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Fluorescence correlation spectroscopy evidence for structural heterogeneity in ionic liquids†

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In this work, we provide new experimental evidence for chain length-dependent self-aggregation in room temperature ionic liquids (RTILs) using fluorescence correlation spectroscopy (FCS). In studying a homologous series of *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, [C_nMPy][Tf_2N] RTILs of varying alkyl chain length (n = 3, 4, 6, 8, and 10), biphasic rhodamine 6G solute diffusion dynamics were observed; both the fast and slow diffusion coefficients decreased with increasing alkyl chain length, with the relative contribution from slower diffusion increasing for longer-chain [C_nMPy][Tf_2N]. We propose that the biphasic diffusion dynamics originate from self-aggregation of the nonpolar alkyl chains in the cationic [C_nMPy]$^+$.

In recent years, room-temperature ionic liquids (RTILs) have gained immense popularity owing to their desirable properties such as negligible volatility, high electrochemical and thermal stability, and high ionic conductivity.[1–3] Those attractive properties have led to many applications of RTILs in separations, catalysis, and energy-related applications, such as fuel cells, photovoltaics, supercapacitors, and batteries.[4–8] Despite rapid growth in the rate of publication on RTILs, some of the most fundamental questions concerning their structure and dynamics remain unanswered. To exploit the great potential of RTILs, an understanding of the liquid structure and microscopic dynamics, such as ionic diffusion and solvation dynamics, is essential.[9]

In spite of broad interest in RTILs, local liquid structures and microscopic dynamics are relatively unexplored and few details are currently known about the nanoscale organization of RTILs. The liquid structure of a neat RTIL is largely determined by a combination of intermediate- and long-range Coulombic and hydrogen-bonding interactions as well as packing factors.[10] Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) can provide highly informative local structures.[11] Prepeaks or first sharp diffraction peaks (FSDPs) at q = 0.2–0.5 Å^{-1} were observed for RTILs using X-ray and neutron scattering techniques.[12–18] However, the origin of these FSDPs has been a subject of extensive debate recently.[12–13,17] Further experiments and simulations are therefore warranted to clarify details of the local liquid structures and microscopic dynamics in RTILs.

Here, we explore the utility of fluorescence correlation spectroscopy (FCS) to investigate model solute diffusion dynamics toward elucidating local liquid structures in RTILs. FCS monitors the motion of a small number of dye molecules by measurement of spontaneous fluorescence fluctuations when the dye molecules undergo Brownian motion through an extremely small observation volume (femtoliters) determined by the focus of a confocal microscope.[19–21] The technique is exquisitely sensitive, offering detection down to the single-molecule level. This method has been extensively used to study translational diffusion, blinking dynamics, biochemical reactions, local polymeric/biomolecular structures[22–24] and, most recently, solute transport in RTILs.[20,25] To better understand the local liquid structure of RTILs, five *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_nMPy][Tf_2N], homologs with alkyl chain lengths n = 3, 4, 6, 8, and 10 were selected, using rhodamine 6G (R6G) as a reporter probe. FCS results revealed biphasic diffusion dynamics for the entire series, suggesting that heterogeneous liquid structures exist in these RTILs.

The molecular structures of [C_nMPy][Tf_2N] and R6G are shown in Fig. 1a. Fig. 1b displays FCS autocorrelation curves for R6G in the five [C_nMPy][Tf_2N] RTILs. As is evident, the R6G diffusion rate decreases with an elongation of the alkyl chain, mirroring the increasing bulk viscosity. For multiple chromophores experiencing different local environments, diffusion in the focal volume can be described by a three-dimensional Gaussian function as:[21,26]

$$G(t) = \frac{1}{N}\sum_{i=1}^{n} a_i\left(1+\frac{t}{\tau_{D_i}}\right)^{-1}\left(1+\frac{t}{\omega^2\tau_{D_i}}\right)^{-1/2} \quad (1)$$

where N is the mean number of molecules, a_i is the contribution of the ith local environment component to the total amplitude of the autocorrelation function, τ_D is the characteristic diffusion time, and ω (= z_0/r_0) defines the focal dimensions, where z_0 and r_0 are the axial and radial dimensions of the

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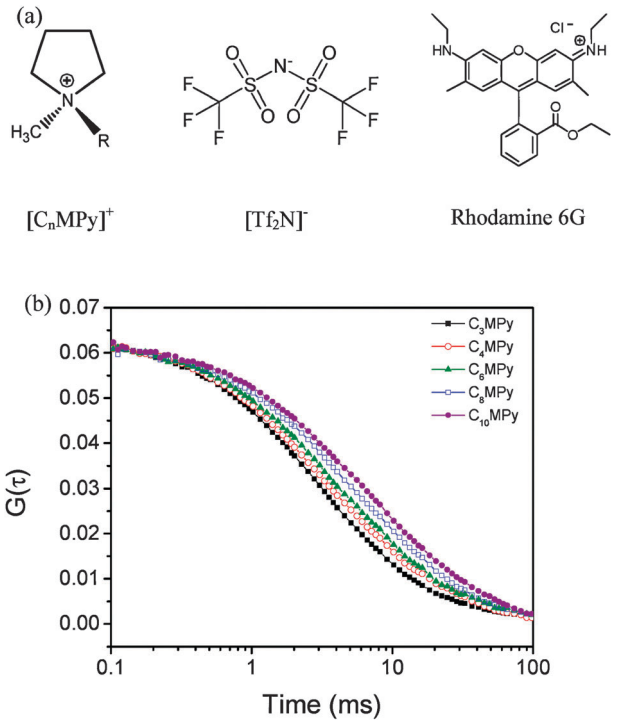

Fig. 1 (a) Molecular structures of R6G and $[C_nMPy][Tf_2N]$. (b) Normalized autocorrelation curves for 2.5 nM R6G in $[C_nMPy][Tf_2N]$ for n = 3,4,6,8, and 10.

confocal volume. The diffusion coefficient, D, is related to τ_D by $\tau_D = r_0/4D$. When $i = 1$, the model reduces to the case for simple diffusion (SD) and when $i = 2$, a two-component diffusion (TD) model is realized.

As shown in Fig. 2 (black solid line), the SD model failed to produce an acceptable fit to the FCS results for $[C_8MPy][Tf_2N]$. Similar fitting discrepancies were observed for the other RTILs (not shown). Anomalous diffusion (AD) models or two-component diffusion (TD) models are often used to explain deviation from simple diffusion. In the anomalous diffusion case, the mean square displacement follows a power law, $\langle r(t)^2 \rangle \propto t^\alpha$. The autocorrelation function expression becomes:[22,27,28]

$$G(t) = \frac{1}{N}\left(1 + \left(\frac{t}{\tau_D}\right)^\alpha\right)^{-1}\left(1 + \frac{1}{\omega^2}\left(\frac{t}{\tau_D}\right)^\alpha\right)^{-1/2} \qquad (2)$$

Fig. 2 compares the fits for R6G-$[C_8MPy][Tf_2N]$ using the SD, TD and AD models. The fit residuals are shown in the bottom panel of Fig. 2. Both AD and TD models show reduced residuals relative to the SD model. The reduced χ^2 obtained from a Levenberg–Marquardt minimization procedure in Origin™ are 10×10^{-7}, 1.4×10^{-7}, and 1.8×10^{-7} for the SD, TD, and AD models, respectively. Based on the reduced χ^2 and the residuals, the TD model gives the most satisfactory fit. Thus, the following discussion will be based on the TD model.

Table 1 lists the D_1 and D_2 values averaged from 60–80 data sets for each of the five RTILs. With increasing alkyl chain length, both the fast and slow diffusion coefficients decrease. Notably, as n goes from 3 to 10, the fraction A_2 associated with the slow component increases. As a result, the average

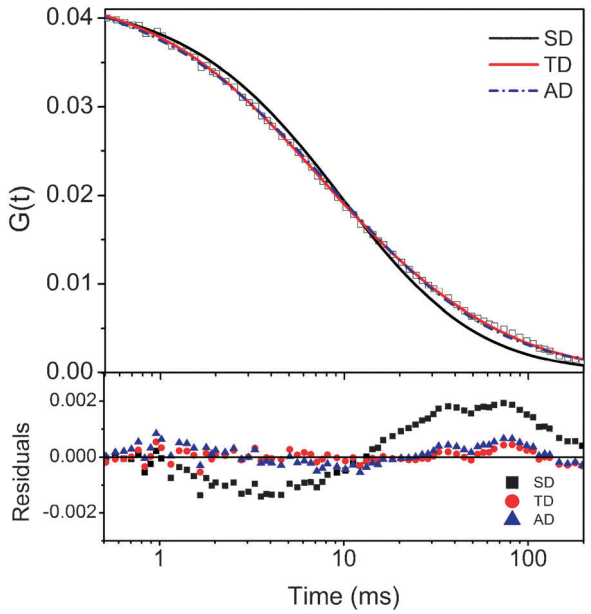

Fig. 2 (a) Fits for the autocorrelation curve for R6G in $[C_8MPy][Tf_2N]$ by use of three diffusion models. (b) Shows the residuals of the fits with the SD, TD, and AD models. The typical N range is between 20 and 40 and the concentration of R6G ranges from 2.5 nM to 5 nM.

Table 1 Summary of fits using the TD model

RTILs	D_1/μm^2 s^{-1}	A_1/%^{a}	D_2/μm^2 s^{-1}	D_{avg}/μm^2 s^{-1}	η/cP^b
$[C_3MPy][Tf_2N]$	9.4	76	1.2	7.4	56
$[C_4MPy][Tf_2N]$	8.7	71	1.1	6.5	74
$[C_6MPy][Tf_2N]$	6.9	68	0.94	5.0	108
$[C_8MPy][Tf_2N]$	5.7	68	0.76	4.1	127
$[C_{10}MPy][Tf_2N]$	5.5	57	0.66	3.4	177

^{a} Amplitude $A_2 = 100 - A_1$. The average diffusion coefficient $D_{avg} = (D_1A_1 + D_2A_2)/100$. ^{b} η was determined at 298 K.

R6G diffusion coefficient, D_{avg}, decreases from 7.4 to 3.4 μm^2 s^{-1} in going from $[C_3MPy][Tf_2N]$ to $[C_{10}MPy][Tf_2N]$. Moreover, the deviation from simple diffusion expected for an isotropic solvent is consistent with heterogeneity in the liquid phase; that is, the biphasic diffusion dynamics for R6G in $[C_nMPy][Tf_2N]$ suggest two different local solvent structures within the RTIL, giving rise to the disparate diffusional rates seen. We interpret these experimental results to suggest persistent heterogeneous liquid structures in $[C_nMPy][Tf_2N]$. We further posit that the fast and slow diffusion rates for R6G are due to the diffusion within non-aggregated regions and self-aggregated domains, respectively.

Our assertion of structural heterogeneity in RTILs is, of course, not without precedent as this topic has been subject to considerable scrutiny in the past few years.[13–16,29–33] By varying the alkyl chain lengths in 1-alkyl-3-methylimidazolium $[C_nMIM]^+$ systems, self-aggregation for mid-range alkyl chains was first suggested by MD simulations.[31] SAXS results from Triolo *et al.*, which showed scattering patterns in the range of 0.2–0.5 Å^{-1}, confirmed self-aggregated domains formed by the hydrophobic alkyl chains.[13] Although SANS experiments also clearly demonstrated similar peaks, the origin of those peaks has been called into question.[12,17]

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By comparing SANS results on selectively H/D-isotopically substituted $[C_nMIM]^+$ systems, Hardacre and coworkers[12] suggested that these peaks are not due to complex long-range interactions but rather are the consequence of cationic anisotropy. Other lines of experimental evidence for self-aggregation, locally ordered domains/structures, or microphase separation within RTILs include the observation of pronounced "hyperpolarity"[34] and additive optical heterodyne-detected Raman-induced Kerr effect spectra (OHD-RIKES).[35] Although use of our results does not allow us to determine the nature of cationic anisotropy, that effect alone clearly cannot explain the two distinct diffusion regimes observed. Therefore, we tentatively attribute the biphasic diffusion to the existence of self-aggregation, resulting from hydrophobic van der Waals interactions between the alkyl chains of the cations. A more surprising finding from our FCS experiments is evidence for the self-aggregation of the relatively short chain analog $[C_3MPy][Tf_2N]$. Although MD simulations and early SAXS results only identified self-aggregation for alkyl chain lengths longer than $n = 4$ in $[C_nMIM]^+$ systems, more recent SAXS results for the $[C_nMIM]^+$ series from $n = 2$ to 9 suggest the existence of self-aggregation domains for $n \geq 3$. Indeed, Atkin and Warr[36] have noted low q scattering peaks for alkylammonium nitrates with n of 1 or 3. MD simulations and SAXS/SANS studies on the $[C_nMPy]^+$ system are currently ongoing and will be reported elsewhere.

Dispersed kinetics have been observed for the rotation of solutes in RTILs,[37] with solvation dynamics in RTILs also being much more dispersed than for conventional solvents. Along these lines, in the results presented herein, we make the assumption that microphase separation of ionic and nonpolar groups causes dispersion in the observed solute diffusion; in other words, that the translational diffusion rate of R6G differs depending upon which spatial region of the RTIL the probe molecule is experiencing. Following this logic, given the super-molecular length scales over which FCS operates, it must also imply some continuity of discrete environment types within the fluid, leading to persistent diffusion for an appreciable period in any one milieu. Otherwise, a cooperative averaging of the two unique diffusion rates is likely, yielding a homogeneous autocorrelation curve whose characteristic time would simply derive from the relative occupancy of R6G in the two distinct environments. In the interest of completeness, a remarkable study by Khurmi and Berg[38] should be noted in which multiple population-period transient spectroscopy (MUPPETS) was applied to the ground-state recovery of auramine O in the widely studied RTIL $[C_4MIM][PF_6]$ as a direct test for rate heterogeneity. In their work, rate heterogeneity was not found to be the primary cause of the dispersed kinetics but rather, a homogeneous mechanism was proposed to give rise to this unusual phenomenon. Thus, while rate heterogeneity is apparent from our results, conclusions made about mesostructure heterogeneity being responsible for this phenomenon in $[C_nMPy][Tf_2N]$ RTILs should be drawn with caution as the exact mechanism is unknown.

In summary, FCS has revealed disparate solute diffusion rates within $[C_nMPy][Tf_2N]$ RTILs. Significantly, these results contribute to a growing literature advancing the notion that non-imidazolium RTILs also consist of microsegregated or nanostructured regions. Distinctly bimodal diffusion was observed for each homolog investigated. Self-aggregation of the nonpolar alkyl chains of the $[C_nMPy]^+$ cation is believed to give rise to the biphasic diffusion dynamics seen here, though the precise mechanism requires further confirmation. With increasing alkyl chain length of the cationic $[C_nMPy]^+$, both the fast and slow diffusion rate decreased and the contribution of slow diffusion increased, suggesting increased aggregation domain size with increasing chain length. This phenomenon was also observed for $n = 3$, consistent with recent SAXS studies for the $[C_nMIM]^+$ system. This work accords with previous MD simulations and scattering results indicating self-aggregation in RTILs and provides important insight into the local solvent structure, which plays a pivotal role in fluid characteristics impacting applications in areas as diverse as drug delivery, batteries, fuel cells, and solar cells.

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