Dynamics in Organic Ionic Liquids in Distinct Regions Using Charged and Uncharged Orientational Relaxation Probes

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The temperature-dependent fluorescence anisotropy decay (orientational relaxation) of perylene and sodium 8-methoxypyrene-1,3,6-sulfonate (MPTS) were measured in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (alkyl = ethyl, butyl, hexyl, octyl) organic room temperature ionic liquids (RTIL). The two fluorescent probe molecules display markedly different rotational dynamics when analyzed using Stokes-Einstein-Debye theory, demonstrating that they are located in distinct environments within the RTILs and have very different interactions with their surroundings. Perylene rotates with subslip behavior, becoming increasingly subslip as the length of ionic liquid alkyl chain is increased. The dynamics approach those of perylene in an organic oil. In contrast, MPTS shows superstick behavior, likely reflecting very strong coordination with the RTIL cations. These results are consistent with different elements of rotational friction within the ionic liquid structure, which are available to solutes depending on their chemical functionality.

I. Introduction

As experimental studies on organic room temperature ionic liquids (RTIL) converge on a cogent picture of liquid structure and dynamics, important questions remain regarding the influence of local chemical environments on solute molecules. The interaction of an ionic liquid solvent with dissolved solute is of particular importance to many of the proposed applications such as reaction solvents,

1-5 as reaction solvents,1-5 separations,6 and batteries.7 These issues have strong dynamical underpinnings that time dependent studies can address.

A particularly important and distinguishing characteristic of organic ionic liquids is the concept of nanoscale heterogeneity. Originally identified in MD simulations,8 the concept has gained considerable traction as a diverse range of experimental studies appear to confirm the existence of structures that persist on non-negligible time scales.7-11 These proposed ionic liquid structures contain hydrophobic regions of alkyl “tails,” and charge-ordered, hydrophilic “head group” regions. In the context of this liquid structure, strong elements of selective solvation are possible. The resulting diversity of local environments can have a direct impact on the dynamics of processes where solvation environment is important. The effect of environment has been observed in the context of a photoisomerization.12 It is not difficult to consider the importance of dynamic heterogeneity being expanded beyond selective excitation in photochemical reactions to include differences in transport properties and availability of reagents and catalysts in the ionic liquid matrix.

One appeal of RTILs as a reaction medium is the breadth of molecules they can solvate. It is not unreasonable to ascribe this to the presence of multiple chemical environments. Dynamic heterogeneity may have a nontrivial impact on the reaction dynamics, and therefore influence “task-specific” organic ionic liquids.13 The design of task-specific organic ionic liquids may depend on the dynamics of molecules in distinct environments in addition to the specific substrate interactions.

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the ionic liquid local structures that are available to solutes depending on their chemical functionality.

Previous fluorescence studies of orientational relaxation of RTILs have seen Debye–Stokes–Einstein (DSE) behavior and possibly deviations from DSE behavior. Most of the studies examined very polar and charged dye molecules. Mali et al. studied a charged dye molecule and a nonpolar chromophore in a single RTIL. The studies presented here examine a triply charged fluorophore and a neutral nonpolar fluorophore that are similar in size (see Figure 1) in a series of RTILs with increasing hydrocarbon chain lengths. The temperature dependent studies of the orientational relaxation permit the local friction to be extracted from the data. By measuring the orientational relaxation on the series of liquids, it is possible to examine changes in the nature of the local environments experience by the two types of probe molecules.

II. Experimental Procedures

All ionic liquids were purchased from IoLiTec at 99+% HP grade. The fluorophores were purchased from Aldrich and used without further purification. HPLC grade water (Fisher) and DMSO (Mallinckrodt AR grade) were distilled prior to use. Other solvents were purged with nitrogen to remove O2, but the solvents were not further purified. HPLC grade water (Fisher) and DMSO (Mallinckrodt AR grade) were distilled prior to use. The fluorophores were purchased from Aldrich and used without further purification.

Steady-state fluorescence spectra were collected at room temperature using a Fluorolog-3 fluorimeter. Fluorescence spectra were collected in the forward-facing geometry with excitation at 380 nm with correction for lamp fluctuation and monochromator/detector efficiency. Temperature dependent viscosities of paraffin oil were measured using a Cannon-Ubbelohde viscometer in a constant temperature bath. Other viscosities were taken from the literature. Since RTIL viscosity can be dramatically affected by small impurity concentrations, the room temperature viscosities were confirmed in a nitrogen purged environment using a Texas Instruments AR-G2 rheometer with 40 mm parallel plate geometry.

III. Results and Discussion

The fluorescence experiments measure the time dependent anisotropy, r(t), defined as

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

with I\(\parallel\) and I\(\perp\) the time dependent fluorescence intensities polarized parallel and perpendicular to the excitation beam, respectively. Eisenthal and Chuang presented the functional form of the fluorescence anisotropy decay for the most general case of orientational diffusion. The result is a sum of 5 exponentially decaying terms containing rotational diffusion constants \(D_j\) about the jth molecular axis as

$$r(t) = \frac{6}{5} \left[ q_x q_y q_z e^{-3(D_x+D_y)t} + q_x q_y^2 q_z e^{-3(D_x+D_y)t} + q_x^2 q_y q_z e^{-3(D_x+D_y)t} + q_x^2 q_y^2 q_z e^{-3(D_x+D_y)t} + q_x q_y^2 q_z^2 e^{-3(D_x+D_y)t} \right] + \frac{3}{10} (\beta + \alpha) e^{-(6D+2\Delta)} + \frac{3}{10} (\beta - \alpha) e^{-(6D-2\Delta)}$$

for

$$\alpha = \frac{1}{\Delta} \left[ D_x (q_x^2 q_y^2 + q_x^2 q_z^2 - 2q_x q_y q_z) + D_y (q_y^2 q_z^2 + q_x q_y^2 q_z - 2q_x q_y q_z) + D_z q_x q_y q_z^2 - 2q_x q_y q_z^2 + q_x q_y^2 q_z - 2q_x q_y q_z \right]$$

$$\beta = q_x^2 q_y + q_x q_y^2 + q_x^2 q_z - \frac{1}{3}$$

$$D = \frac{1}{3} (D_x + D_y + D_z)$$

$$\Delta = \sqrt{(D_x^2 + D_y^2 + D_z^2) - D_x D_y - D_x D_z - D_y D_z}$$

The quantities \(q_j\) and \(\gamma_j\) are projections of the excitation and emission dipole onto the molecular axes. For most rotators, the similarity of the rotational diffusion constants generally causes there to be fewer than 5 resolvable exponentials, oftentimes generating only a single rotational diffusion constant.

In the experiments presented here, the observed exponential decays were related to hydrodynamic properties through the Debye–Stokes–Einstein relation

$$\tau = \frac{1}{6D} = \eta V fC kT$$

where \(\tau\) is the measured orientational relaxation time constant, \(\eta\) the viscosity, \(k\) is the Boltzmann constant, \(V\) is the molecular volume, \(C\) is a friction coefficient, and \(f\) is the shape factor.
TABLE 1: Shape Factors and Slip Friction Coefficients

<table>
<thead>
<tr>
<th>shape factors</th>
<th>slip coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_x ), ( f_y ), ( f_z ), ( f )</td>
<td>( C_x ), ( C_y ), ( C_z ), ( C )</td>
</tr>
<tr>
<td>perylene</td>
<td>1.86, 1.38, 2.03, 1.76</td>
</tr>
<tr>
<td>MPTS</td>
<td>1.43, 1.01, 1.55, 1.33</td>
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</tbody>
</table>

For a given molecule, the friction coefficient will contain information on the rotational friction experienced by the molecule. For large particles, the stick boundary condition (\( C = 1 \)) almost always holds. For rotators of similar size to the solvent molecules, the continuum approximation of the solvent begins to break down. This is manifest as a decrease in rotational dynamics in the vicinity of the probe molecule. This structuring can lead to effective void spaces through which the molecule can rotate with little hindrance, leading to a decrease in rotational friction below slip.

The results of the analysis are presented in Table 2 as a list of the experimentally determined average friction coefficients (\( C \) in eq 3). As the alkyl chain length increases, the friction coefficient approaches that of perylene in paraffin oil. From the values listed in Table 2, perylene is found to rotate with slip to subslip boundary conditions.

Because perylene is only slightly larger than the ionic liquid ions, some contribution to the subslip behavior can come from the coarseness of solvent media, which can be treated using Gierer–Wirtz theory. The Gierer–Wirtz theory takes the solvent to be concentric shells of spherical particles around the probe.
friction coefficient to its theoretical value for slip boundary conditions. A value of 1 means that the measured and calculated values are the same. A ratio larger than 1 indicates that the measured value is slower than slip, and a ratio smaller than 1 shows that the experimental value is faster than slip. The trends displayed in Table 3 demonstrate that as the length of the ionic liquid alkyl chain length increases, relative to the theoretical slip values, the in-plane rotational diffusion becomes faster with a concurrent slower rotational diffusion out of plane. Both the in-plane and out-of-plane rotational diffusion are converging on the values found in the paraffin oil. The increase in in-plane rotational diffusion constant with alkyl chain length is consistent with previous work on perylene in n-alkanes. For longer alkanes, the results are interpreted as a partial alignment of the alkane chains along the long axis of the perylene. This interpretation is supported by studies of gas phase van der Waal complexes. Therefore, the orientational relaxation trends with RTIL chain length indicate that the environment experienced by perylene is increasingly like that of a partially ordered alkane.

The convergence of the perylene environment to that of an alkane as the RTIL alkyl chain length increases is also manifest in the perylene fluorescence spectra displayed in Figure 3. The spectra are normalized at their peaks for clarity. As the RTIL chain length increases, the spectra become closer to that of perylene in the paraffin oil. The spectra are in accord with the trends seen in the friction coefficient data given in Table 3. The fluorescence spectra are sensitive to the local solvent environment and the orientational relaxation data depend on how the environment influences the dynamic interactions between the nonpolar perylene fluorophore and its environment. Both types of data show that as the chain length increases, perylene finds its environment approaching that of a hydrocarbon liquid.

These convergent trends of perylene demonstrate that the solvation environment of perylene in the ionic liquids becomes more alkane-like as the alkyl chain increases in length. In the context of ionic liquid structure, one might conclude that the aliphatic moiety is dominant in solvating the perylene. This is consistent with simulations on solvation in ionic liquids, as well as a recent optical Kerr effect experiment. The selective solvation constitutes an effective partitioning of the perylene into the hydrophobic regions of the bulk ionic liquid structure. The subslip rotational behavior is describing the structure and microviscosity of the hydrophobic pockets. It is important to note the apparent lack of a “turn-on” of nanoscale segregation. Both the in-plane and out-of-plane friction coefficients change continuously toward those of perylene in paraffin oil.

This interpretation leads to several interesting possibilities. Although not necessarily of the same origin, void spaces in RTILs have been evoked when discussing the solubility of CO2. The directionality of the rotational friction (see Table 3) may provide insight into anomalous Diels–Alder reactions in RTILs. Tiwari and co-workers find that the rate of an intramolecular Diels–Alder reaction involving a nonpolar reactant does not change significantly in going from C2mim+ NTf2− to C2mim+ [BF4], even though the viscosity changes substantially. The reaction involves the rotation of the dienophile over the plane of the molecule. This is the direction of rotation in C2mim+ that is most strongly subslip, indicating a relatively unhindered rotation produced by the ionic liquid structure that should be relatively insensitive to the anion.

B. MPTS. The anisotropy decays of MPTS in all liquids are single exponential, reflecting the lower symmetry of MPTS compared to perylene and indicating similar MPTS rotational diffusion coefficients for the various axes. The decay times vs η/kT are shown in Figure 4 for three RTILs, DMSO, and water. MPTS is essentially insoluble in C2mim+, so this liquid could not be studied. Because of the low viscosity, the data for MPTS in DMSO and water have very fast decays times. The data for these two liquids are shown in the inset. As is the case for perylene, the MPTS temperature dependent data in each liquid is linear within a very small error, demonstrating Debye–Stokes–Einstein behavior.

The friction coefficients for the five liquids are given in Table 4. The friction coefficient for stick boundary conditions is 1. In contrast to the perylene (see Table 2), the MPTS friction coefficients are all greater than 1 for the ionic liquid samples (Table 4), indicating superstick boundary conditions. MPTS in water and DMSO were used as control solvents for comparison. MPTS in these two solvents yield close to stick boundary conditions. Superstick conditions observed in the RTILs are traditionally explained using either the “solventberg” model or Nee-Zwanzig dielectric friction (eq 7). The former assumes

| TABLE 3: Ratios of In- and Out-Of-Plane Exp. Friction Coefficients to Their Theoretical Slip Values |
|----------------------------------|-----------------|-----------------|
| in-plane | out of plane |
| C2mim+ | C4mim+ | C6mim+ | C8mim+ | paraffin oil |
| 1.2  | 1.0  | 0.90 | 0.67 | 0.55 |
| 0.39 | 0.44 | 0.53 | 0.54 | 0.60 |

Figure 4. Orientational relaxation times, τ = 1/6D, for MPTS in five solvents plotted as a function of the viscosity (η) divided by kT (symbols). The lines through the data points are fits using linear least-squares. For clarity, the C2mim+ and C4mim+ data have been shifted up 4 and 2 ns, respectively. Because of the difference in time scale, the data for the solvents DMSO and water are shown in the inset. The axes labels for the inset are the same as for the main panel of the figure.

Figure 3. Normalized fluorescence spectra of perylene in four RTILs and paraffin oil.
specific solvent–solute interactions anchor solvent molecules of non-negligible size to the solute, effectively increasing the rotator volume. The latter involves the electrostatic torque between a dipole and the reactive field of the surrounding dielectric cavity, as

\[ D = \frac{kT}{6\eta V C} + \frac{\varepsilon_{NZ}}{\tau_D} \]

where \( \mu \) is the dipole moment of the solute, \( a \) is the dielectric cavity radius, \( \tau_D \) is the Debye relaxation time, and \( \varepsilon_0 \) and \( \varepsilon_\infty \) are the static and optical dielectric constants, respectively.

Given the structure of MPTS, both mechanisms are expected to contribute in the ionic liquid samples. The three formal −1 charged sulfonate groups should interact very strongly with the charged cations of the ionic liquid. Similarly, the presence of a reasonably strong dipole and long Debye relaxation time could also contribute to a dielectric friction. For alcohol solvents that can hydrogen bond to the solute, research on the relative contributions of the two mechanisms has indicated that the “solventberg” effect dominates.38

For the RTILs studied here, the contribution from the dielectric friction was estimated using eq 7 with aggressive but not unrealistic physical parameters and measured properties of the ionic liquids. Taking \( \mu = 15 \text{ D,} \quad a = 6 \text{ Å,} \quad \tau_D = 500 \text{ ps,} \quad \varepsilon_0 = 10, \quad \text{and} \quad \varepsilon_\infty = 1.4, \) one arrives at an additional contribution to the friction that is \( < 0.8 \). This contribution is in addition to the value of 1, which is the mechanical friction for stick boundary conditions. The actual contribution will most likely be significantly smaller because the RTIL solvents are charged resulting in a reduction caused by the kinetic polarization deficiency and shielding.42 With rotational frictions that exceeds stick boundary conditions by greater than a factor of 2 (see Table 4), the dielectric friction alone cannot account for the observed superstick results.

Figure 5 shows the fluorescence spectra of MPTS in the three RTILs and in DMSO and water. MPTS in the three RTILs shows a significant shift to longer wavelengths and a reduction of vibronic structure relative to DMSO. The loss of vibronic structure and bathochromic shift of the fluorescence is indicative of strong solvent–solute interactions.43 The shift and reduction of vibronic structure increases as the alkyl chain length of the RTIL increases. This trend may indicate stronger solute–solute interactions because of increased segregation of the liquid into ionic regions and alkane-like regions, which is in accord with the trends seen for perylene. The shift in the MPTS spectrum and reduction in vibronic structure with increasing RTIL chain length tracks the observed increase in the friction coefficient (see Table 4). The fluorescence spectrum of MPTS in water shows a very large shift and virtual complete loss of vibronic structure. The spectrum in water indicates that water has a very strong interaction with MPTS. Water is both a hydrogen bond donor and acceptor. Water can solvate the sulfonate anions, and it may also donate \( \pi \)-hydrogen bonds to the aromatic rings. In spite of the spectroscopic evidence for strong interaction between MPTS and water, orientational relaxation occurs with a diffusion constant that is consistent with stick boundary condition. This is in contrast to MPTS in the RTILs that undergoes orientational relaxation that is much slower than stick boundary conditions (see Table 4). Therefore, the strength of the fluorophore-solvent interaction that influences the fluorescence spectrum alone is not sufficient to explain the very slow diffusion, that is, superstick boundary conditions see in Table 4.

The MPTS orientational relaxation data show strongly hindered motion that is likely caused by strongly associated solvent molecules. The most obvious possibility is that RTIL cations are bound to the sulfonate anions. A simple calculation can estimate the number of associated solvent molecules assuming the overall shape factor does not change substantially. Using the cation van der Waals volumes, the results yield 3.0, 2.8, and 3.1 cations that are “attached” to each MPTS in \( \text{C}_2\text{mim}^+, \) \( \text{C}_4\text{mim}^+, \) and \( \text{C}_8\text{mim}^+, \) respectively. These numbers, which are all basically 3, correspond to the number of sulfonate groups on MPTS, supporting the idea that cation coordination is responsible for the slow (superstick) orientational relaxation of MPTS in the RTILs. Furthermore, the friction coefficient increases as the RTIL cation alkyl chain increases. The increase in friction is consistent with larger and larger cations being strongly bound to the MPTS sulfonate groups as RTIL solvent goes from \( \text{C}_2\text{mim}^+ \) to \( \text{C}_4\text{mim}^+ \) to \( \text{C}_8\text{mim}^+. \)

### IV. Concluding Remarks

The rotational friction of perylene and MPTS have been studied in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonfyl)imide ionic liquids from 298 to 333 K. On the basis of these measurements, two distinct rotational environments were found. Perylene undergoes orientational relaxation in the slip to subslip regime, that is orientational relaxation is faster than predicted by hydrodynamic theory. As the alkyl chain length of the cation increases, the in-plane and out-of-plane orientational relaxation friction coefficients converge to those of perylene in paraffin oil (see Table 3). The results indicate that perylene partitions into alkane-like environments. The trends in the in-plane and out-of-plane friction coefficients suggest some degree of alkyl chain alignment along the perylene long molecular axis.

MPTS undergoes orientational relaxation with superstick boundary conditions in contrast to MPTS in DMSO and water, which show approximately stick boundary conditions. The slow
orientational relaxation of MPTS in the RTILs cannot be ascribed to a nonspecific strong solute solvent interaction. The fluorescence spectrum of MPTS in water indicates stronger interactions with water than with the RTILs yet water does not produce anomalously slow orientational relaxation. The results indicate that three RTIL cations are bound to the three MPTS sulfonate anions, and the entire assembly undergoes orientational diffusion. The increased volume of MPTS accounts for the slow orientational relaxation. The results presented here provide clear evidence for solutes partitioning into distinct environments in RTILs. The location of the solute depends on its properties, in this case nonionic/nonpolar (perylene) vs highly charged (MPTS) solutes. For both solutes, the orientational dynamics change with the cation alkyl chain length, but for different reasons. As the alkyl chain length increases, perylene finds itself in an increasingly alkane like environment, while MPTS has increasingly large cations bound to it.

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References and Notes