.23 MHz.

Measurements of deuterated  $[Im_{21}][Tf_2N]$  (Figure 5. 6) were considered in a similar manner to the benzene- $[Im_{41}][BF_4]$  data discussed earlier. Uncertainties were assigned as were those for the benzene sample; 8% for the AV-III-850, 8% for the DRX-400, and 15% for the DPX-300. We saw good agreement of the C(2) signal for d<sub>1</sub> and d<sub>6</sub> measurements when the ring peaks could be separated, as demonstrated by the upper segment of Figure 5. 6. Because the ring peaks were inseparable at low temperatures, we have averaged the responses of the (separate) C(2) and the C(4), C(5) peaks, for continuity across the temperature range. The results of this averaging are shown in the lower segment of Figure 5. 6 and these data are used for the remainder of this analysis.



**Figure 5. 6.** Inversion recovery data for neat  $[Im_{21}][Tf_2N]$ -d<sub>1</sub> and -d<sub>6</sub> with separate C(2) and C(4,5) peaks combined to give one signal for all ring deuteriums.

## 5.4.2.2. Simulated Reorientational Time Correlation Functions

Two different MD simulations of  $Im_{21}^{+}$  were performed to help guide the modeling of the  $[Im_{21}][Tf_2N]$  data. That conducted by Chris Rumble uses the same coarse-grained ILM2 model ionic liquid described previously (Section 5.4.1.2) for the imidazolium solvent, while representing the imidazolium cation assessed as a solute as a rigid, united-atom  $Im_{21}^{+}$ . Although not as accurate as the flexible, all-atom force field simulations<sup>39,40</sup> by Sharad Kyadav, the simplicity of the ILM2 approach allows for longer simulations at higher viscosities. Comparison of ILM2 simulation results with all-atom simulation results, as well as experiments, also provides an opportunity to further assess the reliability of our coarse-grain ionic liquid model (Figure 5. 7).



**Figure 5. 7.** Comparison of temperature-dependent reorientational time correlation functions of ring C-H vectors (averaged over the three C-H vectors) of  $Im_{21}^{+}$  in (a) all-atom simulations of neat  $[Im_{21}][Tf_2N]$  and (b) simulations of a rigid united-atom model of  $Im_{21}^{+}$  in the reduced ionic liquid model ILM2.

As can be seen in Figure 5. 7, there is good general agreement between the two simulation methods. In both, the fast component is relatively temperature-invariant, and accounts for approximately 25% of the decay within about 1 ps. The slow components are shown by both methods to be temperature-dependent, relax fully within 1 ns, and be well-described by a stretched exponential with  $\beta = 0.5$  to 0.6. The simulations differ in their fits of the fast-component, with the all-atom model best described by a stretched exponential, and the ILM2 by a single exponential function. There are also differences in the specific behavior at a given temperature, although this may be expected from the different descriptions of the ionic liquid solvent. While we treat the model ionic liquid ILM2 as representative of most short-chain imidazoliums, the  $[Im_{41}][PF_6]$  on which it was based has a much more compact anion than the Tf<sub>2</sub>N<sup>-</sup> it represents, and a longer-chain cation. Given the solvent differences, a different dependence of viscosity on temperature is expected. To be directly comparable, tcfs should be considered in terms of  $\eta/T$ , rather than just T.

We choose to assign the non-optimized variables and to fit the fast-component of our NMR data according to the functional form suggested by the all-atom simulations, rather than that of the ILM2 simulations. As these motions are likely to be Brownian in nature, and will be more strongly influenced by the specific solvent flexibility and structure, we expect more

accuracy from the all-atom simulations. The difference between the results of the two methods is not large, however, and therefore reinforces the usefulness of the coarse-grain model for lengthy simulations and low temperatures.

To allow direct comparison with NMR data, rotational tcfs have been simulated for the three ring C-D bond vectors. The expected rotational correlation times of the molecule are not so divergent as those considered for benzene. The similar sensitivities of the three ring deuteriums to rotations about the different axes, as a result of the geometry of the molecule, likely contribute to the similarity of the tcfs. All three ring deuteriums must have the same sensitivity to in-plane rotations, and the substantial angles formed by the N-N vector with either the acidic deuterium bond or the C(4)-D and C(5)-D bonds implies a similar sensitivity to rotations about N-N. The only substantial difference in sensitivities of the three deuteriums to the rotations of the molecule is the insensitivity of the acidic deuterium to rotations about the C(2)-D bond, and the contribution of this rotation to the relaxation of the other ring deuteriums may be expected to be small because of the relatively small angle their bonds form with the N-N vector. We therefore expect all three tcfs to be very similar, with slightly more divergence in the acidic deuterium tcf. This is confirmed by the rotational tcfs of the all-atom simulations (Figure 5. 8).



**Figure 5.8.** Simulated all-atom reorientational time correlation functions of ring C-H vectors at positions 2, 4, and 5 for neat  $[Im_{21}][Tf_2N]$  at 273 K.

The rotational tcf was described using two stretched exponentials, since this more accurately depicts the results of the all-atom simulations (Eq. 5. 16).

$$C_{r}(t) = f_{1} exp\left\{-\left(\frac{t}{\tau_{c1}}\right)^{\beta_{1}}\right\} + (1 - f_{1}) exp\left\{-\left(\frac{t}{\tau_{c2}}\right)^{\beta_{2}}\right\}$$
5.16

Fitting this expression to the all-atom simulation tcfs at various temperatures produced the following parameterizations (Table 5. 3). Values that appear to be mostly temperature-independent,  $f_1$ ,  $\tau_{c1}$ ,  $\beta_1$ , and  $\beta_2$ , are averaged across all the simulated temperatures and for all three assessed positions.

H-C(2)										
T/K	$\mathbf{f}_1$	$\tau_{c1}$	$\beta_1$	$\tau_{c2}$	$\beta_2$	$\langle \tau_c \rangle / \mathrm{ps}$				
260	0.21	0.73	0.52	193	0.51	297				
273	0.20	0.67	0.55	84	0.52	125				
285	0.22	0.70	0.55	64	0.53	90				
298	0.23	0.72	0.56	41	0.54	56				
H-C(4)										
T/K	$\mathbf{f}_1$	$\tau_{c1}$	$\beta_1$	$\tau_{c2}$	$\beta_2$	$\langle \tau_c  angle / \mathrm{ps}$				
260	0.19	0.75	0.47	219	0.58	279				
273	0.22	0.86	0.49	107	0.64	117				
285	0.23	0.87	0.49	81	0.65	86				
298	0.25	0.88	0.50	53	0.67	54				
			H-C(5	5)						
T/K	$\mathbf{f}_1$	$\tau_{c1}$	$\beta_1$	$\tau_{c2}$	$\beta_2$	$\langle \tau_c \rangle / \mathrm{ps}$				
260	0.19	0.72	0.49	220	0.59	254				
273	0.22	0.82	0.50	99	0.64	107				
285	0.23	0.80	0.50	75	0.64	80				
298	0.25	0.81	0.52	49	0.67	50				
	Average H-C(2), H-C(4), H-C(5)									
T/K	$\mathbf{f}_1$	$\tau_{c1}$	$\beta_1$		$\beta_2$					
	0.23	0.79	0.52		0.61					

**Table 5. 3.** Dependence of all-atom simulation parameters on temperature for  $Im_{21}^+$  in neat  $[Im_{21}][Tf_2N]$ .

The slow correlation time is strongly dependent on temperature, probably because of the change in viscosity with temperature, and can be characterized as follows (Eq 5. 17).

$$\tau_{c2} = \left(\frac{T_{ref}}{T}\right) \left(\frac{\eta}{\eta_{ref}}\right)^p \tau_{c2}^{ref}$$
 5.17

The fast-component exhibits much less change with temperature and is found to be proportional to  $T^{-1/2}$ , in the same manner that reorientation of a free rotor scales with temperature (Eq 5. 18).

$$\tau_{c1} = \left(\frac{T_{ref}}{T}\right)^{1/2} \tau_{c1}^{ref}$$
 5.18

The viscosity dependence of neat  $[Im_{21}][Tf_2N]$  has been characterized by many researchers and we have again fit these literature data, along with our own measurements, to the VFT equation (Figure 5. 9). The experimental viscosity data do not cover the entire temperature range of our NMR experiments, but inclusion of the glass transition (at  $\eta=10^{13}$  cP) to constrain the fit should provide for reliable extrapolations.



**Figure 5. 9**. Fit of collected literature data<sup>41-45</sup>, including  $T_g = 183.3$  at  $\eta = 10^{13}$  cP (not shown) on the temperature dependent viscosity of  $[Im_{21}][Tf_2N]$  to the VFT equation:  $[Ln(\eta) = A + B/(T - T_0)]$ .

## 5.4.2.3. Fit of NMR Data Using the Functional Form from In-Plane Simulations

Fitting the model to our inversion recovery data (Table 5. 4. Progressive fits to NMR inversion recovery data. An asterisk, \*, denotes a parameter which was optimized in fitting, rather than assigned and fixed. Parameters in bold have been accepted as the best fit.) was conducted in much the same way as for the benzene sample discussed earlier, beginning with the simplest fit and working towards a  $\chi_v^2$  value of 1 or less. The agreement of several of these fits with our NMR data is illustrated in Figure 5. 10. A quadrupolar coupling constant of  $1.871 \times 10^5$  Hz was used for the imidazolium cation.

Fit #	<b>X</b> v <sup>2</sup>	$\mathbf{f}_1$	$\tau_{c1}$	$\beta_1$	$\tau_{c2}$	$\beta_2$	р	Fit Type
1	9.04	0			67*	1	1	single exponential
2	0.61	0			42*	0.51*	1	stretched exponential
3	5.03	0			73*	1	0.68*	single exponential (p varied)
4	4.1	0.23	0.79	0.52	91*	1	1	stretched exp + single exp
4b	3.2	0.23	0.79	0.52	93*	1	0.77*	stretched exp + single exp (p varied)
5	0.37	0.23	0.79	0.52	72.8*	0.649*	1	stretched exp + stretched exp ( $\beta$ varied)
6	0.38	0.23	0.79	0.52	72.4*	0.644*	1.01*	stretched exp + stretched exp ( $\beta$ , p varied)

**Table 5. 4.** Progressive fits to NMR inversion recovery data. An asterisk, \*, denotes a parameter which was optimized in fitting, rather than assigned and fixed. Parameters in bold have been accepted as the best fit.

The simplest fit, fit #1, has been assigned  $f_1 = 0$  and  $\beta_2 = 1$ , making it single exponential. This form would be expected for a spherically-symmetric analyte and, consequentially, is not the ideal form for this data. Allowing  $\beta_2$  to vary from one produces a stretched exponential; fit #2. This function fits the data surprisingly well, partly because the contribution of the fastcomponent observed in the simulations is relatively small and so not essential for fitting the NMR data. In all likelihood, the Brownian nature of rotations of the three axes, with no rotation that should be significantly faster or slower than the others may also play a role, as it would result in three very similar correlation times. Although the stretched exponential in fit #2 agrees tolerably well with NMR data, its failure to in any way address the fast-component which accounts for 25% of the relaxation disqualifies it as the final model (Figure 5. 10).

Attempts to fit the data with a single exponential by allowing the power of viscosity dependence, p, to vary also failed (fit #3). All efforts to fit the fast-component with a stretched-exponential used parameter values determined by the fits of the all-atom tcfs (Table 5. 3), since the NMR data are not sensitive to the details of the short component. Again, this time in conjunction with a stretched-exponential fit of the fast-component, the fit of the slow component is attempted by a single exponential (fit #4), single exponential with optimized p (fit #4b), and stretched exponential (fit #5). The effort to achieve a smaller  $\chi_v^2$  by optimizing both  $\beta_2$  and p, in

conjunction with a stretched exponential for the fast-component (fit #6) did not produce a better  $\chi_v^2$  than that of fit #5. Consequently, the parameterization of fit #5 was chosen for the final  $[Im_{21}][Tf_2N]$  model.



**Figure 5. 10.** Four fits (curves) to ring-averaged experimental  $T_1(T)$  data (points) using the model described in the text with several of the parameter sets listed in Table 5. 4.

Figure 5. 16 illustrates the reorientational time correlation functions derived from fit #5 at different temperatures (solid curves). The points "x" show the correlation function obtained from the all-atom simulations after a (2-fold) renormalization of the times in order to bring the two functions into coincidence. This comparison shows that, apart from a modest scaling of times, the simulated tcfs provide an excellent fit to the NMR data.



**Figure 5. 16.** Time correlation functions derived from the best model fit (#5) of the NMR data (curves). For comparison, the points "x" show the function simulated at 273 K after multiplying the times by a factor of 1.9 (the scaling needed to provide the same 1/e time as the 277 K NMR result).

Individual components, fast and slow, of the time correlation functions calculated from the NMR fits are compared to both the all-atom and the ILM2 simulations in Figure 5. 17. Because we do not have the results of viscosity values from these simulations, we use viscosity values determined by our viscosity-temperature correlation (Figure 5. 9). We are confident in doing this, as the diffusion coefficients predicted by the all-atom simulations agree with other authors' measurements<sup>42,43</sup> as well as our own, suggesting that the viscosities should also be similar. Although there is not exact agreement for a given temperature, deviations are within about a factor of two. The viscosity/temperature dependence of the slow component ( $\tau_{c1}$ ), and overall correlation time for the NMR fit ( $\langle \tau_c \rangle$ ), more closely resemble those of the ILM2 simulations (p=2) than they do the all-atom simulations (p=0.85). The dependence of the fastcomponent correlation time is, of course, a perfect match to the all-atom simulations, as it was specifically fit to these values.



**Figure 5. 17.** Comparison of component times of the ring reorientational time correlation functions derived from fitting NMR data (curves) and from simulations (points) versus viscosity/temperature. Closed symbols are from all-atom simulations of neat  $[Im_{21}][Tf_2N]$  and open symbols from simulations of a rigid, united–atom  $Im_{21}^+$  in ILM2.  $\langle \tau_c \rangle$  is the overall correlation time (calculated by integration of the whole tcf) and  $\tau_{c1}$  and  $\tau_{c2}$  are the correlation times of the fast and slow components, respectively. Viscosities for all-atom simulations are assumed to be the same as experimental viscosities.

For completeness, fits of the inversion recovery data for D-C(2) relaxation (Figure 5. 18) were also performed. Optimal fits were obtained for the same parameterization as in fit #5 above, with the sole alteration of  $\tau_{c2}^{ref}$  from 73 ps for the ring to 60 ps for C(2), specifically. The agreement with this data is not quite as good as with the average data for the three ring positions, but is still reasonable.



**Figure 5. 18.** Fit of D-C(2) inversion recovery data over temperature. All of the same parameters were used as in Fit #5 of Table 4 except that  $\tau_{c2}^{ref} = 60 \ ps$  rather than 73 ps for the ring-averaged result.  $\chi_{v^2} = 1.6$ 

# 5.4.2.4. Fit of Model to Methyl-Group NMR Data Alone

To further illustrate the reliability of this method of analyzing NMR data, we have also fit to the relaxation of the imidazolium methyl group, without inclusion of data for the in-plane C-D vectors. As some of the necessary all-atom simulation data was forthcoming at the time of this work, this analysis does not include it. Because the free-rotor component of methyl-group relaxation should be much too fast to be seen by NMR measurements, the accuracy of a fit to this part of the tcf will not significantly impact the accuracy of the model. We will therefore assume that a simple exponential decay will approximate the fast component of the tcf well enough.

In order to determine the fractional contribution of the fast and slow components, we apply the relation introduced by Lipari and Szabo (Eq 5. 19)<sup>46</sup>. This uses the angle formed by the C-D bonds of the methyl ( $\theta$ ), to calculate the amplitude ( $f_1$ ) of the relaxation due to freerotation of the methyl rotor (Figure 5. 19).

$$S = P_2(\cos \theta) = \frac{3}{2}(\cos \theta)^2 - \frac{1}{2}$$
 5.19

In the above, S is the order parameter (where  $1-S^2 = f_1$ ) and P<sub>2</sub> denotes the second Legendre polynomial. The average angle between C-D bonds was determined by atomic structure

optimization to be 108.83°, based on calculations for dimethylimidazolium yielding a contribution of  $f_1 = 88\%$  for the fast component.



Figure 5. 19. Atomic structure optimization of dimethylimidazolium to determine C-D bond angles.

Efforts to fit CD<sub>3</sub> NMR data to single exponential or stretched exponential functions were inadequate to describe methyl rotation (Table 5. 5). The  $T_1$  minima clearly displayed in the NMR data was not apparent in non-bimodal fits. A simple biexponential function (#5) matched the data to within experimental uncertainties, but agreement of the fit was significantly improved with the use of stretched exponential representation of the slower component (fit #6). Although a biexponential function with a power law dependence on viscosity (fit #7) produced resulted in better agreement with the data, this version was ultimately rejected because of the unrealistic correlation time of the fast component. Because the methyl group is subject to many of the same reorientations experienced by the ring deuteriums, we expect that the slow component of the tcf will resemble that found earlier for in-plane vectors (Table 5. 4). We find, however, that fixing  $\beta_2$  for the slow-component stretched exponential (fit #8) did not match the data to within experimental uncertainties. Fixing  $f_1$  at the Lipari-Szabo predicted value also resulted in  $\chi_v^2$ greater than experimental uncertainties. As a result, we choose fit #6 as the best representation. The larger value of f<sub>1</sub> for the accepted fit, in comparison to the Lipari-Szabo predictions, suggests that the fast component of relaxation at the methyl group includes motions in addition to the free-rotation of the methyl. This agrees with our tcfs for the imidazolium ring deuteriums, which also experienced a fast component relaxation. We conclude, therefore, that the fast component of methyl deuterium relaxation is due in part to the free-rotor behavior of the methylgroup, and in part to a small amount of libration and jump motions of the attached ring.

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Fit #	<b>X</b> v <sup>2</sup>	$f_1$	$\tau_1$	β1	$\tau_2$	$\beta_2$	р	Fit Type
1	32.00	1	24*	1				single exp (linear η-dependence)
2	28.8	0			8.2*	1	1	single exp (linear η-dependence)
3	8.8	0			9.7*	1	0.48*	single exp (power η-dependence)
4	25.1	0			1.0*	0.27*	1	stretched exp (linear $\eta$ -dependence)
5	0.85	0.95*	2.4*	1	141*	1	1	biexponential
6	0.45	0.94*	1.0*	1	120*	0.73*	1	single exp + stretched exp
7	0.41	0.95*	0.05*	1	189*	1	0.81*	single exp + single exp (power $\eta$ )
8	1.45	0.93*	2.9*	1	72.8*	0.649	1	single exp + single exp (fixed $\beta$ )
9	1.7	0.88	1.7*	1	25.5*	0.40*	1	single exp + stretched exp (fixed $f_1$ )

**Table 5. 5.** Fits to NMR rotation data of the methyl group. An asterisk, \*, denotes a parameter which was optimized in fitting, rather than assigned and fixed. Parameters in bold have been accepted as the best fit.

The good agreement of our modeled rotational tcf with measured longitudinal decay times is shown in Figure 5. 11. Our method of deducing rotational tcfs from inversion recovery data has therefore been successful under three very different sets of conditions; a non-ionic ellipsoidal solute at infinite dilution, the non-ellipsoidal cation of a neat ionic liquid, and a small free-rotor ligand. The variation among these systems suggests that this method may be successfully applied in a broad array of studies.



**Figure 5. 11.** Fit #6 of the rotational tcf for longitudinal decay of methyl deuteriums (curves) and its agreement with NMR data (points).

## 5.4.3. Comparison to Hydrodynamic Predictions

As discussed in Section 5.1 prior studies have often reported sub-slip rotational dynamics for imidazolium cations and other solutes in ionic liquids. Comparison to hydrodynamic predictions was usually only considered at the level of the overall correlation time in these studies. Here, however, we have access to experimentally derived approximations to the rotational time correlation functions, which will hopefully provide more insight into the utility of hydrodynamic descriptions. The calculations of SED hydrodynamic rotational tcfs were modeled on the work of Perrin<sup>27</sup> and Youngren and Acrivos<sup>28</sup>, for the dependence of rotational diffusion coefficients D<sub>i</sub> on ellipsoid dimensions. Time correlation functions for benzene were characterized using equation 5. 3 and, for imidazolium, equation 5. 4. As such, the forms of both hydrodynamic tcfs are biexponential. Both solutes were represented as a oblate ellipsoids by approximating the outline of a space-filling model of the solute, seen both on-edge and head-on, with ellipses and normalizing to the van der Waals volume<sup>29</sup> (Figure 5. 12).



**Figure 5. 12.** Ellipsoidal representation of benzene (left) and  $\text{Im}_{21}^+$  (right) used for hydrodynamic calculations. The (*a*, *b*, *c*) are the semi-axis lengths of the ellipsoids.

In Figure 5. 13 the hydrodynamic tcfs calculated with stick and slip boundary conditions are compared to the best-fit correlation functions derived from NMR data in the middle of our temperature range; 277 K. A summary of component times for the benzene and imidazolium samples are provided in Table 5. 2, and Table 5. 4, respectively. Hydrodynamic predictions for imidazolium agree with simulation with regards to the similarity of correlation functions at the three different imidazolium ring positions. We therefore present only an average of these three correlation functions.



**Figure 5. 13.** Comparison of ellipsoidal hydrodynamic predictions to NMR-derived reorientational time correlation functions of (a) benzene and (b)  $Im_{21}^+$  at 277 K.

In both cases, the stick predictions decay much more slowly than the NMR-based correlation functions. The slip predictions are closer to the observed dynamics, especially at longer times. In the case of benzene, after the initial fast decay, the NMR correlation functions become exponential with similar slow-component time constants to the slip predictions (Table 5. 6). In the  $Im_{21}^+$  case, the non-exponential decay of the NMR correlation function is quite similar to the slip predictions at greater times than ~2 ns. However, for both solutes the early portion of the NMR tcf decays much more rapidly than even the slip predictions. Because of the depiction

of benzene as a prolate ellipsoid, in which rotation about the unique semi-axis displaces no solvent, frictionless hydrodynamic slip conditions predict infinite diffusion for the in-plane rotation, and  $\tau_1 = 0$ . This is, of course, unrealistic, and we don't expect accurate hydrodynamic predictions. But even in the case of  $\text{Im}_{21}^+$  where such problems do not exist, ~25% of the NMR correlation function decays in a few picoseconds. Simulations show that this decay is due to inertial librations of the solute, which are absent in a purely hydrodynamic description.

Benzene	a <sub>1</sub>	$\tau_1$ /ns	a <sub>2</sub>	$\tau_2$ /ns	$\tau_c$ /ns
Stick	0.75	6.3	0.25	7.2	6.5
Slip	0.75	0	0.25	1.3	0.33
NMR	0.88	0.0029	0.12	1.1	0.11

$\operatorname{Im}_{21}^+$	<b>a</b> <sub>1</sub>	$\tau_1$ /ns	a <sub>2</sub>	$\tau_2$ /ns	$\tau_c$ /ns
Stick	0.47	2.7	0.53	3.8	3.3
Slip	0.79	0.34	0.21	0.82	0.45
NMR	0.23	0.0015	0.77	0.26	0.20

**Table 5. 6.** Simplified re-parameterizations of hydrodynamic stick and slip rotational tcfs for benzene and  $\text{Im}_{21}^+$  at 277 K, as biexponential functions of time:  $C_r(t) = a_1 \exp(t/\tau_1) + a_2 \exp(t/\tau_2)$ . NMR functions are not simple exponentials (Table 5. 2 and Table 5. 4). Here  $a_1$  is the relative amplitude of the fast component, with  $a_1 = 1 - a_2$ , and  $\tau_1$  and  $\tau_2$  are the correlation times for the fast and slow components.

From the component times in Table 5. 4, it is clear that stick conditions provide a poor depiction of rotational dynamics in ionic liquids, with regards to both correlation times and relative amplitudes. Conversely, slip predictions produce a much closer representation of the slow component dynamics ( $\tau_2$ ), although the relative amplitudes diverge from those predicted by our NMR model. The slip underestimation of the relative amplitude of benzene's fast component (a<sub>1</sub>) is likely due to small amplitude out-of-plane librations that cannot be accounted for by hydrodynamic predictions. This is probably also the case for the much shorter observed  $\tau_1$  of Im<sub>21</sub><sup>+</sup> in comparison to slip hydrodynamics. The poor agreement of slip with fast dynamics is relatively unimportant, for the purpose of our model, as NMR cannot observe rotations in this regime. We expect this type of hydrodynamic prediction to be a useful tool in future NMR and simulation studies of rotational diffusion in ionic liquids.

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# Chapter 6. Conventional Solvent-Ionic Liquid Transition

#### 6.1. Introduction

To further consider how diffusion in conventional solvents compares with that in ionic liquids, we have studied a series of mixtures of  $[Im_{21}][Tf_2N]$  and tetrahydrofuran (THF) over the entire composition range. By assessing the changes in behavior as the solution progresses from a more conventional solvent identity to a more ionic liquid identity, we hope to illuminate some of the factors that distinguish dynamics in ionic liquids from those in conventional solvents.

# 6.1.1. Samples

We chose an imidazolium-based ionic liquid for this study partly because they are among the better characterized ionic liquids, figuring in many publications, partly because of their subslip behavior, and partly as a compliment to the other studies detailed in this work. Tetrahydrofuran (THF) was chosen as an ideal molecular solvent to pair with  $[Im_{21}][Tf_2N]$ because of its similar size to  $Im_{21}^+$  and easily distinguishable chemical shift. Although deuterated THF was not available at the time of these measurements, we do intend to assess the rotational diffusion of deuterated THF across the series.

Singly-deuterated imidazolium was prepared from  $[Im_{21}][Tf_2N]$  (Iolitec, 99%), as described by Wulf, et. al.<sup>1</sup> A mixture of 6.9 mL of  $[Im_{21}][Tf_2N]$  was combined with 3.6 mL of D<sub>2</sub>O (99.9 atom % D, Sigma-Aldrich), so that the IL mole fraction was 0.117. The mixture was stirred and heated to approximately 75 °C overnight. Over 90% deuteration of the acidic position C(2) was achieved this way (Figure 6. 1).



**Figure 6. 1.** 1-Ethyl-3-methyl-imidazolium cation  $(Im_{21}^+)$ , with ring positions labeled in blue.

After deuteration, the imidazolium was dried on a vacuum line to 39 ppm water, as measured by Karl-Fischer titration. Solutions were mixed in a nitrogen glove box. Deuterated

rotational diffusion samples were vacuum sealed in NMR tubes, except for those with higher concentrations of THF, as it was considered that the vacuum step may evaporate significant amounts of THF and change the concentrations. Samples intended for viscosity measurement were also prepared with no vacuum or drying step after mixing in the glove box. Because large concentrations of molecular oxygen can effect diffusion measurements, the THF used in translational diffusion samples (and four rotational diffusion samples, scattered across the concentration range) was repeatedly freeze-dried until the vapor pressure of the solid was negligible. The  $T_1$  measurements resulting from dried THF samples did not show any greater variance than the un-dried samples, or any distinct tendency, so we do not consider this a factor in our rotational results. Compositions of the mixtures were calculated from the NMR spectra, as this has been found to be a more accurate method than calculation by component weight added.

## 6.1.2. Methods

Viscosities were acquired using Cannon-Fenske Routine Glass Viscometers, numbers 50 and 100, as detailed in Section 3.4.2. Solution viscosities were measured at 25 °C. Water contamination was minimized by using ethylene glycol as the fluid in the VWR circulating bath and standard controller, with the measurement apparatus kept within an N<sub>2</sub>-purged volume. Translational diffusion was measured on the AV-III-850 spectrometer, and rotational diffusion on the DRX-400 spectrometer. For more details, see Chapter 3. Calculations of  $\tau_c$  included a quadrupolar coupling constant of  $1.871 \times 10^5$  Hz (used elsewhere for neat  $[Im_{21}][Tf_2N]$ ), which was applied for all mole fractions of  $[Im_{21}][Tf_2N]$ .

# 6.2. Results

The data presented in Table 6. 1 is discussed in the following sections. Because rotation measurements required deuterated analytes, while translation measurements required protonated solutes, samples for rotation, translation, and viscosity measurements were all prepared separately, resulting in slightly different concentrations for each set. The viscosity measurement at 3.30 M ionic liquid was disregarded as an erroneous measurement, as it is the only point significantly deviating from the fit to the IL+THF ratio.

[IL] <sub>trans</sub> / M	$\frac{{Im_{21}}^{+} D_{trans}}{I 0^{-10} m^2 s^{-1}}$	$\frac{THF}{10^{-10}} \frac{D_{trans}}{m^2 s^{-1}}$	[IL] <sub>T1</sub> / M	$T_1 (Im_{21}^+) / s$	$[IL]_{\eta} / M$	η / cP
neat	0.533		neat	0.0324	neat	34.7
3.60	0.584	1.17	3.50	0.0437	3.45	16.3
3.35	0.688	1.42	3.35	0.0456	3.30	3.49
2.41	1.32	2.98	3.03	0.0557	2.91	7.50
1.76	2.29	5.29	2.65	0.0821	2.44	4.49
1.33	3.28	7.20	2.01	0.163	1.99	2.73
1.02	4.25	9.75	1.02	0.180	1.55	1.89
0.696	5.89	12.6	1.00	0.203	1.01	1.07
0.364	6.59	18.2	0.364	0.231	0.388	0.662
0.0966	10.3	25.7	0.113	0.202	0.143	0.527
0.0553	11.1	26.9	0.0966	0.275	0.0448	0.490
0.0000		25.3	0.0517	0.281	0.0000	0.465

**Table 6. 1.** Raw data for: translational diffusion  $(D_{trans})$  of  $Im_{21}^+$  and THF, rotational diffusion of the cation (expressed in terms of longitudinal decay time  $T_1$ ), and viscosity of the solution ( $\eta$ ). The concentrations of ionic liquid in solution, [IL], are given separately for each different measurement.

# 6.2.1. Viscosity Measurements

Viscosities of the samples, fitted below, are considered with respect to volume fraction of ionic liquid and molar fraction of ionic liquid (Figure 6. 2). Although samples were prepared with regard to concentration of ionic liquid in the mixture, the results are discussed in terms of ionic liquid volume fraction,  $\phi_{IL}$ , since it takes into account the relative sizes of molecules in solution, as well as the relative amounts.



**Figure 6. 2.** Viscosity of  $[Im_{21}][Tf_2N]$ +THF solution at 25 °C, fit with respect to volume fraction and to molar fraction.

The reproducibility of viscosity measurements, along with the agreement of density measurements, across the concentration series suggested an uncertainty of 4% overall. The fit of viscosity vs. concentration, however, was determined to have a standard error of estimate of 6%. Ultimately, we have chosen to apply an uncertainty of 10% for our glass viscometer measurements, to account for the possibility of some systematic error (Section 3.4.2).

# 6.2.2. Translational Diffusion Measurements

Signal-to-noise ratios for the  $Im_{21}$ - $d_1^+$  cation in THF are reasonably good across the concentration range (Figure 6. 3). All measurements were taken at 298 K, producing sharp peaks.



**Figure 6. 3.** <sup>2</sup>H NMR spectra of IL+THF mixtures at the highest (3 M) and lowest (0.05 M) concentrations of  $[Im_{21}][Tf_2N]$  measured on the DRX-400 spectrometer at 298 K.

Translational and rotational diffusion measurements were assigned uncertainties of 15% and 8%, respectively. These values were determined as described in Sections 3.6.1.3 and 3.7.2. Diffusion coefficient for the neat THF and neat  $[Im_{21}][Tf_2N]$  compare well with literature values; approximately  $3x10^{-9}$  m<sup>2</sup>/s for THF<sup>2,3</sup> and  $7x10^{-11}$  m<sup>2</sup>/s for  $[Im_{21}][Tf_2N]^{4-7}$ . Although values measured in this study (2.6x10<sup>-9</sup> m<sup>2</sup>/s and 5.8x10<sup>-11</sup> m<sup>2</sup>/s for THF and  $[Im_{21}][Tf_2N]$ , respectively) are slightly smaller than the average literature value, they are well within our assigned uncertainties of 8% for rotational diffusion and 10% for viscosity. The observed rate of translational diffusion for THF is higher than the rate for the imidazolium cation, owing to the difference in molecular sizes ( $r_{THF} = 2.6$  Å,  $r_{[Im_{21}]^+} = 3.0$  Å) and the lack of charge of THF.



**Figure 6. 4.** Dependence of the translational diffusion coefficients on solution viscosity for the  $[Im_{21}][Tf_2N]$ +THF mixture series.

The translational diffusion coefficient does not show a linear dependence on inverse viscosity, as predicted by the Stokes-Einstein equation, but instead demonstrates a logarithmic dependence on inverse viscosity (Figure 6. 4). Although this relation is within experimental uncertainties for both the ionic liquid and the conventional solvent, the fit underestimates diffusion at very high viscosity for both components. Conversely, the dependence of diffusion on solution content is much simpler, relating translational diffusion coefficients to IL volume fractions by an exponential decay (Figure 6. 5, left). Diffusion coefficients for the species have very similar dependences on  $\phi_{IL}$ , despite the significant shift from a nonionic to an ion-dominated solution.


**Figure 6. 5.** Dependence of translational diffusion (left) and of the frictional coefficient (right) on the ionic liquid volume fraction. IL/THF values symbolize the ratio of IL-to-THF frictional coefficient, equal to IL/THF observed diffusion ratio. SE predictions assume a spherical solute and stick boundary conditions.

The dependence of the frictional coefficient on volume fraction (Figure 6. 5, right) is not so simple a relation as that of the diffusion coefficient. Observed friction,  $\zeta_{obs}$ , is close to SE friction,  $\zeta_{SE}$ , for both components across most of the composition range, with the observed THF diffusion faster than the rate predicted by the SE equation, and the observed diffusion of imidazolium slower than predicted. Sub-stick behavior may be expected for THF in general, as the viscosities of the mixtures (used to calculate SE predictions) partially derive from the high viscosity ionic liquid component. Since THF molecules cannot form ionic aggregates with the ionic liquid component and are more compact, they are free to move at faster rates than the solution viscosity would indicate. This behavior is more pronounced in highly ionic solutions, resulting in the significant decrease in  $\zeta_{obs}$ (THF) relative to  $\zeta_{SE}$ (THF) as the imidazolium contribution increases. This is in accordance with the behavior exhibited by most non-ionic solutes at infinite dilution in ionic liquids, as discussed in Chapter 4. The superstick imidazolium dynamics exhibited at low and mid IL volume fraction likely results from the tendency of dilute ionic liquids in conventional solvents to form clusters. This leads to a larger effective radius and a smaller observed diffusion coefficient than predicted by the SE equation. In high enough ion content solutions, the clustering effect is reduced until, around 0.7  $\phi_{IL}$ , the

ions displays stick diffusion, and may be considered as moving more-or-less independently. The subslip diffusion of the cations at very high  $\phi_{lL}$  is puzzling, as the effect strengthens with decreasing THF content, all the way to the neat IL. It is clear, whatever the cause, that this is a general trend for ionic liquids solutions with nonpolar solutes; the value of  $\zeta_{obs}/\zeta_{SE}(Im_{21}^{+}) \approx 0.55$  at  $\phi_{lL} > 0.9$  (Figure 6. 5, right) is similar to values for pyrrolidinium cations in solution with infinitely-dilute non-ionic solutes (0.48 - 0.76). Further investigation is required to understand this feature, and all-atom simulations would be especially useful. At the opposite end of the continuum, both  $\zeta_{obs}(THF)$  and  $\zeta_{obs}(Im_{21}^{+})$  demonstrate a slight decrease at very low  $\phi_{lL}$ . This may be explained, in the case of the cation, if the concentration of ionic liquid is so low as to eliminate clustering. Simulations will also be necessary to explain the decrease in  $\zeta_{obs}(THF)$  at low  $\phi_{lL}$ .

It is interesting to note that the value of  $\zeta_{obs}(Im_{21}^+)/\zeta_{obs}(THF)$  is relatively unchanging across the range of compositions, even at very high  $\phi_{IL}$ . This suggests that the rates of diffusion of one component relative to the other are fairly constant across the range of compositions, although not quite so unchanging as SE predictions. This will be another good topic for a future simulation study.

#### 6.2.3. Rotational Diffusion Measurements

Longitudinal relaxation times of the acidic deuterium, D-C(2), in solutions of d<sub>1</sub>-[Im<sub>21</sub>][Tf<sub>2</sub>N]+THF were measured as a function of composition on the DRX-400 (Figure 6. 6). The relationship of T<sub>1</sub> with IL concentration (or  $\phi_{IL}$ ) requires further study. Although it can be represented to some degree with a linear relation, it appears as though there may be a much more complex relation. Uncertainties were assigned as before for rotation measurements; 8% for the AV-III-850, 8% for the DRX-400, and 15% for the DPX-300.



**Figure 6. 6.** Dependence of  $d_1$ -[Im<sub>21</sub>][Tf<sub>2</sub>N] longitudinal decay time on concentration of ionic liquid (at left). Dependence of  $d_1$ -[Im<sub>21</sub>][Tf<sub>2</sub>N] longitudinal decay time on solution viscosity (at right).

Rotational time correlation functions at the H-C bonds on the imidazolium ring (C(2), C(4), and C(5)) (Figure 6. 1) and on THF were simulated using the flexible, all-atom force field model described earlier (Section 5.4.2.2.). Comparisons of simulation results and  $T_1$  relaxation measurements are preliminary, but clearly within a factor of two for any given composition (Figure 6. 7). Although the correlation time exhibits an approximately linear dependence on ionic liquid mole fraction, according to simulations, the relation is not as simple for the NMR data.



**Figure 6.7.** Dependence of reorientational tcfs on ionic liquid mole fraction for all-atom simulation data and NMR inversion recovery measurements.

T/K	C(2)-H /ps (L=2)	C(4)-H /ps (L=2)	C(5)-H /ps (L=2)	C(2)-H /ps (L=1)	C(4)-H /ps (L=1)	C(5)-H /ps (L=1)
260	259	262	237	351	790	658
273	151	113	103	162	438	358
285	87	87	80	129	353	291
298	54	53	48	82	245	200

All-atom simulations were also conducted for rotational correlation times along the C(4)-H and C(5)-H bonds, and for L=1 as well as L=2 (Table 6. 2).

**Table 6. 2.** All-atom simulations of rotational correlation times for L=1 and L=2 at various C-H ring bonds on the  $Im_{21}^+$  cation.

Overall, results indicate that the all-atom simulations are well-equipped to describe our experimental results. We will therefore continue to use these simulation methods to investigate ion clustering in mixtures of various ionic liquid + conventional solvent ratios, and its effects on solution dynamics.

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# Chapter 7. Conclusion

Our studies of diffusion in ionic liquid (IL) solvents demonstrated that the Stokes-Einstein (SE) equation is able to predict translational diffusion coefficients in ILs to a similar level of accuracy as it does in conventional solvents. The translational friction ratio ( $\zeta_{obs}/\zeta_{SE}$ ) exhibits a strong dependence on the solute-to-solvent size ratio in both ILs and in conventional solvents, with smaller size ratios corresponding to much smaller friction ratios. Conditions of very high solute to solvent size ratios approach conditions under which the Stokes-Einstein equation was derived, in which a sphere moves through a continuous fluid. As the size ratio drops below one, SE predictions become less accurate, with SE friction coefficients typically dropping below one and into the subslip regime.

The friction ratio for translational diffusion is also strongly dependent on the various intermolecular forces present in a solution. For both ILs and conventional solvents, the translational friction ratio is smaller for solutes that are unable to form intermolecular interactions that are as strong as those among solvent molecules. In conventional solvents, the strongest interactions are those of hydrogen bonds. Observed friction coefficients are relatively close to SE-predictions for solutions in which neither the solute nor the solvent can form hydrogen bonds, and also for solutions of hydrogen bonding solutes in hydrogen bonding solvents. Solutes that cannot participate in hydrogen bonding but are dissolved in hydrogen bonding solvents have smaller translational friction ratios than solutes that can form hydrogen bonds. This is likely due to the use of solvent viscosity in the SE equation. If the solute is able to form the same strength of bonds with the solvent as the solvent forms with itself, then both are sensitive to the same factors that play into viscosity. If, however, the solute is incapable of forming the stronger intermolecular interactions that the solvent molecules form with each other, the solute molecules will be relatively insensitive to the causes of the high viscosity, and are consequently free to move at a faster rate. The situation in ionic liquids is similar, with the distinguishing feature being the ionic nature of solute and solvent, rather than the ability to form hydrogen bonds. The dependence of the friction ratio on solute-solvent charge density in ILs disappears at larger solute-to-solvent size ratios, indicating that the effects of size ratio are stronger than the effects of relative intermolecular forces. The effect of solute shape on

translational friction coefficient is so much smaller than that of relative size and intermolecular forces as to be comparably unimportant.

We considered several different SE adjustments, proposed for conventional solvents by other researchers, re-calculating any fitting parameters to IL data measured in our group, as well as additional data published in the literature. Of those considered, two models demonstrate good agreement with IL solutions; that proposed by Chen and Wei,<sup>1</sup> and that proposed by Kooijman.<sup>2</sup> Although the model put forth by Geirer and Wirtz<sup>3</sup> provided a good fit to the available IL data, predicted translational friction ratios did not level off at high solute-to-solvent size ratio, as should be expected for any SE-based model. The Wilke-Chang<sup>4</sup> model did not provide an acceptable fit to the IL data, even with the addition of an exponential fitting parameter.

In the course of these studies, we have attempted to contribute to the understanding of deviations from the Stokes-Einstein relation, both in ionic liquid solvents and, through our compilation of literature data, in conventional solvents. On this topic, we reaffirm the importance of solute-solvent size ratio for solutions of both molecular and ionic liquids, and advocate consideration of the effects of different intermolecular forces for solute and solvent compounds. We also find that, of several popular models which have been proposed to correct for SE deviations from data in conventional solvents, only those proposed by Kooijman<sup>2</sup> and by Chen and Wei<sup>1</sup> are capable of representing ionic liquid solutions with enough accuracy to deserve continued consideration.

Rotational diffusion measurements, in conjunction with MD simulations, indicate that at infinite dilution in ILs, benzene displays a relatively slow relaxation component as well as a much faster component. This behavior is expected of oblate molecules, with slower dynamics corresponding to rotation of the six-fold symmetry axis, and faster dynamics corresponding to rotation also displays bimodal rotational time correlation functions, although with much smaller contribution from the fast component and much less difference in the form of the functions describing the different rotations. Fitting the functional form of simulated time correlation functions to NMR data demonstrated good agreement between simulations and experimental measurements, and this approach shows promise for extracting some degree of time-resolved data from inversion recovery experiments. Likewise, the agreement between our coarse-grained ILM2 model and the much more precise (and time-consuming) all-atom measurements supports the continued use of

ILM2. Because of its simplicity, the ILM2 model allows for much longer simulations and simulations at much lower temperatures than are easily accessible with all-atom calculations.

In the field of rotational diffusion in ionic liquids, we contributed what we hope to be a valuable approach, allowing much more extensive analysis of reorientations by inversion recovery measurements through the close comparison of simulations. As inversion recovery is a technique sensitive to a much wider range of analytes than are many other methods of rotational measurements, and yielding much less convoluted results than some, we hope this will allow for investigation of a broader range of solutes in ionic liquids. The verification of ILM2 results by all-atom calculations will also, we hope, lead to the increased use of these simpler, faster simulations, which would be particularly useful because of the vast time-requirements of all-atom simulations of ionic liquids. This would also, therefore, allow for greater exploration into the field.

In the ionic liquid-conventional solvent composition series, translational diffusion coefficients of both tetrahydrofuran (THF) and the imidazolium cation  $(Im_{21}^+)$  exhibit a simple exponential dependence on ionic liquid volume fraction. The friction ratio for both the cation and the THF remained relatively constant for mid to low IL volume fraction, decreasing bit at very low IL volume fractions and, a bit more significantly, above about 0.6 IL volume fraction. The smaller reduction in IL friction ratio may be a signal of the dilution of cations beyond the limits of cluster formation. The larger reduction in THF friction ratio is likely due to the increasing dilution of THF in a solvent of much stronger intermolecular interactions. It is interesting to note that the ratio of observed diffusion coefficients for THF and  $Im_{21}^+$  remained relatively constant across the entire composition range.

In contrast to the exponential dependence of translational diffusion on volume fraction, the  $Im_{21}^+$  rotational correlation time displays a linear dependence on the IL mole fraction and neither a linear nor an exponential dependence on volume fraction. Our rotation measurements are generally confirmed by flexible, all-atom simulations of the system across the range of compositions. Future work with this system will shed further light on this topic.

There are many studies that we believe will serve as a valuable continuation of this work. Translational diffusion studies will be continued by investigating the effect of charge density on the frictional coefficient ratio of ionic solutes in ionic liquids. Enough insight on this effect may enable us to suggest our own model for adjusting the SE equation for use in ionic liquid systems. Our rotational work will be furthered by repeating inversion recovery measurements for benzene in  $[Im_{21}][Tf_2N]$ , in order to allow for direct comparison with all-atom simulations of the same, which are already in progress. Results of the coarse-grain ILM2 model for the benzene system will be compared with the results of the all-atom simulations to further verify the ILM2 model. Measurements will also be repeated for the  $[Im_{21}][Tf_2N]$ +THF composition series using deuterated THF in order to analyze the time correlation functions of the conventional solvent, and compare them with those of the imidazolium cation. Inversion recovery measurements of a  $[Im_{21}][Tf_2N]$ +benzene-d<sub>6</sub> composition series would allow us to expand on our THF composition data while simultaneously relating it more directly to the translational and rotational results of our NMR studies. Studies involving rotations of anthracene and pyrene would also allow for direct comparisons to fluorescence anisotropy measurements.

# **Conclusion References**

(1)Chen, S.-H.; Wei, S. K.-H. Ind. Chem. Eng. Res. 2011, 50, 12304.

- (2)Kooijman, H. A. Ind. Eng. Chem. Res. 2002, 41, 3326.
- (3)Gierer, V. A.; Wirtz, K. Zeitschrift fur Naturforschung A 1953, 8a, 532.
- (4) Wilke, C. R.; Chang, P. American Institute of Chemical Engineers Journal 1955, 1, 264.

# Appendix A. NMR Measurement Instructions

#### THESE INSTRUCTIONS ARE FOR USE ONLY AFTER ADVANCED TRAINING

<u>Key:</u>

"quotes"—typed commands CAPITOLS—buttons to click *Blue italics*—explanatory notes

## A.1. General Procedures on the DRX-400 and DPX-300

## A.1.1. Shut Down

-undo special settings when finished
-LOCK window →LOCK POWER: regular setting (-15.1), SWEEP: on
-tune back to standard
-eject sample and put in one with a deuterium lock solvent

-"re scoob" → (for <sup>1</sup>H probe) "rpar PROTON all"; (for <sup>13</sup>C probe) "rpar C13CPD all"
-"wobb", "acqu", etc
-return temperature to standard (298.1 K)
-"edte"
-return any hardware to previous position
-re-connect low pass X filter and deuterium band stop filter on XBB channel
-re-connect cable for <sup>2</sup>H lock channel

# A.1.2. Saving and Finding Data

-"edc" (opens a new space to begin writing/saving onto) -new name (new file)

-new experiment number (allows addition of new data to existing file without overwriting)

-new procedure number (allows addition of new data / multiple analyses of same data, within one parameter file and set of conditions)

-procedure numbers other than 1 cannot be analyzed in SpinWorks -"search" (finds a previously-created measurement from the directory) -"re X" (returns to saved data of interest)

-where X is a file name, the experiment number, or procedure number of interest -to move from experiment 3 to experiment 2 in the same file; "re 2"

-to move to a procedure 1 from procedure 999, both in experiment 2; "re 2 1"

-to move to another file; "re file\_of\_interest", "re file\_of\_interest 2 1", etc. -scoob file (a "throw-away" file)

- return to scoob at the end of NMR time; data on any file left open may be overwritten

by other users

### A.1.3. Temperature Control

-"edte"

-allow a minimum of 20 minutes for temperature equilibration if changing temperature *-low temperatures require higher gas flow rates* 

-very low temperatures require liquid nitrogen cooling: get training for this -do not raise temperature above 40  $\,^{\circ}\!\!C$ 

-lower temperatures need more scans per row (higher "ns") for good signal-to-noise ratio

## A.1.4. 1D Phasing

-PHASE  $\rightarrow$  BIGGEST, PH0 (select and hold down left mouse button while dragging up or down to flatten baseline around the biggest peak), PH1 (drag the same way to flatten the rest of the spectrum)

-RETURN  $\rightarrow$  SAVE AND RETURN

-expand peak, UTILITIES  $\rightarrow$  O1  $\rightarrow$  center click on the intended center of the spectrum -RETURN

-resize spectral width if necessary:

-too narrow a spectral width: "sw", enter larger number

-too wide a spectral width: zoom in to display desired spectral width/placement, select SW-SWO button (*do not enter below 13 ppm unless necessary, then* > 8 *ppm*)

# A.1.5. Integration

-after phasing and baseline correction ("abs" for 1D, "abs2" for 2D)

-Zoom in enough to select peaks precisely, left-click spectrum to get curser, and middleclick to the left and right of each peak. To move to a peak out of range of the window while zoomed, click arrow pointing in the opposite direction from the intended peak (for example, select "'⇔" to move upfield).

-DELEATE CURRENT (*to undo mistake*) -RETURN → SAVE AS 'INTRNG' & RETURN

# A.1.6. Printing Commands

-zoom in on spectrum of interest, leaving some empty space on the sides

-"view" (preview of spectrum before printing)

-"edg" (change printing settings)

-DP1  $\rightarrow$  agree to all three settings  $\rightarrow$  SEEN (<u>Important</u>: screen must show intended domain- for printing or paropt- when select DP1. Otherwise, redo DP1.)

-"cy": input larger value to zoom-in y-scale on printout

-"view" (Check iteratively to find desired zoom)

-"setti": input desired title and hit return at the end of the line

-"edo" (to choose printer: only necessary if it can't find the printer/thinks it's unavailable)

-"pscal": GLOBAL (*change minimum cutoff for labeled peaks in printout*) -"mi": input desired value for minimum peak size/height -"pps" (*view peaks for labeling*) -"plot" (*to print*)

### A.2. Translational diffusion measurements on the DRX-400

#### A.2.1. Basic Setup

-LIFT ON, wait for loud air noise, insert sample, LIFT OFF

-"edc" → increment experiment number (*prevents overwriting previous 1D experiment*) -SAVE

-"rpar PROTON all" (read parameter file for  $1D^{1}H$ )

-"wobb", "acqu", tune probe ~if trained~, (when done) "stop", RETURN.

(All IL samples will need tuning, even if running <sup>1</sup>H NMR. Will need to re-tune for different IL samples.)

-"eda"  $\rightarrow$  "sol"  $\rightarrow$  LOCNUC: OFF, and PROSOL: TRUE  $\rightarrow$  SAVE ("off" necessary for no lock solvent; "true" loads best values for parameter file, unless corrupted. Must choose "true" after loading parameter file ("rpar") and before changing values of parameters.)

#### -In LOCK window;

-SWEEP: off

-(if no lock solvent) LOCK POWER: minimum value (-60)

-(if running with lock solvent) "lock": choose solvent from list

-"edte", check for 298.1 K (brings up temperature controller window)

-Allow a minimum of 20 minutes equilibration time with the sample in the spectrometer. Half an hour is better, unless the temperature change is large, in which case, allow minimum 20 min equilibration after target temperature is reached.

-"ns": 1 (Number of scans can be 1 unless S/N ratio is small. If  $ns \neq 1$ , it must be a multiple of four so the phase cycling doesn't get messed up.)

-"ds": 0 (Only reduce from ds=2 for tuning and shimming)

-"rsh": choose most recent shim file (They are recorded in the spectroscope's notebook.)

#### ~Shimming on the fid~

-"gs", "acqu"  $\rightarrow$  open SHIM window. (There is often substantial improvement in shimming, rather than just using the "rsh" shim files. Have to shim on the fid if no lock solvent.)

-Select Z and shim, then X, Y,  $Z^2$ ,  $Z^3$ , then back to Z and repeat so long as the integral size keeps increasing significantly

(Important: do NOT try to increase or decrease by clicking on or dragging the bar. This will cause the number for the chosen value (i.e.  $Z^2$ ) to begin drifting randomly. In order to stop it, you will have to close down XWINNMR and re-open it. Alan warns against doing that, but I have always had it work when I've needed to do it.)

-It is often easiest to watch for increase/decrease in the pop-up box showing the integral size, but in theory, it is also possible to shim by watching the lengthening of

the actual fid -left click for decrease, right click for increase -"stop", close SHIM window, RETURN

#### A.2.2. Basic 1D Spectrum Acquisition

After <u>Basic Setup</u> (above)

-"p1": input calculated value for  $\pi/2$  spin rotation (*If have*)

-"rga", "rg", record rg value for later use

-"ns": input desired value (only 1 or multiples of 4)

-"ds": 2

-"ii", "zg", "ft", PHASE (as in P1 Optimization)

-"abs" (baseline correct over region- usually 10 ppm to 0 ppm. Change in "edg".)

#### A.2.3. P1 Optimization

After <u>Basic Setup</u> (above)

-"edp" → PH\_MOD: pk → SAVE (allows you to use the same phase settings for subsequent runs, so long as all after the model phasing are processed with "fp")
-"ns": input desired value (usually 1; may use multiples of 4 if necessary)
-"ds": 0

-"ii", "zg", (when run is complete) "ft" (uploads conditions, runs receiver gain automatically, runs experiment, and Fourier transforms data) -(if uncertain of T1 relaxation, use a large D1 value- but not for rga; it takes forever. 30 sec is ok for most. Can do without, but will make results unreliable until very close to  $2\pi$ , so that the value of P1 at  $2\pi$  will appear to jump around.)

-phase as in <u>1D Phasing</u>

-"pulprog": zg

-"p1": input a number that would be a relatively low guess for a  $2\pi$  rotation (for example: 30)

-"ii", "zg", (when run is complete) "fp" (*Important*: "fp" keeps phasing from last "ft".) -With increasing p1, peaks start positive. Input p1 should be at or near a maximum positive value ( $\pi/2$  spin rotation). With increasing p1, the peak amplitude will eventually begin decreasing, will pass zero ( $\pi$  spin rotation), attain a maximum negative value ( $3\pi/2$ spin rotation), return to zero ( $2\pi$  spin rotation), and begin growing in a positive direction again. P1=30 should be a negative peak for most of our samples.

-Continue running "zg"s with different p1 values, processing with "fp", until the p1 for  $2\pi$  spin rotation is found. This will be a flat zero-line or a peak with equal positive and negative areas. (*Be sure this is the correct p1 value for an overall zero area, since all integer*  $\pi$  *spin rotations will have the same zero area peaks.*)

-Divide the value of p1 at  $2\pi$  spin rotation by 4 to find p1 for  $\pi/2$  spin rotation -Run with p1=1/4( $2\pi$  value). Raise baseline to mid vertical scale, with peak at top of window, so peak occupies upper half of y-scale.

-Run with  $p1 = 3/4(2\pi \text{ value})$ , "fp"

(Correct  $2\pi$  value gives  $3/4(2\pi$  value) =  $-1/4(2\pi$  value).)

-Repeat run and phasing at  $p1=1/4(2\pi \text{ value})$ . (For 1D spectrum for future reference.) -record values for next experiment: -"sw": record, "o1": record

-"rga", when finished "rg": record value

# A.2.4. $\Delta$ (D20) and $\delta/2$ (P30/P16) Parameter Optimization

*After <u>Inversion Recovery</u> (not necessarily same day, but must have run for each component previously)* 

-"edc" → increment experiment number (*prevents overwriting previous 1D experiment*) -SAVE

-"rpar diffgrad1d all" (read parameter file for 1D parameter optimization of  $\Delta$  and  $\delta$ /2 for translational diffusion measurement)

-"eda"  $\rightarrow$  "sol" (in pop-up window)  $\rightarrow$  LOCNUC: OFF, and PROSOL: TRUE  $\rightarrow$  SAVE ("off" necessary for no lock solvent; "true" necessary for anything.)

-"o1": input value recorded earlier

-"ased":

-input previously recorded values for: rg, D1, sw, P1, and (if changed) td and si

-P19: input 2000  $\mu$ sec ( $\tau$ ; necessary wait time for gradient recovery before the next *pulse*)

-input guesses for  $\Delta$  (D20) and  $\delta/2$  (P30)

( $\Delta$  is the time allowed for diffusion, and  $\delta$  is the time duration of the gradient pulse)

-P30 cannot exceed 4000 µsec, and is not practically effective below 1000 µsec
- D20 is only limited by minimum electronics response time: 1E-7 sec

-SAVE

-"ii", "zg", (when completed) "ft", PHASE (as in *1D Phasing*)

-zoom in on only a very small section of the spectrum- one peak or a small cluster (Otherwise, it may cause negative peaks which look like the phasing is terrible, but cannot be phased better. This renders the paropt useless until the negative peaks are removed. Alan said it is likely from overwhelming the memory with too much data.)

-DP1 (as in *Printing Commands*)

-"paropt"  $\rightarrow$  "gpz6"  $\rightarrow$  "5"  $\rightarrow$  "10"  $\rightarrow$  "10"

(Parameter Optimization for the values input above, with gradient strength stepping from 5% up, in 10% increments, for 10 steps (ending at 95%). This will take a while to runanywhere from ~7 minutes to >15 minutes. A message will appear when all 10 steps are completed.)

-Adjust the scale to show the full peak height while the paropt is running

-Parameterization is complete when, in the final step, the peak of interest is 10% its value in the first step

-If the peak heights decay too quickly,  $\Delta$  (D20) or  $\delta/2$  (P30) should be decreased. If the decay is too slow, the parameters should be increased.

(P30 has a much stronger, and less linear, effect on the rate of decay than D20 does. If the initial guess is far off- showing hardly any decay over the 10 steps, or decaying to 10% by the  $3^{rd}$  step- I will change P30 by 500 or 1000  $\mu$ sec. If the decay rate is only off by a smaller amount- for example, reaching 10% by the  $6^{th}$  step or reaching 50% by the  $10^{th}$  step- then I will change D20 by some tenths of seconds)

-(if necessary) "kill"  $\rightarrow$  PAROPT

(Interrupts paropt before completion, for use when parameters are clearly far off)

-"ased"  $\rightarrow$  input new D20 or P30 values  $\rightarrow$  SAVE  $\rightarrow$  "ii"

-"re # 1" where "#" is the experiment number and "1" is the first procedure (*It is necessary to return to procedure 1, since paropt automatically goes to procedure 999, but you cannot begin a new paropt from there. For example, if experiment 3 is being used for ∆ and δ/2 parameterization, the command would be "re 3 1".*)

-"paropt"

-Continue running paropts, changing  $\Delta$  and  $\delta/2$ , and returning to procedure 1 to repeat until the 10<sup>th</sup> step shows a decay to 10% of the peak height in the 1<sup>st</sup> step, then record D20 and P30(P16) for future use.

#### A.2.5. Translational Diffusion Experiment (DOSY)

After  $\Delta$  (D20) and  $\delta$ /2 (P30/P16) Parameter Optimization

-"edc"  $\rightarrow$  advance the experiment number again  $\rightarrow$  SAVE

-"rpar diffgrad2d all" (reads parameter file for 2D DOSY translational diffusion experiment)

-"eda"  $\rightarrow$  "sol"  $\rightarrow$  PROSOL: TRUE  $\rightarrow$  SAVE

-"o1": input value recorded earlier

-"ased": input recorded values for: rg, ns, D1, sw, P1, D20, P16(P30), and (IF CHANGED) td and si

-P19: input 2000 µsec

-SAVE

-"ii" (sends all inputs to the consol)

-"xau dosy 2 95 16 l y n" (Run command for DOSY; begin at 2% max gradient, finish at 95% max gradient, use 16 steps overall with a Linear gradient ramp; Yes to beginning run now; No to running an rga immediately before the DOSY. The Bruker-suggested command includes the rga, but we found that this resulted in several unusually-noisy rows early on in the decay. Run is sometimes long enough to warrant leaving for a while.)

-OK (agree to start acquisition)

-(when completed) "xf2" (2D Fourier transform of data)

-PHASE (*Important*: slightly different than for T<sub>1</sub> measurements)

-ROW, middle click lowest row, MOVE TO 1

-ROW, middle click middle row, MOVE TO 2

-BIGGEST OF 1

-PH0 (Hold down left mouse button and scroll up or down to flatten baseline around largest peak in window 1. Spectrum in window 2 may not be ideally-phased.)

-PH1 (Use as with PH0, but for baseline around other peaks in window 1.)

-RETURN → SAVE AND RETURN

-OK (agree to apply xf2p phasing to data)

-"abs2" (2D baseline correction)

-"re scoob" (*Important*: return to throw-away file before signing off so no one overwrites your data)

### A.3. Inversion Recovery (T1 measurement) for DRX-400, DPX-300

-for All:

-"edc" → increment experiment number (*prevents overwriting previous 1D experiment*) -SAVE

-In LOCK window;

-SWEEP: off

-(if no lock solvent) LOCK POWER: minimum value (-60)

#### -for d1 determination, only:

After <u>P1 Optimization</u>

-"rpar ionict1 all" (read parameter file for T<sub>1</sub> experiment) -"eda" → "sol" → PROSOL: TRUE → SAVE

-for Rotation, only: (measure <sup>2</sup>H: quadrupolar nuclei give simpler relation between  $T_1$  and rotational reorientation time.)

-for very small amounts of deuterated sample:

-tune and shim for <sup>1</sup>H, as in <u>Basic Setup</u>, and do NOT shim again for <sup>2</sup>H -Remove the low pass X filter and the deuterium band stop from the XBB channel and hook up the cable without them (Low pass filter blocks high frequency signals; <sup>31</sup>P, <sup>2</sup>H, <sup>1</sup>H. Need to use this channel to measure deuterium signal, but can't run <sup>2</sup>H with deuterium filters in place.)

-Detach the <sup>2</sup>H lock channel cable from the magnet and cap the end where it was previously attached. (*Ensures against slim possibility of radio transmission of* <sup>2</sup>H lock signal by un-capped cable interfering with measurement of <sup>2</sup>H signal)

-<u>for DRX-400</u>: "rpar h2xchannel all" (*reads parameter file for 1D of deuterium nucleus*) -Tune the Carbon probe to <sup>2</sup>H

-"eda"  $\rightarrow$  "sol"  $\rightarrow$  PROSOL: TRUE  $\rightarrow$  SAVE

-"pl1: change from 0 to -3 (<u>Important</u>: do this after eda or it will be undone) -<u>for DPX-300:</u> "rpar deuterium all" (*reads parameter file for 1D of deuterium nucleus*)

-Tune probe to  $^{2}$ H

-(do NOT set PROSOL to TRUE (until fixed) messes up parameter values)

#### -for Rotation, only:

-shim as in *Basic Setup*, unless already shimmed for <sup>1</sup>H

-determine p1, as in <u>P1 Optimization</u> (if have not already)

-"pl: change from 0 to -3

#### -<u>for All</u>:

-"o1": input value recorded earlier

-"rg": input value recorded earlier

-"p1": input value recorded earlier

-"sw": input value recorded earlier (not below 13 ppm)

-(if large  $T_1$  is expected) "d1": input value  $\geq 5x$ (expected  $T_1$ ) (fitting for  $T_1$  takes into account some underestimation, but can't fix extreme underestimations)

-"ns": input necessary value (1 or a multiple of 4. Use smallest value with good S/N.) -"ds": 2

-"expt" (Gives estimated experiment time. Often long enough to leave for a while.) -"ii", "zg" (runs experiment) -(when complete) "xf2" (Fourier transforms the 2D data set)

#### -for Rotation, only:

- for DRX-400: "eda"  $\rightarrow$  "td"(F1): 50

- for DPX-300: "eda"  $\rightarrow$  "td"(F1): 62

-for All:

-PHASE (Important: slightly different than for translational diffusion)

-ROW, middle click lowest row, MOVE TO 1

-ROW, middle click highest row, MOVE TO 2

-BIGGEST OF 2

-PH0 (Hold down left mouse button and scroll up or down to flatten baseline around largest peak in window 2. Spectrum in window 1 will be upside-down.)

-PH1 (Use as with PH0, but for baseline away from biggest peak in window 2.)

-RETURN  $\rightarrow$  SAVE AND RETURN

-OK (agree to apply xf2p phasing to data)

-"abs2" (2D baseline correction)

-for d1 determination, only: "edt1" → NUMPNTS: 16, FCCTYPE: INVREC → SAVE -for Rotation, only:

- for DRX-400: "edt1"  $\rightarrow$  NUMPNTS: 50, FCCTYPE: INVREC  $\rightarrow$  SAVE

- for DPX-300: "edt1"  $\rightarrow$  NUMPNTS: 62, FCCTYPE: INVREC  $\rightarrow$  SAVE

-for All:

-"rspc", move baseline to top of window and zoom in on negative peak(s) enough to be able to precisely choose a point close to the tip

-"basl"  $\rightarrow$  DEF-PTS, middle-click on (negative) peaks

-for multiplets, only select once at largest magnitude

-for peaks of interest outside zoomed-in window:

-RETURN  $\rightarrow$  SAVE AND RETURN  $\rightarrow$  change zoom

-"basl", DEF-PTS, "a" (to append more peaks to already-selected peaks)

-continue selecting (negative) peaks of interest until finished

#### -RETURN $\rightarrow$ SAVE AND RETURN

-"t1/t2", "pd" or "pd0" (whichever gives more points)

-"ct1", record T1 (T<sub>1</sub>), "nxtp"

-repeat until T<sub>1</sub> values recorded for all selected peaks

-RETURN

-"eda"  $\rightarrow$  PARMODE: 2D  $\rightarrow$  SAVE  $\rightarrow$  OK

(Do this even though it already says "2D". Returns data to 2D format.)

#### -for d1 determination, only:

-For D1 values based on T<sub>1</sub> measurements; D1  $\ge$  5x(longest T<sub>1</sub>). To be safe, I use  $D1 \approx 7(T_1)$ .

(D1 is the wait time after every 1D measurement- including all of the 1Ds that make up a 2D or go into parameter optimization- to allow all the spins to relax to their equilibrium state before beginning another run. Too short a D1 will ruin the data. *Too long a D1 will make measurements unbearably long.*)

-D1 VALUES CALCULATED FOR <sup>2</sup>H ARE NOT INTERCHANGEABLE WITH <sup>1</sup>H

#### -for All:

-"re scoob" (Important: return to throw-away file before signing off so no one overwrites *your data)* 

### A.4. Troubleshooting the DRX-400 and DPX-300

### A.4.1. ICONNMR open

-close all smaller windows -for main window, FILE  $\rightarrow$  "EXIT to XWINNMR"

#### A.4.2. XWINNMR suddenly closes

-DESKTOP  $\rightarrow$  OPEN UNIX SHELL -"xwinnmr –r"  $\rightarrow$  "y" (agree to stop functions of user) -(all work from that session is saved automatically)

### A.4.3. Open bsms display and lock display

-"get bsmsdisp" -"get lockdisp"

# A.4.4. Shim (un)adjusting itself

-close XWINNMR and re-open

### A.4.5. Very slow shim/rga

-"ns": 1 -"d1": 1

### A.4.6. Oscillations at peak bases

-SWEEP: off -check that "td" is long enough for spectral width

### A.4.7. Bad signal/noise (S/N) ratio

-increase ns (<u>Important</u>: if "ns"  $\neq$ 1, must be a factor of 4) -if no time to increase ns:

-" $\ell$ b": increase value as needed ( $\ell$ b = "line broadening"; moving average for each point in spectrum. Artificially reduces noise, but also decreases peak intensity and resolution)

-"efp" (Fourier transform using same phasing AND line broadening)

### A.4.8. Temperature won't equilibrate

-If not cold enough: turn down heater and/or increase flow rate -If not warm enough: turn up heater and /or reduce flow rate

# A.4.9. Very large P1

-"pulprog": "zg"

-"p1": original guess (*PROTON parameter file p1=6.45 µsec, often ~10 µsec for my samples*)

-"zg"  $\rightarrow$  (when done) "ft"  $\rightarrow$  PHASE

-begin looking for p1 again, from scratch

-check that measured large P1 is for  $2\pi$  (rather than  $4\pi$ , etc) by checking that  $\pi/2$  and  $3\pi/2$  are approximately equal and opposite in magnitude.

## A.4.10. Difficulty narrowing in on P1 for $2\pi$

-"d1": input larger value (P1 Optimization usually works with d1 set to 1 sec.) ~AND/OR~

-"paropt": "p1": input p1 guess for  $\pi/2$ : input increment for p1: input number of p1 tests (P1 range should span from  $\pi/2$  guess to past  $2\pi$  guess. Will run like paropt for gpz6. Even if does not span  $\pi/2$  to  $2\pi$ , so long as it spans  $\frac{1}{2}$ -phase, should be able to narrow-in on p1 for  $2\pi$ .)

## A.4.11. Strange program behavior

-if cannot find error in parameter values; reload parameter file and start over on that section -if problem continues; load parameter file into a new file and start over on that section - if problem continues AND no one can help; close XWINNMR and re-open it

# A.4.12. Crazy "gpz6" paropt

-zoom in on a small range of chemical shift (1 peak or a small cluster)
-DP1 → enter, enter, enter, agree
-return to procedure number 1
-"paropt", etc.

### A.4.13. DOSY error- won't start

-"ased"  $\rightarrow$  input values again, especially P1, P19 (=2000 µsec), and P16(P30) -"ii"  $\rightarrow$  "xau dosy 2 95 16 l y n"

### A.4.14. Ruined first few DOSY rows

-repeat with "n", not "y" in the last position of the command: "xau dosy 2 95 16 l y n"

### A.4.15. Crazy DOSY results

-re-process with "xf2" (don't use "xfb", despite directions on screen)

### A.4.16. Much less precision in 2D than in 1D

-check that 2D measurement uses the same "sw" and "o1" as the 1D (*much broader spectrum sacrifices precision*)

-increase "td" (longer fid collection time = more precise frequencies in fourier transform)

#### A.4.17. Delete data

-DESKOP  $\rightarrow$  OPEN UNIX SHELL

-"cd/bigboy/data/Maroncelli/nmr"  $\rightarrow$  "rm –r filename", where "filename" is the actual file name

-(to delete several at once, for example, all ending in "DMA") "rm -r \*DMA"

#### A.4.18. Process DOSY on Bruker software

-INTEGRATE

-Zoom in enough to select peaks precisely, left-click spectrum to get curser, and middleclick to the left and right of each peak. To move to a peak out of range of the window while zoomed, click arrow pointing in the opposite direction from the intended peak (for example, select "⇔" to move upfield).

-FILE  $\rightarrow$  COPY 'INTRNG' TO  $\rightarrow$ INTRNG

-RETURN

-go to next procedure number "re exp# proc#"

-INTEGRATE  $\rightarrow$  FILE  $\rightarrow$  COPY 'INTRNG' FROM

-FILE  $\rightarrow$  READ 'INTRNG'

-LASTSCAL

-(the above will allow spectra for all rows to be integrated relative to the 1.000 area in the first integrated row.)

#### A.4.19. Temperature Calibration

-Choose necessary standard sample for temperature range: 100% methanol (175 K – 295 K), or 100% ethylene glycol (295 K – 420 K)

-"edte"  $\rightarrow$  change to desired temperature and allow equilibration for  $\geq$ 30 minutes -tune and shim sample

-"zg"  $\rightarrow$  "ft"  $\rightarrow$  phase peaks  $\rightarrow$  zoom in on peaks, record chemical shift of each in ppm, subtract to find difference in chemical shift between the two peaks ( $\Delta\delta$ )

-Measure at both a low temperature extreme and at a high extreme. Compare to the standard graph (relating  $\Delta\delta$  to Temperature).

-Actual temperatures may then be calculated from measured temperatures by setting measured  $\Delta\delta$  equal to  $\Delta\delta$  from the standard graph.

### A.4.20. Gradient Calibration

-Measure translation diffusion constants for known samples. Find the exponential decays of  $\log[I(f^2)]$  vs.  $f^2$  for the different peaks in the spectrum, where I is the observed peak area

and  $f^2$  is the square of the fraction of maximum gradient applied for a given row. Average the exponential parameter of the fit to find  $\alpha_{avg}$ . Then, solve  $\alpha_{avg} = D(\delta \gamma g_{max})^2 (\Delta - \delta/3 - \tau/2)$  for  $g_{max}$ , where D is the diffusion coefficient,  $\delta$  the gradient pulse duration,  $\gamma$ the gyromagnetic ratio,  $g_{max}$  the maximum gradient strength,  $\Delta$  the delay between gradient pulse pairs, and  $\tau$  the gradient recovery time. A well-known literature value must be used for D. Doing this for several well-known liquids will allow for calculation of an average  $g_{max}$ .

#### A.5. Translational diffusion measurements on the AV-III-850

#### ONLY RUN ON 850 IF APPROVED FIRST

-"bsmsdisp" or click  $\mathbb{B} \rightarrow$  (brings up bsms display) -LIFT (on)  $\rightarrow$  insert sample (Important: don't lean on magnet)  $\rightarrow$  LIFT (off)SWEEP: off -"edc"  $\rightarrow$  input file name  $\rightarrow$  "rpar protonnolock all" -ACQUPARS  $\rightarrow$  click -"ii" -SPECTRUM  $\rightarrow$  "wobb"  $\rightarrow$  use gold posts with grey heads  $\rightarrow$  (when done) "stop" -SPECTRUM  $\rightarrow$  "rga"  $\rightarrow$  "zg"  $\rightarrow$  (when enough signal in ACQU) "halt" -MANUAL PHASING  $\rightarrow$  click  $| \mathcal{V} |$  (*like BIGGEST on 400*) -use **0** and **1** to finish phasing (*like PH0 and PH1 on 400, respectively*) -click to save -"abs", "rg": record value for later -drag mouse (left button) from desired downfield edge to desired upfield edge of spectrum -click -"sw": record value for later -"o1": record value for later -"td": generally 8k -"rsh": most recent shim file -"gs"  $\rightarrow$  watch FIDAREA (if fluctuating a lot, wait for temperature equilibration) -click  $|B| \rightarrow$  SHIM (as with DRX-400)  $\rightarrow$  Z, X, Y, Z<sup>2</sup>, Z<sup>3</sup>  $\rightarrow$  "stop" -"pulsecal" (measures p1)  $\rightarrow$  record p1; record \_\_\_\_ dB -"edc"  $\rightarrow$  increment experiment number  $\rightarrow$  "rpar diffusion all" -ACQUPARS  $\rightarrow$  click  $\bigcup \rightarrow$  "ii" -"01": input recorded value  $\rightarrow$  "sw": input recorded value  $\rightarrow$  "rg": input (1/3) recorded value -"ased"  $\rightarrow$  input value for P1 (radio pulse duration for  $\pi/2$  rotation); input value for P2 (radio pulse duration for  $\pi$ ) -"diff" (window appears on left monitor) -ACTIVE METHOD: STEBP -LOADED PROTOCOL: STEBPWATER -input expected diffusion coefficient

-REPETITION TIME (T1): input 20,000 if unsure of T<sub>1</sub> -input desired ns -**Only if** MAX GRADIENT  $\ge 800$ -change  $\delta$  to 2.00 msec (or 3.00 msec, if expected diffusion coeff =  $10^{-12}$ ) -"aq" (gives experiment time) -"zg" -(when complete) "xf2"  $\rightarrow$  (shows all spectra) -click 1 to phase 2D -right-click towards the bottom of the 2D spectra  $\rightarrow$  "all" -right-click towards the middle of the 2D spectra  $\rightarrow$  "all" -right-click towards the top of the 2D spectra  $\rightarrow$  "all" -click  $\stackrel{R}{\longleftarrow}$ -(to set main phasing around a small peak) right-click point  $\rightarrow$  "set pivot point" -click  $\bigcirc$  (save and return)  $\rightarrow$   $\checkmark$  (return) -"abs2" -ANALYSIS → T1/T2 RELAXATION -EXTRACT SLICE  $\rightarrow$  SPECTRUM  $\rightarrow$  1 -PEAKS/RANGES  $\rightarrow$  MANUAL INTEGRATION  $\rightarrow$  left-click and drag across intended range of integration -click  $\square_{A}$  (save region as)  $\rightarrow$  EXPORT REGION TO RELAXATION MODULE -RELAXATION WINDOW  $\rightarrow$ -FIT FUNCTION  $\rightarrow$  CLOSE  $\rightarrow$  APPLY  $\rightarrow$  OK -exit windows and begin again for next peak -exit diff (left monitor) when done analyzing (should open a new one when ready to run *another*)

# Appendix B. Spectral Analysis

# B.1. SpinWorks 3.1.7 Analysis

-FILE  $\rightarrow$  OPEN

-find the ser file of the final data set—the experiment corresponding to the DOSY -EDIT PARS (or EDIT -> Edit Processing Parameters)

-(in F2 Detection) PHASING: CONSTANTS, WINDOW FUNCTION: LORENTZ (EXPONENTIAL)

-(in F1 Evolution) SIZE: larger (slightly) than the number of 1D scans

(for 16 scans per DOSY, SIZE = "64", the smallest)

-OK

-PROCESSING → PROCESS ARRAY (BRUKER) (*takes Fourier transform*) -VIEW → DEFINE STACKED TRACE PROPERTIES (*changes size/offset of scans*)

-Do separate baseline corrections for solute peaks and for ionic liquid peaks, at least if IL and solute are in separate parts of the spectrum.

-zoom in on solute peaks and increase size to see baseline noise clearly

-BL POINT (to select points for baseline correction)

-Choose several points immediately bordering both sides of any peaks which returns to baseline, without encroaching on foot of peak. Also choose several points spreading across empty sections of baseline and extending for some distance away from peaks. -RETURN

-PROCESSING  $\rightarrow$  LEAST SQUARES BASELINE CORRECT ARRAY

-INTEGRATE (to choose ranges for peak area integrations)

-zoom in around peak(s) of interest

-left click at limits of integration

-CLOSE (when done selecting domains for integration)

-(can close box, zoom to a different place, re-open box, and continue choosing ranges)

#### -PROCESSING $\rightarrow$ INTEGRATE STACKED ARRAY

-(integrates all rows of DOSY simultaneously)

-FILE  $\rightarrow$  SAVE

-EDIT → COPY METAFILE TO FILE (saves displayed image/zooming of spectra)

# B.2. Excel and SigmaPlot Data Extraction

-in Excel: OPEN saved stacked array
-DELIMITED → NEXT → TAB, SPACE →FINISH
-select alternate format of data (bottom of Excel sheet)
-COPY → PASTE SPECIAL →TRANSPOSE

-(this should show data with each peak in its own column, and scans in their own rows) -select peak areas, leaving out incrementation of peaks and integration ranges -COPY

-in SigmaPlot: PASTE

-input a column of  $f^2$  (where  $f = fraction \ of \ max \ gradient$ )

-remove any peak areas which are less than 10% their own maximum value -graph X MANY Y, with peak areas vs.  $f^2$ 

-FIT CURVE  $\rightarrow$  EXPONENTIAL DECAY  $\rightarrow$  SINGLE, TWO PARAMETER

-these fits provide the value of:  $-D(\gamma \delta g_{max})^2 \left(\Delta - \frac{\delta}{3} - \frac{\tau}{2}\right)$ , where  $g = g_{max} * f^2$ 

-values of  $\Delta$  and  $\delta$  for a given experiment can be found in the ACQUS file of the DOSY experiment

 $-\Delta$  (D20) = the 20<sup>th</sup> number under D= (0..31) -  $\delta$  (P16/P30) = the 16<sup>th</sup> under P= (0..31)

-(values are numbered beginning with zero)

-the diffusion coefficient (D) can easily be calculated from the above values

-  $\tau$  (=D16),  $\gamma,$  and  $g_{max}$  are known

# Appendix C. Peak Assignments

For samples run without a lock solvent, the absolute chemical shifts will vary, although the relative shift (between peaks on any given spectrum) should match that given in the literature. The components of mixtures will also have some effect on chemical shifts.

The following are example spectra of several chemicals which were used particularly often in this study.



### C.1. Dimethylaniline (DMA)

**Figure C. 1.** <sup>1</sup>H peak assignment of DMA, measured at 0.05 M in  $[P_{14,6,6,6}][Tf_2N]$  (IL peaks are all below 2.8 ppm).

C.2. N-Alkyl-N-methyl-pyrrolidinium Bis(trifluoromethylsulfonyl)imide  $([Pr_{N1}][Tf_2N])$ 



**Figure C. 2.** <sup>1</sup>H peak assignment of  $[Pr_{31}][Tf_2N]$ . Longer chain  $[Pr_{N1}][Tf_2N]$  show a very similar spectrum, with f peaks forming a large multiplet at approximately 0.095 ppm.

C.3. 1-Alkyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide ([Im<sub>N1</sub>][Tf<sub>2</sub>N])



**Figure C. 3.** <sup>1</sup>H peak assignment of  $[Im_{41}][Tf_2N]$ . The presence of a different anion may change the relative peak shifts to some degree, but they should be in this approximate positioning, regardless.

# Appendix D. DMA Concentration Series in $[Pr_{n1}][Tf_2N]$

Diffusion measurements of dimethylaniline (DMA) were conducted in N-alkyl-Nmethyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide  $[Pr_{n1}][Tf_2N]$  at several concentrations from the neat ionic liquid up to solutions of 0.3 M DMA. Raw data is presented here, for data taken at 297.88 K on the DRX-400 spectrometer.

[Pr <sub>31</sub> ][Tf <sub>2</sub> N]	$\frac{D_{IL}}{/10^{-12} \text{ m}^2 \text{s}^{-1}}$	$\frac{unc_{IL}}{/10^{-12} \text{ m}^2 \text{s}^{-1}}$	$\frac{D_{DMA}}{/10^{-12} \text{ m}^2 \text{s}^{-1}}$	$\frac{unc_{DMA}}{/10^{-12} \text{ m}^2 \text{s}^{-1}}$
0.00 M	81	3		
0.05 M	92	1	148	4
0.10 M	93	1	151	3
0.15 M	94	1	152	3
0.20 M	95	2	167	2
0.30 M	97	2	161	4
[Pr <sub>41</sub> ][Tf <sub>2</sub> N]*				
0.00 M	16	1		
0.05 M	17.7	0.9	37	0.3
0.10 M	18.1	0.9	37	0.3
0.15 M	18	1	36	0.2
0.20 M	17.9	0.6	36	0.3
0.30 M	18.9	0.7	37	0.3
[Pr <sub>61</sub> ][Tf <sub>2</sub> N]				
0.00 M	10	1		
0.05 M	12.1	0.8	35.8	0.2
0.10 M	11.2	0.9	30	1
0.15 M	12.0	0.5	34	3
0.20 M	11.2	0.5	32	2
0.30 M	13	1	34	2
[Pr <sub>81</sub> ][Tf <sub>2</sub> N]				
0.00 M	75	0.3		
0.05 M	78	0.4	27	3
0.10 M	81	0.4	27	5
0.15 M	83	0.5	28	3
0.20 M	85	0.3	29	4
0.30 M	92	0.5	31	3
[Pr <sub>10,1</sub> ][Tf <sub>2</sub> N]				
0.00 M	5.5	0.1		
0.05 M	5.8	0.5	26	0.3

0.10 M*	6.2	0.2	27	0.3
0.15 M	6.4	0.2	28	0.2
0.20 M	6.7	0.3	30	0.4
0.30 M	7.2	0.3	31	0.3
0.10 M, 275.0 K	1.59	0.06	6.12	0.06
0.10 M, 286.2 K	3.1	0.1	14.4	0.6
0.10 M, 316.5 K	14.5	1	59	5

**Table A. 1.** Translational diffusion coefficients of solvent pyrrolidinium ionic liquid and of DMA at various concentrations. Unless otherwise stated, all measurements are at 297.88 K. An asterisk, \*, denotes a field where values are the average of two measurements.

# Vita

#### Anne Kaintz

Anne E. Kaintz was born in Minneapolis, Minnesota in 1982 to John H. Kaintz and Beverly A. Johnsen. She was awarded a National Merit Scholarship and a Presidential Scholarship by the University of Minnesota in 2000, from which she earned her Bachelor's of Science in Chemistry in 2004 with minors in Mathematics and Geography. In 2009, she defended her Master's Degree in Chemistry, "Mechanistic Studies in Water Splitting Systems," with Dr. Tom Mallouk at The Pennsylvania State University, and moved on to work on her Ph.D. with Dr. Mark Maroncelli, two floors up, in a very different branch of chemistry. She now intends to return to Minnesota, where she will stop referring to herself in the third person, and seek out a fulfilling career that makes use of her chemical knowledge. Her publications include:

Liang, M.; Kaintz, A.; Baker, G. A.; Maroncelli, M. Bimolecular Electron Transfer in Ionic Liquids: Are Reaction Rates Anomalously High? *J. Phys. Chem. B*, **2012**, *116*, 1370.

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