

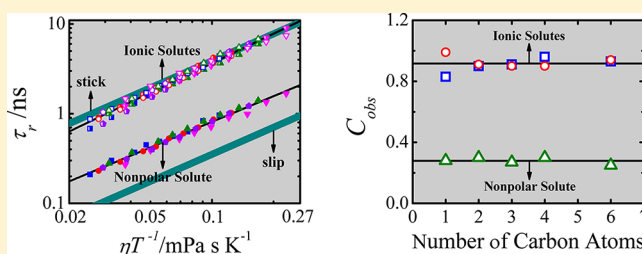
Rotational Diffusion of Nonpolar and Ionic Solutes in 1-Alkyl-3-Methylimidazolium Bis(trifluoromethylsulfonyl)imides: Is Solute Rotation Always Influenced by the Length of the Alkyl Chain on the Imidazolium Cation?

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Supporting Information

ABSTRACT: In an attempt to find out whether the length of the alkyl chain on the imidazolium cation has a bearing on solute rotation, temperature-dependent fluorescence anisotropies of three structurally similar solutes have been measured in a series of 1-alkyl-3-methylimidazolium (alkyl = methyl, ethyl, propyl, butyl, and hexyl) bis(trifluoromethylsulfonyl)imides. Solute–solvent coupling constants obtained from the experimentally measured reorientation times with the aid of Stokes–Einstein–Debye hydrodynamic theory indicate that there is no influence of the length of the alkyl chain on the rotation of nonpolar, anionic, and cationic solutes 9-phenylanthracene (9-PA), fluorescein (FL), and rhodamine 110 (R110), respectively. It has also been noticed that the rotational diffusion of 9-PA is closer to the predictions of slip hydrodynamics, whereas the rotation of negatively charged FL and positively charged R110 is almost identical and follows stick hydrodynamics in these ionic liquids. Despite having similar shape and size, ionic solutes rotate slower by a factor of 3–4 compared to the nonpolar solute. Interplay of specific and electrostatic interactions between FL and the imidazolium cation of the ionic liquids, and between R110 and the bis(trifluoromethylsulfonyl)imide anion, appear to be responsible for the observed behavior. These results are an indication that the length of the alkyl chain on the imidazolium cation does not alter their physical properties in a manner that has an effect on solute rotation.



1. INTRODUCTION

Research dealing with ionic liquids has received considerable attention during the past decade due to numerous applications in chemistry and material science.^{1,2} Fundamental aspects, such as chemical reactivity in ionic liquids and their structure, have been investigated by a wide range of techniques.^{3–5} It has been well-established that the presence of a cooperative network of hydrogen bonds between the cations and anions induces structural directionality.³ Thus, ionic liquids form organized structures on various length scales and these structural features in turn cause dynamic heterogeneity in fast processes such as solvation, isomerization, charge transfer, and intramolecular electron and proton transfer reactions. However, the influence of organized structure of the ionic liquids on these dynamical processes is not always conclusive.⁴ Alkyl chains of varying lengths, either on the cation or on the anion of the ionic liquid, are known to facilitate the formation of organized structures in these systems. As a result of their structural inhomogeneity, solutes dissolved in ionic liquids, depending on their chemical nature, tend to reside in varied environments of an ionic liquid, and such a hypothesis has been substantiated from the rotational diffusion study of nonpolar and charged solutes in a series of 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imides by Fruchey and Fayer.⁶ Thus,

rotational diffusion studies provide a convenient means to explore different interactions experienced by a solute molecule with its surroundings in a complex system such as an ionic liquid.

Apart from the work of Fruchey and Fayer,⁶ several groups have investigated various aspects of solute rotation in ionic liquids.^{7–24} Maroncelli and co-workers⁸ have noticed that anisotropy decays of a number of charged and neutral solutes in ionic liquids follow stretched exponential functions of time, which is akin to the type of dynamics observed in supercooled liquids and glasses.⁹ This result has been rationalized on the basis of non-Markovian friction effects rather than the organized structure of the ionic liquids.¹⁰ Another aspect of solute rotation that has been extensively investigated is the influence of specific interactions between the solutes and the constituents of the ionic liquids.^{6,12–23} Recent work from our laboratory addressed the influence of the nature of the anion of the ionic liquid on solute rotation.¹⁶ Results obtained indicate that rotation of the cationic solute rhodamine 110 (R110) is significantly hindered due to specific interactions between the

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solute and the anion of the ionic liquid, and the extent of hindrance is governed by the hydrogen bond basicity of the anion.

The third and perhaps least-explored aspect is how the length of the alkyl chain on one of the constituents of the ionic liquid influences solute rotation. Strehmel et al.²¹ have investigated rotational diffusion of piperidine-1-yloxy spin probes in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides at room temperature by electron spin resonance (ESR) spectroscopy. They have observed that the rotational correlation time of the neutral spin probe follows a linear dependence on ionic liquid viscosity, whereas ionic spin probes display nonhydrodynamic behavior in ionic liquids with longer alkyl chains. This result has been explained on the basis of phase separation at a molecular level between the charged part of the ionic liquid and the longer alkyl chains bound to the imidazolium cation. As mentioned earlier, from temperature-dependent anisotropy measurements of a nonpolar solute perylene and a triply charged anionic solute, 8-methoxypyrene-1,3,6-sulfonate (MPTS), in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, Fruchey and Fayer⁶ have shown that nonpolar and charged solutes are located in distinct environments within the ionic liquids. Rotational diffusion of perylene follows slip hydrodynamics in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and reaches subslip behavior in the octyl derivative. Essentially, the solute–solvent coupling constant (C_{obs}) decreases by 50% from ethyl to octyl derivative, and such a steep variation could not be accounted by the quasihydrodynamic theories. Thus, the observed result has been rationalized on the basis of the solute molecule experiencing an alkane-like environment with an increase in the length of the alkyl chain on the imidazolium ring. In contrast, rotational diffusion of the triply charged anionic solute MPTS follows superstick behavior and C_{obs} increases by 25% from ethyl to hexyl derivatives, which has been explained by the solventberg model. A somewhat similar trend has been noticed for the cationic solute R110 in a series of 1-alkyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (FAP) ionic liquids.¹⁴ Das and Sarkar²² have shown that an increase in the length of the alkyl chain, not only on the cation but also on the anion of the ionic liquid, influences solute rotation. They have observed significantly slower rotation for the dipolar solute coumarin 153 in the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate compared to its octyl analogue, and this observation has been rationalized with the aid of quasihydrodynamic theories.

The examples presented in the preceding paragraph unambiguously establish that the length of the alkyl chain on one of the components of the ionic liquid has a significant bearing on solute rotation. However, the debatable issue is whether the observed trends are generic or specific to a particular class of solutes. In other words, from the data available in literature it is not obvious whether solute rotation is always influenced by the length of the alkyl chain on one of the components of the ionic liquid. Thus, to address this issue, rotational diffusion of three structurally similar solutes has been investigated in the ionic liquid series comprising the cations 1,3-dimethylimidazolium ($[\text{mmim}^+]$), 1-ethyl-3-methylimidazolium ($[\text{emim}^+]$), 1-methyl-3-propylimidazolium ($[\text{mpim}^+]$), 1-butyl-3-methylimidazolium ($[\text{bmim}^+]$), and 1-hexyl-3-methylimidazolium ($[\text{hmim}^+]$) and the anion bis(trifluoromethylsulfonyl)imide ($[\text{Tf}_2\text{N}^-]$). The three solutes chosen are nonpolar 9-phenylanthracene (9-PA), anionic fluorescein (FL), and

cationic R110; Figure 1 gives their molecular structures. By carrying out temperature-dependent anisotropy measurements

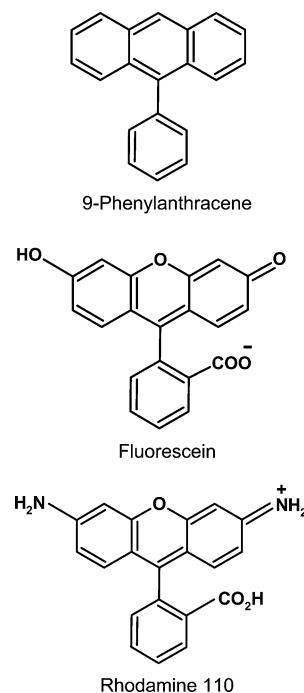


Figure 1. Molecular structures of the solutes.

of the three structurally similar but chemically distinct solutes in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, we hope to find out whether the length of the alkyl chain on the imidazolium cation influences solute rotation.

2. EXPERIMENTAL SECTION

All the ionic liquids were purchased from io-li-tec, and the stated purity of the ionic liquids is >99% with <100 ppm water content and <100 ppm halide ion concentration. Water content of the ionic liquids was estimated by Karl Fischer titration with the aid of a Metrohm 831 KF Coulometer and found to be within limits specified by the manufacturer. The fluorophore 9-PA was obtained from Aldrich, whereas FL and R110 were from Exciton. All these fluorophores and ionic liquids are of the highest available purity and were used without further purification. Concentrations of the fluorophores in ionic liquids were chosen such that the absorbance is in the range of 0.1–0.2 at the wavelength of excitation, which corresponds to a concentration range of $(0.5\text{--}1.0) \times 10^{-5}$ M.

Time-resolved fluorescence measurements were carried out with a setup that works on the principle of time-correlated single-photon counting.²⁵ The setup used in the present study was purchased from IBH and employs a diode laser as the excitation source. The instrumental details have been described in our earlier publication.¹⁴ Samples containing the probe 9-PA were excited with a 374 nm diode laser and the emission from the samples was collected at 420 nm. On the other hand, samples with the probes FL and R110 were excited with a 445 nm diode laser and the emission was monitored at 550 nm. The decays were collected in 4096 channels with a time increment of 14.4 ps/channel. The instrument response function (IRF) of the setup was measured by collecting the scattered light from a TiO_2 suspension in water and the full-width at half-maximum was found to be around 100 ps. For lifetime measurements,

decays were collected by keeping the emission polarizer at magic angle (54.7°) with respect to polarization of the excitation laser to ensure complete depolarization of the fluorescence. Anisotropy decay measurements were carried out by collecting parallel and perpendicular decay components with respect to the polarization of the excitation laser. The two decay components were acquired for at least 900 s each, such that a good signal-to-noise ratio was obtained. To account for the discrepancies in transmission efficiency of the monochromator, the perpendicular component was corrected for the G -factor of the spectrometer. All the anisotropy measurements were carried out over the temperature range 298–348 K. The temperature of the sample was controlled with the aid of a thermoelectric controller (model DS) from IBH. Each measurement was repeated 2–3 times and the average values are reported. Analyses of fluorescence and anisotropy decays were performed with the software supplied by IBH.

3. RESULTS AND DISCUSSION

A single-exponential function is adequate to fit the anisotropy decay of each solute at a given temperature. Anisotropy decays of the three solutes in $[\text{emim}^+][\text{Tf}_2\text{N}^-]$ measured at 298 K along with the fitted curves are displayed in Figure 2, and it can

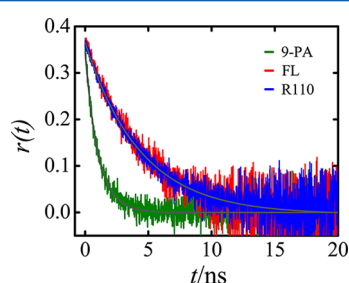


Figure 2. Anisotropy decays of 9-PA, FL, and R110 in $[\text{emim}^+][\text{Tf}_2\text{N}^-]$ at 298 K, together with the fitted curves. It can be noticed that the anisotropy decays of FL and R110 are almost identical and are significantly slower compared to that of 9-PA.

be noticed from the figure that the anisotropy decay of 9-PA is significantly faster compared to those of the ionic solutes FL and R110. Another point to be noted from the figure is that the anisotropy decays of FL and R110 are identical. The measured reorientation times (τ_r) of the three solutes in the five ionic liquids over the temperature range 298–348 K and the viscosities (η) of the solvents are given in the Supporting Information. The viscosities of these ionic liquids have been taken from our earlier publication.²⁶ The experimentally measured reorientation times have been analyzed within the framework of Stokes–Einstein–Debye (SED) hydrodynamic theory.^{27,28} According to the SED theory, the rotational diffusion of a solute molecule in a solvent continuum occurs by small step diffusion and the experimentally measurable quantity, the solute reorientation time, is related to the bulk viscosity of the solvent by

$$\tau_r = \frac{\eta V_h}{kT} \quad (1)$$

where k and T are the Boltzmann constant and absolute temperature, respectively. V_h is the hydrodynamic volume of the solute, which is a product of van der Waals volume (V), shape factor (f), and boundary condition parameter (C). A

brief description of how these parameters have been obtained from the SED hydrodynamic theory is given below.

The solute axial radii have been obtained from Corey–Pauling–Koltun scaled atomic models by treating them as asymmetric ellipsoids, and van der Waals volumes were calculated by Edward’s increment method.²⁹ Friction coefficients with slip and stick boundary conditions were estimated from the axial radii by interpolating the numerical tabulations available in literature.^{30,31} These friction coefficients, in turn, were used to calculate the diffusion coefficients with the aid of the Einstein relationship.³² It may be recalled that the expression for anisotropy $r(t)$ of an asymmetric ellipsoid contains at most five exponentials with five time constants.²⁷ However, no more than two reorientation times have ever been recovered from the experimentally measured anisotropy decays. The reason is the closely spaced nature of the five time constants, and for typical solutes such as the ones used in the present study, only one τ_r is sufficient to fit the experimentally measured anisotropy decays. Under such circumstances, the reorientation times can be obtained from the diffusion coefficients via the following relationship; the details have been described in literature:³³

$$\tau_r = \frac{1}{12} \left[\frac{4D_x + D_y + D_z}{D_x D_y + D_y D_z + D_z D_x} \right] \quad (2)$$

where D_x , D_y , and D_z are the diffusion coefficients along the three principal axes of rotation and eq 2 is derived under the assumption that the direction of the transition dipole coincides with the long symmetry axis of the solute molecule. The details of the calculation for the three solutes used in this study have been described in our earlier publications.^{13,17} Solute dimensions, van der Waals volume, shape factor, and boundary condition parameter (C_{slip}) for the three solutes have been calculated and are listed in Table 1. It is evident from the table

Table 1. Solute Dimensions, van der Waals Volumes, Shape Factors, and Boundary Condition Parameters Calculated from SED Hydrodynamic Theory

solute	axial radii/Å ³	$V/\text{Å}^3$	f	C_{slip}
9-PA	$5.7 \times 5.5 \times 1.8$	236	1.73	0.119
FL	$6.4 \times 5.5 \times 1.8$	267	1.93	0.139
R110	$6.7 \times 5.5 \times 1.8$	275	2.02	0.147

that the solutes 9-PA, FL, and R110 have similar dimensions and volumes, and as a consequence their shape factors and the boundary condition parameters are almost identical. In other words, the SED hydrodynamic theory predicts that the rotational diffusion of the three solute molecules should be similar.

To find out how the experimentally measured reorientation times match with the predictions of SED hydrodynamic theory, τ_r is plotted as a function of η/T in Figure 3 for the three solutes, along with the stick and slip lines. It can be noticed from the figure that rotational diffusion of the nonpolar solute 9-PA is faster by a factor of 3–4 compared to the ionic solutes FL and R110. Furthermore, the reorientation times of 9-PA in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides are closer to slip hydrodynamics, whereas the rotational diffusion of FL and R110 is more or less identical and follows stick predictions. Linear fits of log–log plots give the following

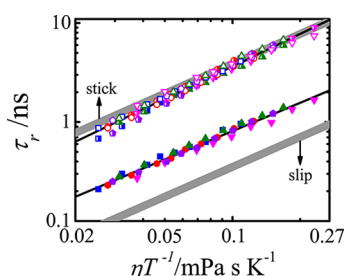


Figure 3. Plots of τ_r versus η/T for 9-PA (solid symbols), FL (open symbols), and R110 (half-open symbols) in [mmim⁺][Tf₂N⁻] (red), [emim⁺][Tf₂N⁻] (blue), [mpim⁺][Tf₂N⁻] (violet), [bmim⁺][Tf₂N⁻] (green), and [hmim⁺][Tf₂N⁻] (magenta). The lines passing through data points were obtained by fitting the data to nonlinear η/T relationships as described in the text. The SED slip line for 9-PA and stick line for FL and R110 are also shown in the figure.

relationships between τ_r and η/T for 9-PA and the two ionic solutes FL and R110:

$$\tau_r = (7.2 \pm 0.4)(\eta/T)^{0.95 \pm 0.02}$$

($N = 45$, $R = 0.990$) for 9-PA

$$\tau_r = (44.9 \pm 1.9)(\eta/T)^{1.09 \pm 0.02}$$

($N = 90$, $R = 0.991$) for FL and R110

In the above expressions, τ_r is in ns and η/T is in mPa s K⁻¹, and the parameters N and R represent the number of data points and the regression coefficient, respectively. To get a better appreciation of these results, the observed solute–solvent coupling constants of the three solutes in the five ionic liquids have been obtained from the experimentally measured reorientation times with the aid of SED hydrodynamic theory and are listed in Table 2. This information is displayed

Table 2. Boundary Condition Parameters of 9-PA, FL, and R110 in Five Ionic Liquids, Obtained from Measured Reorientation Times

ionic liquid	C_{obs}		
	9-PA	FL	R110
[mmim ⁺][Tf ₂ N ⁻]	0.28 ± 0.01	0.99 ± 0.08	0.83 ± 0.04
[emim ⁺][Tf ₂ N ⁻]	0.30 ± 0.01	0.91 ± 0.09	0.90 ± 0.03
[mpim ⁺][Tf ₂ N ⁻]	0.27 ± 0.01	0.90 ± 0.07	0.91 ± 0.02
[bmim ⁺][Tf ₂ N ⁻]	0.30 ± 0.01	0.90 ± 0.03	0.96 ± 0.06
[hmim ⁺][Tf ₂ N ⁻]	0.25 ± 0.01	0.94 ± 0.06	0.93 ± 0.07

pictorially in Figure 4 by plotting C_{obs} versus number of carbon atoms in the alkyl chain attached to the imidazolium ring. A quick glance at the table and figure reveals that there is no systematic variation in the C_{obs} values of the three solutes with an increase in the length of the alkyl chain on the imidazolium cation. This result is in complete contrast to what has been reported in literature so far.^{6,14,21} In other words, solute rotation is not influenced by the length of the alkyl chain on the imidazolium cation. The observed behavior has been rationalized by carrying out further analysis of the data.

The rotational diffusion of a nonpolar solute such as 9-PA depends not only on its size but also on the size of the solvent, and this aspect has been addressed in our earlier publication.¹³ Quasihydrodynamic theories of Gierer–Wirtz (GW)³⁴ and Dote–Kivelson–Schwartz (DKS)³⁵ have been used to account

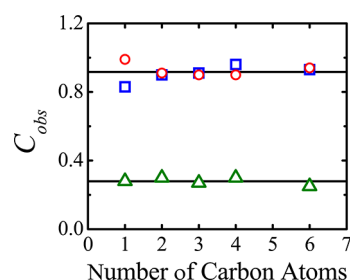


Figure 4. Plots of C_{obs} for 9-PA (Δ), FL (\circ), and R110 (\square) versus number of carbon atoms in the alkyl chain attached to the imidazolium cation of the ionic liquid. The lines passing through data points represent average values of C_{obs} . It can be noticed that there is almost no variation in C_{obs} for the three solutes with an increase in length of the alkyl chain attached to the imidazolium cation.

for the observed solvent size dependence on solute rotation.^{36–41} Since there is a 30% increase in van der Waals volume from [mmim⁺][Tf₂N⁻] to [hmim⁺][Tf₂N⁻], it will be interesting to find out how the boundary condition parameters of 9-PA calculated by the GW and DKS theories match with the experimental numbers. According to GW theory,³⁴ the solvent is made up of concentric shells of spherical particles surrounding the spherical solute molecule at the center. The boundary condition parameter C_{GW} is calculated by considering how the angular velocity of the solvent molecules in successive shells surrounding the solute decreases as a function of distance away from it. The expression for C_{GW} is given by

$$C_{\text{GW}} = \sigma C_0 \quad (3)$$

In eq 3, σ is the sticking factor, which is given by

$$\sigma = [1 + 6(V_s/V_p)^{1/3}C_0]^{-1} \quad (4)$$

and

$$C_0 = \left\{ \frac{6(V_s/V_p)^{1/3}}{[1 + 2(V_s/V_p)^{1/3}]^4} + \frac{1}{[1 + 4(V_s/V_p)^{1/3}]^3} \right\}^{-1} \quad (5)$$

In these equations, V_s and V_p are the volumes of the solvent and solute, respectively. When the ratio V_s/V_p is very small, the solvent becomes continuous and C_{GW} approaches unity, which is the SED equation with the stick boundary condition. van der Waals volumes of 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imides are given in Table 3. The van der Waals volumes of ionic liquids were obtained by addition of volumes of the individual cation and anion. However, a molecular dynamics simulation study⁴² indicates that the distribution of cations and anions about a medium-sized

Table 3. van der Waals Volumes of the Ionic Liquids and Boundary Condition Parameters Obtained via Hydrodynamic and Quasihydrodynamic Theories

ionic liquid	$V_s/\text{\AA}^3$	C_{slip}	C_{GW}	C_{DKS}^a
[mmim ⁺][Tf ₂ N ⁻]	275	0.119	0.157	0.077
[emim ⁺][Tf ₂ N ⁻]	292	0.119	0.154	0.074
[mpim ⁺][Tf ₂ N ⁻]	309	0.119	0.151	0.071
[bmim ⁺][Tf ₂ N ⁻]	326	0.119	0.148	0.068
[hmim ⁺][Tf ₂ N ⁻]	360	0.119	0.143	0.063

^aCalculated at 298 K.

organic solute is not random. In view of this scenario, the procedure adopted here to calculate the van der Waals volume of the ionic liquid is not rigorous. Moreover, because of the significant degree of order present in these systems due to ion–ion interactions, the applicability of concepts such as solvation shell and the utility of continuum models for the solvent are somewhat suspect. Nonetheless, in the absence of an alternative treatment, we have resorted to the methodology that has been applied in the case of conventional solvents. The C_{GW} values of 9-PA calculated in this manner, along with C_{slip} , are also given in Table 3. It can be noticed from the table that C_{GW} decreases by less than 10% from $[\text{mmim}^+][\text{Tf}_2\text{N}^-]$ to $[\text{hmim}^+][\text{Tf}_2\text{N}^-]$ and these numbers are higher by 20–30% compared to C_{slip} . This exercise confirms that the 30% increase in the size of the solvent from $[\text{mmim}^+][\text{Tf}_2\text{N}^-]$ to $[\text{hmim}^+][\text{Tf}_2\text{N}^-]$ has no influence on the rotation of 9-PA, which is consistent with the experimental findings. However, it may be noted that the absolute value of C_{GW} depends on the method used for estimation of V_s .

The other quasihydrodynamic model, proposed by Dote–Kivelson–Schwartz,³⁵ not only considers the solvent size but also incorporates the cavities or free spaces created by the solvent around the probe molecule while calculating the boundary condition. The boundary condition parameter is assumed to depend on the ratio of solute volume to total volume available for solute rotation. According to this theory, the solute–solvent coupling parameter C_{DKS} is given by

$$C_{\text{DKS}} = (1 + \gamma/\phi)^{-1} \quad (6)$$

where γ/ϕ is a measure of the ratio of the free volume of solvent to the effective size of the solute molecule, with

$$\gamma = \frac{\Delta V}{V_p} \left[4 \left(\frac{V_p}{V_s} \right)^{2/3} + 1 \right] \quad (7)$$

and ϕ is the ratio of the rotation time predicted by slip hydrodynamics to the stick prediction for a sphere of the same volume or essentially ϕ is a product of fC_{slip} . ΔV is the smallest volume of free space per solvent molecule and is empirically related to viscosity, the Hilderbrand–Batschinski parameter B , and also the isothermal compressibility k_T of the solvent:

$$\Delta V = Bk_T\eta kT \quad (8)$$

However, Anderton and Kauffman³⁸ suggested that the Frenkel hole theory and the Hilderbrand treatment of solvent viscosity were developed for simple liquids. Thus, eq 8 is not a valid measure of the free space per solvent molecule for highly associative solvents such as the ionic liquids used in the present study. For associative liquids, ΔV can be calculated by³⁸

$$\Delta V = V_m - V_s \quad (9)$$

where V_m is the ratio of solvent molar volume and the Avogadro number. It may be noted that molar volume of a liquid depends on its density, which decreases with temperature. Thus, ΔV and consequently C_{DKS} are also dependent on temperature. C_{DKS} values of 9-PA calculated from eq 6 at 298 K are also listed in Table 3, and it can be noticed from the table that there is a 20% decrease in these numbers from $[\text{mmim}^+][\text{Tf}_2\text{N}^-]$ to $[\text{hmim}^+][\text{Tf}_2\text{N}^-]$. Moreover, they are a factor of 4 lower compared to C_{obs} , which is an indication that DKS theory is not successful in explaining the observed behavior.

Although they are structurally similar in size and shape, rotational diffusion of ionic solutes FL and R110 is significantly slower compared to that of the nonpolar solute 9-PA. The observed behavior is a consequence of specific interactions between the ionic solutes and the constituent ions of the ionic liquids, and this aspect has been well-established. However, the important finding from the study is that there is no change in the rotational diffusion of both solutes from $[\text{mmim}^+][\text{Tf}_2\text{N}^-]$ to $[\text{hmim}^+][\text{Tf}_2\text{N}^-]$, which is surprising given that there is a significant increase in the length of the alkyl chain on the imidazolium cation. As already mentioned in the Introduction, Fruchey and Fayer⁶ have observed a 25% increase in C_{obs} values of a triply charged anionic solute MPTS in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, which has been rationalized on the basis of increased size of the imidazolium cations that are bound to the three sulfonate groups of the solute. It may be noted that the increase is not uniform: from $[\text{emim}^+]$ to $[\text{bmim}^+]$, C_{obs} increases by a mere 6%, but from $[\text{bmim}^+]$ to $[\text{hmim}^+]$, the enhancement is 17%. In the same vein, we have noticed that C_{obs} values of R110 increase by 32% in 1-alkyl-3-methylimidazolium tris-(pentafluoroethyl)trifluorophosphate ionic liquids, although the solute experiences specific interactions with FAP anion of the ionic liquids.¹⁴ Even in the case of R110, the increase in C_{obs} is not uniform: 27% from $[\text{emim}^+]$ to $[\text{bmim}^+]$ and a negligible 4% from $[\text{bmim}^+]$ to $[\text{hmim}^+]$. These examples along with results obtained in the present work illustrate that the solventberg model is perhaps not suitable for explaining the specific solute–solvent interactions in a quantitative manner.

Recent work from our laboratory^{16,17} addressed the importance of understanding specific solute–solvent interactions in terms of solute–solvent interaction strengths by considering hydrogen-bond acidities and basicities of the ionic liquids. The anionic solute FL and the cationic solute R110 experience specific interactions with the imidazolium cation and $[\text{Tf}_2\text{N}^-]$ anion, respectively. Since FL and R110 are hydrogen bond accepting and donating solutes, respectively, their rotation is governed by the corresponding hydrogen-bond acidity and basicity of the ionic liquid. Thus, to assimilate the experimental results, Kamlet–Taft acidity (α) and basicity (β) parameters for 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imides have been considered. According to the data available in literature,⁴³ as the length of the alkyl chain increases, from ethyl to hexyl in the case of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, α decreases marginally from 0.71 to 0.65, whereas β increases from 0.23 to 0.26. Essentially, this implies that the hydrogen bond donating and accepting abilities of these ionic liquids more or less remain the same with an increase in the length of the alkyl chain on the imidazolium cation, and as a consequence there is no variation in the solute–solvent interaction strength. Thus, C_{obs} values of the ionic solutes FL and R110 remain invariant from $[\text{mmim}^+][\text{Tf}_2\text{N}^-]$ to $[\text{hmim}^+][\text{Tf}_2\text{N}^-]$. This aspect can be further examined by undertaking similar studies in imidazolium-based bis(trifluoromethylsulfonyl)imides with longer alkyl chains from octyl to octadecyl derivatives, as the domain structure is likely to play a role on the rotational diffusion of solute molecules, and efforts are underway for carrying out such measurements.

Another observation that needs some discussion is the almost identical rotational reorientation times obtained for the anionic solute FL and the cationic solute R110, even though the hydrogen-bond acidities of 1-alkyl-3-methylimidazolium bis-

(trifluoromethylsulfonyl)imides are higher compared to their hydrogen-bond basicities. A similar pattern has been noticed for FL and R110 in a protic ionic liquid, *n*-propylammonium nitrate,¹⁷ which also possesses a higher α than β . It may be noted that the strength of the solute–solvent interaction depends not only on the α and β of the ionic liquids but also on the respective hydrogen bond accepting and donating abilities of FL and R110. Thus, the experimental trends in conjunction with α and β parameters available for the ionic liquids used in the study are probably an indication that FL is a weak hydrogen-bond acceptor, whereas R110 a strong hydrogen-bond donor. Another possible explanation for the observed identical rotational diffusion of FL and R110 in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides could be the strong electrostatic interactions of comparable strength between the ionic solutes and the constituent ions of the ionic liquids. In other words, the strength of strong ion–ion interactions between anionic solute FL and imidazolium cation and also that between cationic solute R110 and bis(trifluoromethylsulfonyl)imide anion is similar. This hypothesis can be verified by carrying out rotational diffusion studies involving nonionic but hydrogen-bonding solutes in a homologous series of ionic liquids.

CONCLUSIONS

Rotational diffusion studies involving three structurally similar solutes in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides indicate that solute rotation is not influenced by the length of the alkyl chain on the imidazolium cation. Reorientation times of the nonpolar solute 9-PA are closer to the predictions of slip boundary condition, and C_{obs} values are independent of the solvent size. Analysis of the experimental results by Gierer–Wirtz quasihydrodynamic theory reveals that a 30% increase in the size of solvent from [mmim⁺][Tf₂N[−]] to [hmim⁺][Tf₂N[−]] has no bearing on the rotation of 9-PA. In contrast to the nonpolar solute, rotational diffusion of ionic solutes FL and R110 is significantly slower and follows stick hydrodynamics as a consequence of specific interactions between the solutes and constituents of the ionic liquids. The effect of alkyl chain length on solute rotation is not apparent even in the case of hydrogen-bonding ionic solutes. Lack of variation in the hydrogen-bond acidities and basicities across the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide series appears to be responsible for the observed behavior. Alternatively, ion–ion interactions of comparable strength between the ionic solutes and constituent ions of the ionic liquids could be the reason for the observed behavior.

ASSOCIATED CONTENT

Supporting Information

Five tables listing reorientation times of 9-PA, FL, and R110 in the five ionic liquids and the viscosities of these ionic liquids as a function of temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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