

Intermolecular Dynamics, Interactions, and Solvation in Ionic Liquids

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ABSTRACT

Ionic liquids can simultaneously assume multiple solvent roles, because they are strongly polar and polarizable solvents and binary solutions and frequently contain very hydrophobic components. When the cation and anion functional groups are tuned appropriately, ionic liquids can be used as designer solvents for a broad range of applications. In this Account, we discuss our spectroscopic studies on the intermolecular interactions, dynamics, solvation, transport, and friction in ionic liquids, as compared with information obtained from macroscopic experiments including viscometry and calorimetry.

Introduction

A substantial new level of understanding of the physical chemistry of ionic liquids has been obtained in the past few years.¹ Experiments and theory have been successfully employed to characterize the unique properties of these binary (and higher-order) solutions. Our own contributions to this growing literature on the physical chemistry of ionic liquids have focused on detailed spectroscopic investigations of solvation, intermolecular interactions, and vibrational dynamics.^{2–7} We are attempting to connect

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the dynamics and interactions that we probe on the molecular scale with both the electronic structures of the component ions, together with the more macroscopic properties such as the viscosity, glass transition temperatures, fragility, and translation diffusion coefficients. This Account will provide an overview of our work on the physical chemistry of ionic liquids to date.

Recent work on the physical chemistry of ionic liquids has included ab initio electronic structure calculations and molecular dynamics simulations, which are both used to calculate the properties of these highly polarizable as well as highly polar liquids. Various insights into the local order on the nanometer scale have been provided from a number of spectroscopy and scattering experiments.^{8–14} Molecular dynamics simulations using both atomistic and coarse-grained methods demonstrated the interaction between hydrophobic alkyl tails on the cations, providing local liquid structures reminiscent of membranes and worm-like micelles.^{15–17} The recent X-ray scattering paper by Triolo and co-workers has demonstrated rather unambiguously that structures having length scales ranging from 14 to 26 Å must exist in imidazolium ionic liquids having alkyl chains with 4–10 carbons.¹⁸ Many researchers have investigated the glass-forming nature of these liquids, showing that they span the range from fragile to medium-strength glass formers, with glass transition temperatures typically in the range from 180 to 220 K.^{19–21}

Spectroscopic methods have been widely applied to ionic liquids, to probe their dynamics, structure, interactions, solvation, and transport. Results from inelastic neutron scattering,¹² NMR,²² terahertz and dielectric,^{23–25} optical Kerr effect,²⁶ and interfacial nonlinear optical spectroscopy have provided some of the intricate details of dynamics and interactions in neat ionic liquids. In order to investigate solvation dynamics and local friction that is most directly relevant to charge-transfer processes, time-resolved fluorescence spectroscopy of a suitable solvatochromic probe molecule has been widely applied.^{1,27,28}

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Spectroscopic Methods

To investigate the interactions and dynamics in ionic liquids, we use a combination of time-resolved nonlinear optical and fluorescence spectroscopy methods. The femtosecond optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES) method is a powerful tool for characterizing the intermolecular dynamics occurring in complex fluids, including both the inter- and intramolecular vibrational dynamics as well as the longer time scale orientational relaxation.^{26,29} Several groups have used the method to characterize the dynamics in ionic liquids.^{2–5,13,14,30–34}

In our laboratory, we use OHD-RIKES to measure the depolarized Raman signals for ionic liquids in the spectral range from less than 0.1 to greater than 750 cm^{-1} .^{2–5} The OHD-RIKES method is a means to observe the depolarized Raman spectra of the intramolecular normal modes of the cation and anion species. More significantly, we can measure the lower frequency part of the spectrum that includes the intermolecular vibrational dynamics resulting from both single-particle and collective motions in the liquid. As with other polar organic solvents, librational dynamics of the ions make substantial contributions to the intermolecular spectral density. Because of the binary nature of the ionic liquids and the asymmetric character of the component ions, OHD-RIKES can also detect those translational dynamics that are coupled to orientational motions. At the lowest frequencies (or longest time scales), we observe the nonexponential relaxation of the liquid. The slowest time scale dynamics, analogous to the α -relaxation observed in glass-formers, extend to several nanoseconds for room temperature ionic liquids.^{31,34} The time constants obtained from the longer time delay portion of these Kerr transients show a linear correlation with viscosity, showing relaxational behavior similar to that predicted by the Stokes–Einstein–Debye hydrodynamic law. We note that translational self-diffusion coefficients obtained from pulse-gradient spin-echo NMR experiments did not display hydrodynamic behavior for some of the samples we measured.⁶

The dynamics of the local environment relevant for understanding solvation and elementary chemical processes can be studied using time-resolved fluorescence spectroscopy of a solvatochromic fluorescence probe molecule, such as coumarin 153 (C153, Figure 1).³⁵ The fluorescence anisotropy experiment^{36,37} provides the second-rank orientational time correlation function for the probe molecule, and thus samples the local friction. The time-dependent spectral shift of the emission spectrum to lower frequencies has been correlated with the reorganization dynamics of the ionic liquid in response to the substantial increase in interaction strength of the probe electronic excited state relative to its ground state. The fluorescence response thus is a measure of the solvation dynamics.³⁵ The femtosecond time resolution needed to fully resolve the frequency shift of the emission can be obtained by recording the time-gated emission spectral dynamics using fluorescence upconversion, stimulated

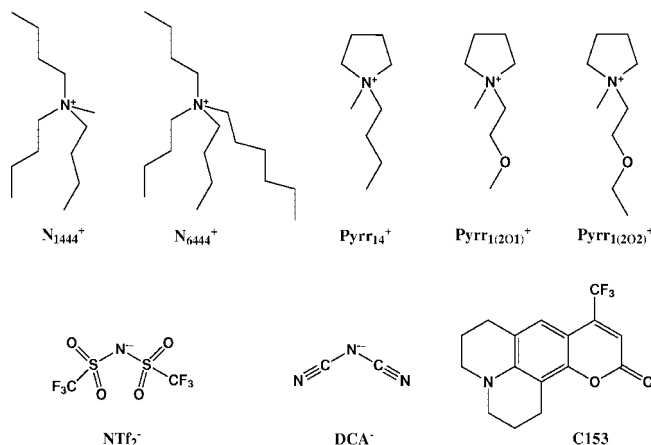


FIGURE 1. Components of ionic liquids with aliphatic cations and anions, together with the solvatochromic fluorescence probe C153.

emission, or an optical Kerr shutter with sub-100 fs optical pulses.^{28,38–41} Greater sensitivity and dynamic range of fluorescence intensity is obtained by using the time-correlated single photon counting (TCSPC) methods, though this comes at the cost of a nearly 2 orders of magnitude decrease in time resolution. Because most of the observed spectral shift of the C153 probe molecule occurs on the picosecond to nanosecond scales for the four ionic liquids we investigated, TCSPC was better suited for resolving the greatest breadth of time delay after the photoexcitation pulse.⁷ Ito and Richert have shown that triplet emission from quinoxaline can be used to probe much slower relaxation phenomena in supercooled ionic liquids.^{42,43}

Ionic Liquids with Aliphatic Cations

Interest in reducing the viscosities of ionic liquids led us, as well as other groups, to substitute ether functionalities^{44,45} in place of alkyl chains in ionic liquid cations or anions. The cations considered were *N*-butyl-*N*-methyl-pyrrolidinium (Pyr₁₄⁺), *N*-methoxyethyl-*N*-methyl-pyrrolidinium (Pyr₁₍₂₀₁₎⁺) and *N*-ethoxyethyl-*N*-methyl-pyrrolidinium (Pyr₁₍₂₀₂₎⁺). In the case of alkyl-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide (NTf₂⁻) salts, the substitution of methoxyethyl (Pyr₁₍₂₀₁₎⁺) and ethoxyethyl (Pyr₁₍₂₀₂₎⁺) groups (Figure 1) reduced the room-temperature viscosities by approximately one-third as compared with the corresponding butyl (Pyr₁₄⁺) and pentyl (Pyr₁₅⁺) derivatives.⁴⁶ Whereas Pyr₁₄⁺/NTf₂⁻ and Pyr₁₅⁺/NTf₂⁻ melt at 255 and 281 K, respectively, Pyr₁₍₂₀₁₎⁺/NTf₂⁻ and Pyr₁₍₂₀₂₎⁺/NTf₂⁻ show no melting point above their glass transition temperatures, as shown in Figure 2.

Preparation of the *N*-ethoxyethyl-*N*-methyl-pyrrolidinium salt from *N*-methylpyrrolidine and bromo-ethyl-ethyl ether led to the fortuitous discovery that the ionic product Pyr₁₍₂₀₂₎⁺/Br⁻ is liquid at room temperature. Indeed, no melting point is observed above the glass transition temperature of 220 K. This rare liquid bromide salt is extremely viscous (estimated to be 14 900 cP at 293 K). The bromide, dicyanoamide (DCA⁻), and NTf₂⁻ salts of the Pyr₁₍₂₀₂₎⁺ cation formed a convenient series for

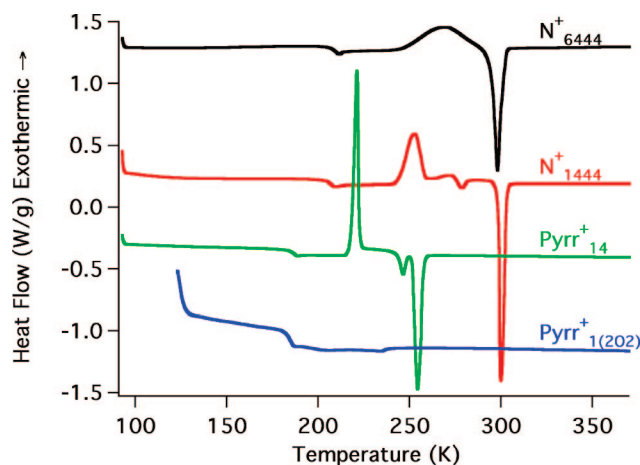


FIGURE 2. DSC plots for the ionic liquids pairing NTf_2^- with N_{6444}^+ , N_{1444}^+ , Pyr_{14}^+ , and $\text{Pyr}_{1(202)}^+$. The traces are displaced vertically for clarity.

detailed spectroscopic studies of ionic liquid dynamics as described below.

Differential scanning calorimetry (DSC) characterization of the tetraalkylammonium NTf_2^- salts used in our earlier radiolysis studies^{47,48} and solvation dynamics work⁷ (see below) provided one additional surprise: methyl-(tributyl)ammonium NTf_2^- ($\text{N}_{1444}^+/\text{NTf}_2^-$), first reported by Bard and co-workers,⁴⁹ melts at 300 K (Figure 2). Thus, this salt and hexyl(tributyl)ammonium NTf_2^- ($\text{N}_{6444}^+/\text{NTf}_2^-$, mp 298 K)⁵⁰ are both persistently supercooled liquids at room temperature.

The temperature dependence of ionic liquid viscosities typically shows a non-Arrhenius behavior where the proportional rate of viscosity decrease (or conversely, fluidity increase) varies sharply with temperature. Data of this sort are empirically described using a three-parameter Vogel-Fulcher-Tammann (VFT) expression, shown here for the fluidity, $\varphi = 1/\eta$, where η is the shear viscosity.²⁰

$$\varphi = \varphi_0 \exp\left(\frac{B}{T - T_0}\right) = \varphi_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (1)$$

The curvature of the Arrhenius plot for viscosity or fluidity is associated with the parameter D , which is inversely related to the fragility of the liquid, or the rate of change in the viscosity with temperature near the glass transition point. Fragile liquids decrease in viscosity very quickly near the glass transition and change less at higher temperatures, whereas strong glass-forming liquids show Arrhenius behavior over the whole temperature range. In general, ionic liquids having NTf_2^- anions fall into the category of fragile glass formers.

We have made detailed spectroscopic studies of several groups of ionic liquids, each based on non-aromatic organic cations.² The molecular structures of the component cations and anions for these liquids are shown in Figure 1, together with the structure for the solvatochromic fluorescence probe coumarin 153 (C153). Our first spectroscopic study of five ionic liquids was made from the two intersecting series of liquids. The first was a trio

of liquids having the NTf_2^- anion paired with Pyr_{14}^+ , $\text{Pyr}_{1(201)}^+$, and $\text{Pyr}_{1(202)}^+$. The intersecting series was comprised of the $\text{Pyr}_{1(202)}^+$ cation paired with three anions: bromide, dicyanoamide (DCA^-), and NTf_2^- . The intermolecular interactions for the ambient temperature ionic liquids were characterized using the femtosecond OHD-RIKES method.²

The second series of four ionic liquids was comprised of Pyr_{14}^+ , $\text{Pyr}_{1(202)}^+$, N_{1444}^+ , and N_{6444}^+ cations paired with the NTf_2^- anion. The structures for N_{1444}^+ and N_{6444}^+ are also given in Figure 1. Solvation dynamics and reorientational dynamics were studied for these liquids using picosecond time-resolved fluorescence from the C153 solvatochromic fluorescence probe.⁷

Intermolecular Interactions and Dynamics in Aliphatic Cation Liquids: Kerr Spectroscopy

A series of typical OHD-RIKES spectra for the pyrrolidinium cation ionic liquids is shown in Figure 3 for the spectral range from 0 to 200 cm^{-1} . It is important to clarify that the longer time scale orientational relaxation dynamics have been fit to nonexponential decay functions and subtracted from the OHD-RIKES transients prior to the Fourier-transform deconvolution procedure that provides the spectrum.²

The spectra shown in Figure 3 have been fit to a combination of asymmetric multimode Brownian oscillator functions plus a number of Lorentzian functions.² This line shape analysis is necessary to separate the contributions from the Lorentzian normal modes so that the underlying intermolecular dynamics can be analyzed in more detail. For the three NTf_2^- ionic liquids having the Pyr_{14}^+ , $\text{Pyr}_{1(202)}^+$, and $\text{Pyr}_{1(201)}^+$ cations, there is a band at 121 cm^{-1} that is assigned to a torsional mode of the NTf_2^- anion. For the $\text{Pyr}_{1(202)}^+/\text{DCA}^-$ ionic liquid spectrum, the band at 180 cm^{-1} is assigned to the bending mode of the DCA^- anion. Because the bromide anion has no internal modes and is of spherical symmetry, it makes no single-particle contributions to the depolarized Raman spectrum. Thus, the intermolecular spectrum for $\text{Pyr}_{1(202)}^+/\text{Br}^-$ arises overwhelmingly from the librational dynamics of the $\text{Pyr}_{1(202)}^+$ cation.² We note that these spectra are similar to the intermolecular spectra of imidazolium-based ionic liquids with the same anions, which have been observed by several research groups.^{2-5,13,14,30,32,33}

A unique feature of the intermolecular spectra for the pyrrolidinium NTf_2^- ionic liquids is that the band centers of the overall intermolecular bands are of lower frequency than the spectra for the ionic liquids having the smaller, lighter anions, DCA^- and bromide. In the original paper, we speculated that the NTf_2^- anion will have intermolecular motions that are strongly coupled to the predominantly torsional low-frequency modes of this ion, while the DCA^- and bromide anions may actually contribute a projection from a unique intermolecular stretching coordinate between the cation and anion.² This speculation is consistent with the frequencies predicted by AM1 semiempirical calculations for such intermolecular stretch-

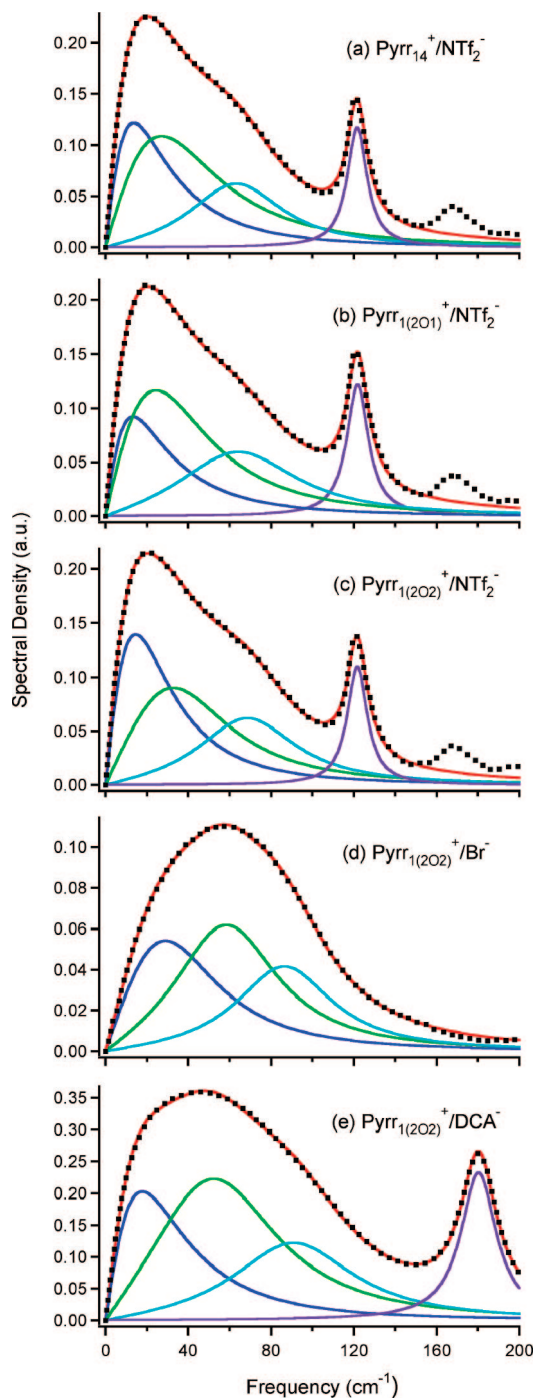


FIGURE 3. OHD-RIKES spectra for ionic liquids with pyrrolidinium cations.

ing coordinates in cation–anion dimers and anion–cation–anion trimers.²

Solvation Dynamics in Aliphatic Cation Liquids Probed by C153

Solvation dynamics in neutral organic solvents has been investigated with a high level of detail by time resolving the emission red shift of a solvatochromic probe molecule such as C153.³⁵ The total emission shift that is typically resolved while using femtosecond laser pulses is often in excess of 10% of the total excitation energy. A normalized

solvation response is obtained from the time-dependent shift of the emission. Horng et al. showed that the solvation response required three or four exponential terms to adequately fit the response.³⁵ The fastest subpicosecond time constants are normally assigned to underdamped librational motions of the dipolar solvent molecules, while the longer time constants are assigned to diffusive reorientational motions of the solvent.³⁵ These diffusive dynamics are shown to strongly correlate with the time constants obtained from dielectric spectroscopy, and to correlate (albeit less strongly) with the time constants for diffusive reorientation obtained from femtosecond Kerr spectroscopy methods.⁵¹

Recently, a substantial amount of research has been done using fluorescence dynamics to investigate ionic liquids.^{7,27,28,38,41,42,52–60} Because the individual ions of an ionic liquid frequently have large effective dipole moments, the same types of orientational motions of the ions will make substantial contributions to the solvation energy. At the same time, translational reorganization of the ions can add substantially to the solvation energy.⁶¹ Though femtosecond fluorescence is widely used to understand solvation dynamics, the experiments commonly require that the sample be rapidly flowed to avoid heating. Because the viscosities of ionic liquids are typically 2 orders of magnitude or more higher than for most organic solvents, a more limited number of subpicosecond fluorescence (or stimulated emission) experiments have been done on ionic liquids.^{28,38–41} These results show that ionic liquids having imidazolium cations do have a component of the fluorescence shift that has a subpicosecond time constant. Curiously, the emission shift data for the tetraalkyl-ammonium and -phosphonium and dialkylpyrrolidinium ionic liquids show that only a very small fraction of the emission shift occurs with subpicosecond dynamics at room temperature.^{54,62} A general consensus seems to be that the ionic liquids have solvation dynamics that are nonexponential, with the time correlation functions being best fit to either Kohlrausch (stretched-exponentials) or two-exponential functions. Maroncelli and co-workers have shown that the average solvation time constants obtained from fluorescence dynamics scale with the ionic liquid viscosity.^{54,63}

Using the C153 fluorescence probe and a time-correlated single-photon counting (TCSPC) instrument (with a 70 ps instrument response, fwhm), we have investigated the temperature-dependent solvation response of the four ionic liquids shown in Figure 1.⁷ Log–log plots of the C153 emission frequency vs time are shown in Figure 4. The plots of log frequency vs log time clearly show more than one inflection point for N_{1444}^+ / NTf_2^- at 293.2 K and for N_{6444}^+ / NTf_2^- at 278.2, 293.2, 308.2, and 353.2 K, indicating that a stretched exponential function is not an appropriate model function for these temperatures. Best fits to the solvation response functions are obtained using sums of three- and typically four-exponential functions for all four of the ionic liquids studied, at each of the six temperatures. For the lowest experimental temperature of 278.2 K, the time constants span a range from less than 25 ps

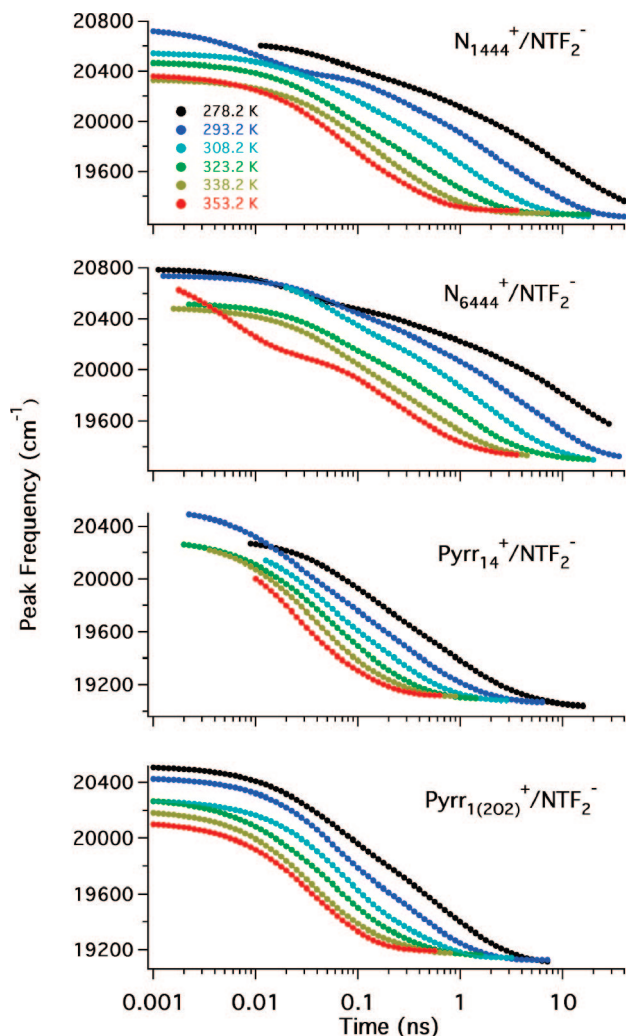


FIGURE 4. Temperature-dependent C153 time-dependent fluorescence shifts in four ionic liquids $N_{1444}^+/\text{NTf}_2^-$, $N_{6444}^+/\text{NTf}_2^-$, $\text{Pyr}_{14}^+/\text{NTf}_2^-$, and $\text{Pyr}_{1(202)}^+/\text{NTf}_2^-$.

to 22 ns. At the highest experiment temperature of 353.2 K, the time constants span a range from 10 ps to 1 ns. Graphs of these time constants vs temperature show behavior that is close to Arrhenius; however, slightly better fits are obtained using the VFT model.²⁰

Orientalional Friction of Coumarin 153

The solution-phase reorientational dynamics of C153 have been characterized in detail for neutral solvents.⁶⁴ We carried out time-dependent fluorescence anisotropy experiments on C153 solutions of the NTf_2^- ionic liquids with N_{6444}^+ , N_{1444}^+ , Pyr_{14}^+ , and $\text{Pyr}_{1(202)}^+$ cations (Figure 4). The same sample temperatures were used. Each anisotropy data set was analyzed using a convolute-and-compare algorithm with the Levenberg–Marquardt minimizer with a simultaneous analysis of the I_{vv} , I_{vm} , and I_{vh} ³⁶ emission transients. In general, three-exponential decay functions were required to obtain adequate fits to our data. Kohlrausch functions never provided an adequate fit to the TCSPC fluorescence anisotropy data for C153 in these four liquids.⁷

Generally, the amplitude-averaged fluorescence anisotropy was in rough accord with hydrodynamics laws, as there was reasonable agreement with a graph of this averaged time constant for reorientation with the ratio of measured viscosity to absolute temperature. Significant deviations from normal hydrodynamic behavior were observed when the three individual time constants obtained from the fits to the time-dependent anisotropy were graphed versus viscosity over temperature.

Fluorescence anisotropy fits to the C153 data taken in the tetraalkylammonium ionic liquids $N_{1444}^+/\text{NTf}_2^-$ and $N_{6444}^+/\text{NTf}_2^-$ show a dominant longest time constant that does show the appropriate scaling with viscosity. However, as with aqueous polymer solutions,^{65,66} faster time constants are also obtained in the fitting procedure. In polymer solutions, these time constants are assigned to reduced local friction or microviscosity effects. We speculate that in certain locations within the local structure of the ionic liquid, the approximately planar C153 probe can undergo reorientation in the plane that samples a substantially lower friction.⁷

The two dialkylpyrrolidinium ionic liquids $\text{Pyr}_{14}^+/\text{NTf}_2^-$ and $\text{Pyr}_{1(202)}^+/\text{NTf}_2^-$ display rather different behavior. For the C153 fluorescence anisotropy in these two liquids, very long time constants ranging from 110 to 860 ns are recovered from the analysis. Since the probe average fluorescence lifetime is 5 ns, the values for these long reorientation time constants have a large degree of uncertainty. However, the quality of the fits is much poorer when these longer time scale exponential decay functions are not included in the fit. We have speculated that these longer reorientational time constants might result from either the C153 becoming part of long-lived structures in the ionic liquid or some of the C153 experiencing a higher friction if they are sampling some of the nanostructure in the liquids predicted by a number of groups.^{8–14,67}

The temperature dependence of the C153 fluorescence anisotropy time constants is in accord with an Arrhenius model for the $\text{Pyr}_{14}^+/\text{NTf}_2^-$ and $\text{Pyr}_{1(202)}^+/\text{NTf}_2^-$ liquids. For the $N_{6444}^+/\text{NTf}_2^-$ and $N_{1444}^+/\text{NTf}_2^-$ liquids, the Arrhenius model does not fit the time constants well; instead a VFT model provides a reasonable fit.⁷

Ionic Liquids and Neutral Binary Organic Solution Homologues

One of the important questions for understanding room temperature ionic liquids is: what is the difference between ionic liquids and neutral organic molecular liquids? More specifically, what elements from the set of the unique properties of ionic liquids result from the fact that an ionic liquid is a solution with a very high concentration of charges and what parts result from the complexities inherent in any binary solution of polar, polarizable, flexible, and asymmetric components? To address these questions, we have compared an ionic liquid, *N*-methoxyethylpyridinium dicyanoamide ($\text{MOEPy}^+/\text{DCA}^-$) with

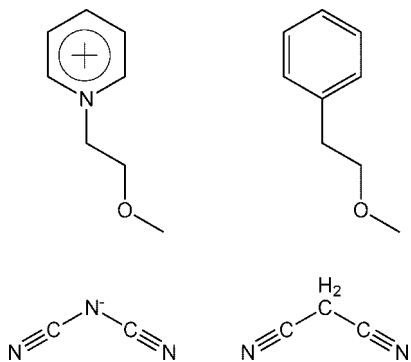


FIGURE 5. Ionic liquid (MOEPy⁺/DCA⁻) and homologous neutral pair (MOEBz/DCM).

the homologous neutral binary solution, an equimolar mixture of methoxy-ethylbenzene and dicyanomethane (MOEBz/DCM), shown below in Figure 5.³ The MOEPy⁺ cation and MOEBz are isoelectronic and isomorphous. The DCA⁻ anion and dicyanomethane are isoelectronic and nearly isomorphous. The shear viscosity at room temperature of MOEPy⁺/DCA⁻ is about 30 times larger than that of MOEBz/DCM, and the room temperature density of the ionic liquid is about 20% larger than that of the neutral binary solution.³

The data from a femtosecond OHD-RIKES study of these liquids is shown in Figure 6. Figure 6a shows the picosecond overdamped transients, Figure 6b shows the femtosecond dynamics, and Figure 6c shows the spectra obtained by Fourier-transform deconvolution of the transients in Figure 6b. In the slowest relaxation observed in this study, the ratio of the relaxation time constants between MOEPy⁺/DCA⁻ and MOEBz/DCM is relatively similar to the ratio of the shear viscosities. This result implies that the longest time scale reorientation time constants for ionic liquids are similar to those for neutral binary solutions and that this behavior is consistent with the predictions of Stokes–Einstein–Debye hydrodynamics.³

However, the intermolecular vibrational dynamics of the ionic liquid are somewhat different from that of the neutral binary solution. As shown in Figure 6c, the peak and the first moment of the intermolecular vibrational spectrum of MOEPy⁺/DCA⁻ are higher frequency than that of MOEBz/DCM. Although there are many possible origins for this spectral difference between the two liquids, it is likely that the primary difference arises from the differences in intermolecular interactions for the ionic liquid relative to the homologous neutral binary solution. Thus, the intermolecular interaction strength in ionic liquid is stronger than that for the neutral binary solution. The macroscopic properties such as liquid density and shear viscosity are consistent with stronger intermolecular interactions.³

Electronic Properties of the Ionic Liquid and Homologous Neutral Pair

To further understand the ionic liquid and its isoelectronic, isostructural neutral binary homologue, we carried

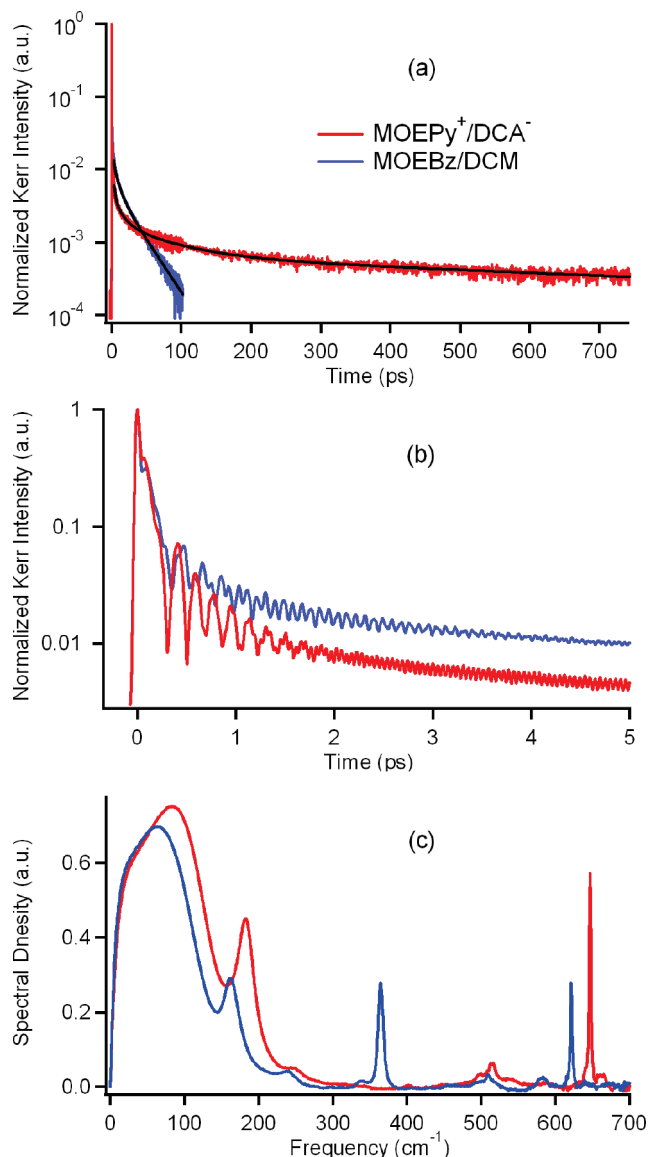


FIGURE 6. OHD-RIKES transients (a, b) and spectra (c) for the ionic liquid MOEPy⁺/DCA⁻ (red) and the homologous neutral binary liquid MOEBz/DCM (blue).

out geometry optimizations and harmonic normal-mode analyses for the individual molecular components.³ Geometry optimizations were made using the B3LYP density functional theory with the 6-311+G(d,p) basis set. Effective atom-centered charges were obtained by fitting the resulting electrostatic potential.

The harmonic normal mode predictions enable us to assign all of the observed low-frequency vibrations from the Kerr spectrum shown in Figure 6 to either the cation or anion species. The charge distributions of the ground-state molecular species are shown in Figure 7, with green colors indicating positive charge and red negative charge. It is clear from inspecting the charge distributions of MOEBz and MOEPy⁺ that the geometries and charge distributions are quite similar, as would be expected for an isoelectronic pair. The DCA⁻ anion and its isoelectronic homologue DCM display the same trend, but the effective charges on the C and N atoms of the nitrile groups are

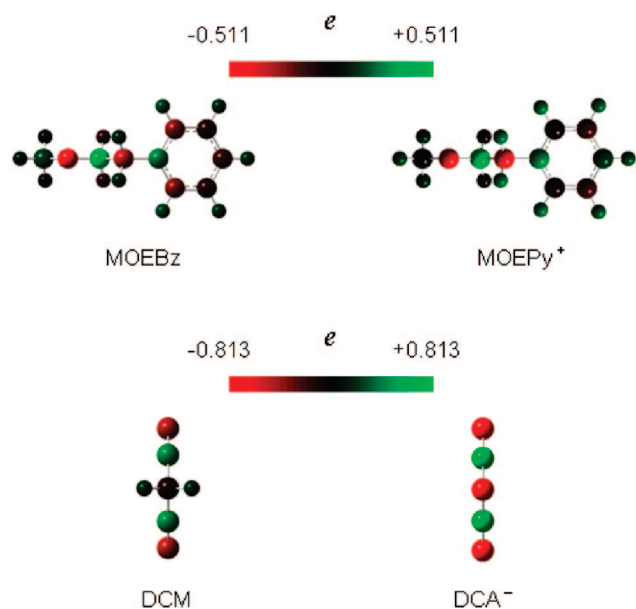


FIGURE 7. Effective atom-centered charges obtained from fits to the electrostatic potential for B3LYP/6-311+G(d,p) optimized geometries.

approximately double for the DCA⁻ anion relative to the DCM neutral.³

Novel Ionic Liquids with Silicon-Substituted Cations

Because of the observed reduction in viscosity upon changing one methylene group to an ether oxygen (viz., Pyr₁₄⁺/NTf₂⁻ and Pyr_{1(2O1)}⁺/NTf₂⁻),² we began to consider whether other chemical substitutions to the cation or anion side chains might offer even better means of tuning the viscosity. Our early discussions included the fact that the ether side chain is more flexible than the alkyl chain. Other concepts discussed included ideas about increased charge asymmetry for the alkylsilyl chains relative to alkyls and conformational heterogeneity.⁶⁷ Our ideas turned to the question, “What would make for a more flexible side chain than an ether?” The answer was that alkylsilyl side chains would be more flexible and that alkylsiloxy chains would be even more so. Our hope was that more side-chain flexibility might lead to a broader range of cation conformations and that this would lead to a reduction in T_g and hence viscosity.

Synthesis of Novel Silicon-Substituted Ionic Liquids

Standard synthetic methods are used to convert *N*-methylimidazole to 1-alkyl-3-methylimidazolium halides, where the alkyl group may be replaced by an alkylsilyl or alkylsiloxy group, and the halides are either chloride or bromide. Anion substitution of the halide for a bulkier anion is accomplished using lithium bis(trifluoromethylsulfonyl)imide (Li⁺ NTf₂⁻) or sodium tetrafluoroborate.^{4,5} Structures of the silyl- and siloxy-substituted imidazolium cations are shown in Figure 8.

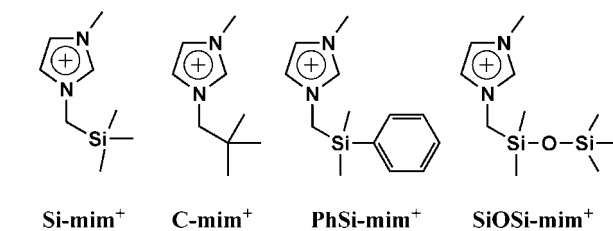


FIGURE 8. Si-substituted cations for low viscosity ionic liquids.

We prepared a series of novel ionic liquids with the *N*-methylimidazolium cation decorated on the other *N'* nitrogen with an alkylsilyl or alkylsiloxy functional group.^{4,5} The first studies involved comparing the trimethylsilyl-methyl-substituted imidazolium with the analogous neopentyl-substituted imidazolium.⁴ Both Si-mim⁺ and C-mim⁺ were prepared as ionic liquids paired with the NTf₂⁻ and the BF₄⁻ anions.⁶

Physical Properties: Low Viscosities and Fragile Glass Formation

Though the room temperature shear viscosities of these novel ionic liquids were not spectacularly low, the intriguing finding was that the Si-mim⁺/NTf₂⁻ liquid viscosity was 100 cP at ambient temperatures, while the C-mim⁺/NTf₂⁻ liquid had a viscosity of about 160 cP.⁴ On measurement of the BF₄⁻ ionic liquids with Si-mim⁺ and C-mim⁺, the former had an ambient viscosity of 631 cP while the latter had a viscosity of 4640 cP, a factor of 7.4-fold larger.⁴

Semilog plots of the viscosities versus temperature for the ionic liquids with silicon-substituted cations are shown in Figure 9. In Figure 9a, the viscosities for Si-mim⁺/BF₄⁻ (blue) are compared with C-mim⁺/BF₄⁻. Figure 9b shows that the viscosities for Si-mim⁺/NTf₂⁻ and C-mim⁺/NTf₂⁻ are both substantially lower than the corresponding BF₄⁻ liquids. Figure 9c shows the log of the viscosities plotted vs temperature for the second generation Si-substituted ionic liquid cation series.

The initial hypothesis as we began this work was that alkylsilyl and alkylsiloxy side groups would permit a greater flexibility of the side chain on the imidazolium, thus leading to a greater degree of conformational heterogeneity of the cation, and hence a lower glass transition temperature. When the glass transition temperatures were measured using differential scanning calorimetry,^{5,6} this was shown to be the case. The T_g values for Si-mim⁺/NTf₂⁻ and C-mim⁺/NTf₂⁻ were 201 and 203 K, while the Si-mim⁺/BF₄⁻ and C-mim⁺/BF₄⁻ ionic liquids had measured T_g values of 216 vs 221 K.⁶

The next investigation of silicon-substituted ionic liquids involved comparing the Si-mim⁺/NTf₂⁻ liquid with two new cations, PhSi-mim⁺ and SiOSi-mim⁺, each paired with the NTf₂⁻ anion.⁵ The SiOSi-mim⁺ cation has a branched yet highly flexible side chain with nine heavy atoms. The PhSi-mim⁺/NTf₂⁻ liquid had a T_g value of 216 K and a viscosity at 295 K of 312 cP.⁵ The SiOSi-mim⁺/NTf₂⁻ liquid had the lowest T_g of the series at 197 K and also had the lowest measured viscosity of 89 cP at 295 K.⁵

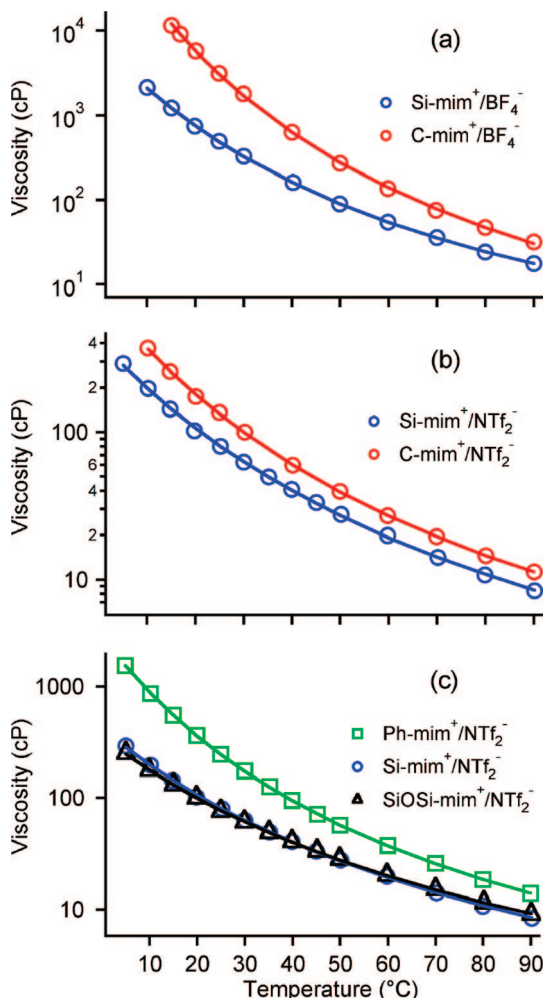


FIGURE 9. Temperature-dependent viscosity plots for the novel ionic liquids with Si-substituted cations.

Intermolecular Interactions, Dynamics, and Structure

The depolarized Raman spectrum from the OHD-RIKES experiment provides a detailed look at the forces determining both inter- and intramolecular vibrational dynamics.²⁶ The intramolecular Raman spectrum has been used to unambiguously demonstrate the presence of both *trans* and *gauche* conformers of the *n*-butyl group in several bmim⁺ ionic liquids.⁶⁷

In a similar fashion, our OHD-RIKES spectra demonstrate that the NTf₂⁻ anion shows similar intensities of both the *trans* and *cis* conformers. Figure 10 shows the spectra for Si-mim⁺/NTf₂⁻, C-mim⁺/NTf₂⁻, SiOSi-mim⁺/NTf₂⁻, and PhSi-mim⁺/NTf₂⁻.⁵ The spectral region from 250 to 410 cm⁻¹ is a fingerprint region for the NTf₂⁻ anion. The *trans* and *cis* conformers of NTf₂⁻ both are known to have eight unique bands in this region, with two of the eight bands having a shift between the two conformers.^{68,69} The observation of the 10 bands assigned to the NTf₂⁻ anion in this region of the spectrum demonstrates that the anion, as well as the cation, can introduce static conformational heterogeneity in the ionic liquid.²⁻⁵

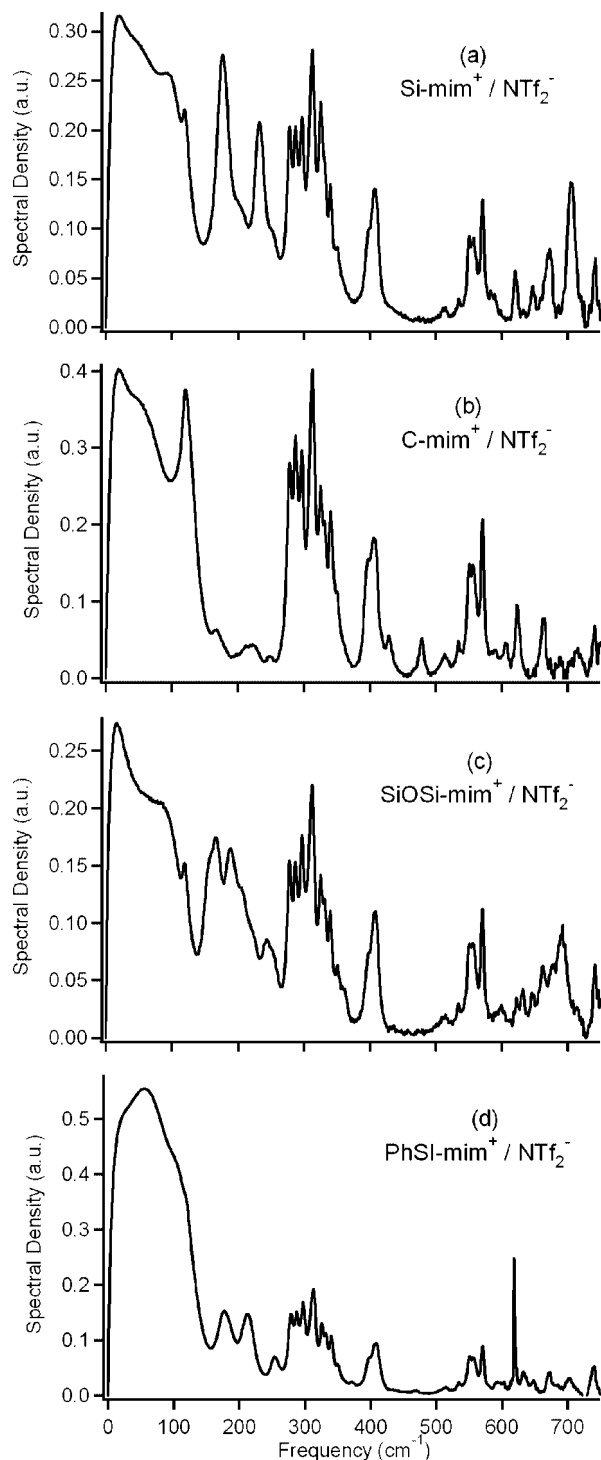


FIGURE 10. OHD-RIKES spectra for NTf₂⁻ ionic liquids with silicon-substituted cations.

Electronic Structure and Harmonic Vibrational Analysis of the Cations and Anions

As with the ionic liquid vs neutral binary pair comparisons above, we also carried out electronic structure calculations for the ions shown in Figure 8 plus the NTf₂⁻ anion, all using the B3LYP method for ground-state geometry optimization of the isolated molecular species.^{4,5} Because the number of electrons is much greater for these systems, the 6-31+G(d,p) basis set was used for the calculations.

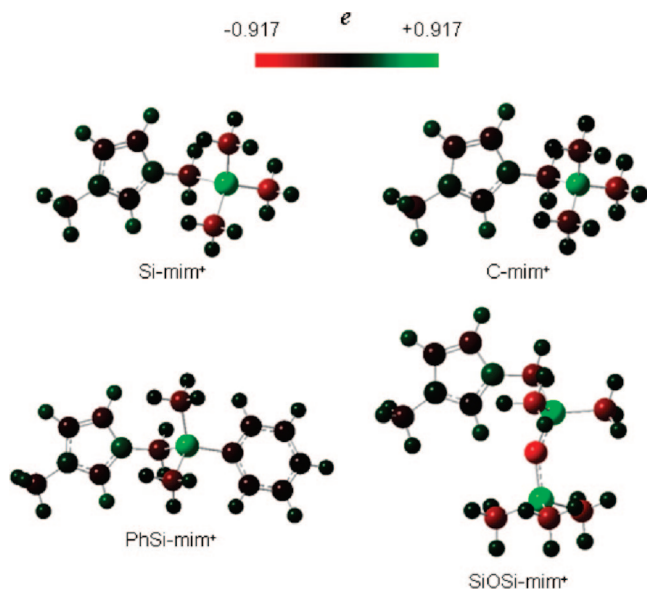


FIGURE 11. Effective atom-centered charges for Si-mim⁺, C-mim⁺, PhSi-mim⁺, and SiOSi-mim⁺ obtained from fits to the electrostatic potential for B3LYP/6-31+G(d,p) optimized geometries.

Again, the harmonic normal-mode analyses enabled full assignment of the observed depolarized Raman modes in the range from 0 to 750 cm⁻¹.⁵ It is interesting to note that the effective charges obtained from application of the CHelpG algorithm show that the net charges on the imidazolium ring system remain the same to better than 5% for this series of four cations, as shown in Figure 11. It is also clear that the presence of the methylene bridging unit between the imidazolium ring and the Si atom in PhSi-mim⁺ is likely part of the reason that there is no apparent delocalization of the positive charge from the imidazolium ring toward the phenyl ring. The striking difference between the Si-mim⁺ and the C-mim⁺ cations is that though the net charge of the Si atom on Si-mim⁺ is +0.76 while the central C atom of the neopentyl functional group on C-mim⁺ is +0.60, this excess charge is compensated by a 20% increase in the Si-C bond lengths relative to the C-C bond lengths.⁵ We note that the same trends for effective charges are also observed in the simpler Mulliken population analysis.

Summary

We learned several significant things from our studies of ionic liquids with non-aromatic cations. The phase behavior is highly sensitive to small changes in the structure. For example, N₁₄₄₄⁺/NTf₂⁻ and N₆₄₄₄⁺/NTf₂⁻ are persistently supercooled liquids with the melting temperature T_m observed at about 300 K. Dialkyl-pyrrolidiniums paired with the same NTf₂⁻ anion either have lower T_m values, as in the case of Pyr₁₄⁺/NTf₂⁻ and Pyr₁₅⁺/NTf₂⁻, or crystalline melting transitions may not be observed at all, as for the DSC scans for Pyr₁₍₂₀₁₎⁺/NTf₂⁻ and Pyr₁₍₂₀₂₎⁺/NTf₂⁻.⁷

Our OHD-RIKES transients and spectra for five ionic liquids at room temperature presented several interesting features.² We were able to study just one component of

the binary fluid by making use of a monatomic bromide anion, since the spherical anion has no intramolecular vibrations and contributes nothing to the depolarized Raman spectrum from reorientation. Thus we isolated the spectrum for the intermolecular dynamics arising from motions of the Pyr₁₍₂₀₂₎⁺ cation. Similarly, we were able to isolate the orientational relaxation dynamics of solely the cation in Si-mim⁺/BF₄⁻ and C-mim⁺/BF₄⁻, since the tetrahedral symmetry of the anion eliminates any contribution to the spectrum from reorientation.³

Just as Hamaguchi and co-workers have shown that substantial conformational heterogeneity exists between the trans and gauche conformers of the butyl chain on the cation of bmim⁺/Cl⁻,⁶⁷ we have shown that both cis and trans conformers of NTf₂⁻ are present in each NTf₂⁻ ionic liquid that we have studied by the OHD-RIKES method.^{2,3,5}

Our fluorescence dynamics studies provided overall agreement with the growing body of literature in this area. Subtle differences were observed in some areas. While solvation dynamics of the ions surrounding the C153 probe showed very nearly Arrhenius character, the temperature dependence of the polarization anisotropy dynamics was better fit to a VFT profile.⁷ Each of the time correlation functions for solvation dynamics derived from the time-dependent fluorescence shift of C153 required three- or four-exponential models in the numerical analysis; in no case did Kohlrausch functions provide an adequate fit. Somewhat different behavior was observed for the C153 orientational relaxation in tetraalkylammonium NTf₂⁻ liquids relative to those with dialkylpyrrolidinium cations. The former liquids are more viscous by about an order of magnitude at room temperature and show faster time constants consistent with microviscosity effects. The dialkylpyrrolidinium liquids show smaller microviscosity effects, but the simultaneous nonlinear least-squares fitting analysis shows the presence of very long time constants. We speculated that these long time constants may result from embedding of C153 in some locally structured region or in some kind of ion cluster.⁷

In another project, we compared the interactions and dynamics of an ionic liquid with its isoelectronic, isostructural homologue. The first moment of the intermolecular spectrum is about 20% larger for the ionic liquid than the neutral binary homologous solution. The longest time constants obtained by fitting the orientational relaxation decay are consistent with hydrodynamic scaling. This is because the ratio of the longest orientational relaxation time constant for the ionic liquid vs the neutral is similar to the ratio of the viscosities.

The novel cations with alkylsilyl and alkylsiloxy substituents have branched rather than straight chains. The Si-mim⁺ ionic liquids (with NTf₂⁻ and BF₄⁻ anions) are 1.6- and 7.4-fold lower in ambient temperature shear viscosity than are the analogous ionic liquids having the same anions paired with the C-mim⁺ cation. The T_g values for the Si-mim⁺ ionic liquids are 2–5 K lower than those for the C-mim⁺ liquids. A notable feature of the self-diffusion coefficients obtained from the PG-SE NMR

experiments is that these coefficients showed sub-linear scaling of the ratio of absolute temperature to viscosity, indicating that their transport behavior is more complex than would be predicted from a hydrodynamics perspective.⁶

Future research directions for understanding the physical chemistry of ionic liquids will span a vast range of ideas. From our perspective, these will include understanding the solvation dynamics and local friction in different regions of these complex and nanostructured liquids, especially with an eye toward predicting chemical reactivity and transport mechanisms. It will be quite interesting to observe the various structural and dynamical features of ionic liquids having both very small and large concentrations of water or organic solvents. As with all solvents, the continued investigation of the coupling between fast and slow dynamics will be of interest in ionic liquids, particularly when there is the possibility for observation of non-Markovian effects. Finally, it will be interesting to do longer time scale emission anisotropy experiments using probes with triplet emissive states.^{42,43} By doing so, we can investigate further the tantalizing hints of slow relaxation suggested by our C153 fluorescence anisotropy studies of $\text{Pyrr}_{14}^+/\text{NTf}_2^-$ and $\text{Pyrr}_{1(2\text{O}2)}^+/\text{NTf}_2^-$.

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