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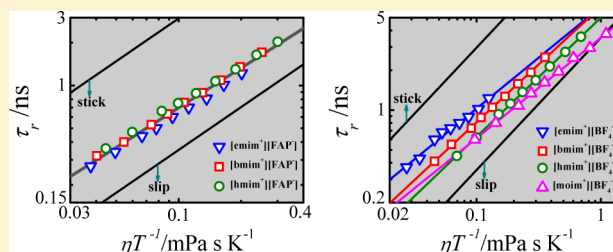
Fluorescence Anisotropy of a Nonpolar Solute in 1-Alkyl-3-Methylimidazolium-Based Ionic Liquids: Does the Organized Structure of the Ionic Liquid Influence Solute Rotation?

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S Supporting Information

ABSTRACT: Temperature-dependent fluorescence anisotropies of a nonpolar solute 9-phenylanthracene (9-PA) have been measured in 1-alkyl-3-methylimidazolium-based ionic liquids with anions such as bis(trifluoromethylsulfonyl)imide ($[\text{Tf}_2\text{N}^-]$), tris(pentafluoroethyl)trifluorophosphate ($[\text{FAP}^-]$), tetrafluoroborate ($[\text{BF}_4^-]$), and hexafluorophosphate ($[\text{PF}_6^-]$) to find out if the organized structure of the ionic liquid has a bearing on solute rotation. Analysis of the experimental data using the Stokes–Einstein–Debye hydrodynamic theory indicates that there is no significant variation in the solute–solvent coupling constants (C_{obs}) with an increase in the length of the alkyl chain on the imidazolium cation for the ionic liquids with $[\text{Tf}_2\text{N}^-]$ and $[\text{FAP}^-]$ anions. However, in the case of ionic liquids with $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ anions, the rotation of 9-PA for a given viscosity at constant temperature becomes progressively faster and C_{obs} decreases by a factor of 2.4 from ethyl to octyl derivatives. Quasihydrodynamic theories of Gierer–Wirtz and Dote–Kivelson–Schwartz could not account for the significant decrease in the C_{obs} values. The observed behavior has been rationalized in terms of the organized structure of the ionic liquids having $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ anions, which results as a consequence of the high charge-to-size ratio of these anions compared to $[\text{Tf}_2\text{N}^-]$ and $[\text{FAP}^-]$.



INTRODUCTION

Ionic liquids, as their name implies, are composed of ions and are in liquid state at ambient temperature. Due to their negligible vapor pressure, they are being used as green alternatives to volatile organic solvents in catalysis, synthesis, as well as in many other fields of chemistry.^{1–3} Besides low vapor pressure, ionic liquids also display interesting physicochemical properties as a consequence of numerous interactions prevailing between the cations and anions. The presence of long alkyl chains on one of the ions and the ensuing van der Waals interactions in addition to the Coulombic and hydrogen bonding interactions between the constituent ions lead to the formation of organized structure. Molecular dynamics simulations indicate that the organized structure can be considered as a three-dimensional network comprising aggregation of alkyl chains in nonpolar domains and ionic channels formed by the anions and cations.^{4–7} Such an organized structure is known to cause dynamic heterogeneity in fast processes, which can be defined as the distribution of relaxation rates due to molecules residing in distinct environments of the ionic liquids.^{4,8,9}

Solute rotation is one of the fast processes that has been extensively investigated in ionic liquids by us^{10–16} as well as others.^{9,17–28} From recent studies, it has become evident that the length of the alkyl chain attached to one of the constituents of the ionic liquid significantly affects solute rotation;^{21,24,25} however, exceptions to this trend have also been reported.^{12,16}

These results assume importance, since the presence of long alkyl chains on one of the ions of the ionic liquid facilitates the formation of organized structures. In other words, these studies can be used to gauge how the organized structure of the ionic liquids influences dynamical processes. Recently, Khara and Samanta²⁴ have carried out fluorescence anisotropy measurements of a dipolar solute coumarin 153 (C153) in a series of *N*-alkyl-*N*-methylmorpholinium bis(trifluoromethylsulfonyl)imides and found that, for a given viscosity at constant temperature (η/T), the solute rotation becomes faster from ethyl to octyl derivatives. The observed result has been rationalized on the basis of the organized domain structure of these ionic liquids, which offers lower microviscosity to the rotating solute molecule. On the basis of excitation wavelength and temperature-dependent studies, it was also concluded that *N*-alkyl-*N*-methylmorpholinium ionic liquids are more structured and heterogeneous compared to imidazolium-based ionic liquids. Similar studies have been performed by Fruchey and Fayer,²¹ using a nonpolar solute perylene in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, and it has been noticed that, for a given η/T , the solute rotation becomes faster from ethyl to octyl derivatives. However, this result has been explained on the basis of a perylene molecule

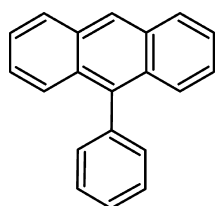
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experiencing an alkane-like environment with an increase in the length of the alkyl chain. In contrast, our results indicate that there is no significant variation in the rotational diffusion of another nonpolar solute, 9-phenylanthracene (9-PA), in the same series of ionic liquids where methyl to hexyl derivatives have been employed.¹⁶ For a given η/T , faster rotation of the solute has been noticed upon the variation of the alkyl chain length from ethyl to octyl on the anion of the ionic liquids as well.^{25,26} It may be noted that the examples discussed here are merely illustrative and by no means exhaustive.

From the results portrayed in the preceding paragraph, however, it is not conclusive whether the organized structure of the ionic liquid or the increasingly nonpolar environment is responsible for the observed behavior. Thus, to address this issue, the present study has been undertaken, wherein temperature-dependent fluorescence anisotropies of the nonpolar solute 9-PA (Figure 1 gives the molecular structure of the



9-Phenylanthracene

Figure 1. Molecular structure of the solute.

solute) have been measured in 1-alkyl-3-methylimidazolium ($[\text{Rmim}^+]$) based ionic liquids with anions such as bis(trifluoromethylsulfonyl)imide ($[\text{Tf}_2\text{N}^-]$), tris(pentafluoroethyl)trifluorophosphate ($[\text{FAP}^-]$), tetrafluoroborate ($[\text{BF}_4^-]$), and hexafluorophosphate ($[\text{PF}_6^-]$). In the case of ionic liquids with $[\text{Tf}_2\text{N}^-]$ and $[\text{FAP}^-]$ anions, ethyl, butyl, and hexyl derivatives have been employed, whereas, for ionic liquids involving $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ anions, octyl derivatives have also been used. The present work will also address the influence of the anion and how the resulting association with the cation of the ionic liquid affects the rotational diffusion of a nonpolar solute molecule.

EXPERIMENTAL SECTION

1-Alkyl-3-methylimidazolium ionic liquids with $[\text{Tf}_2\text{N}^-]$, $[\text{BF}_4^-]$, and $[\text{PF}_6^-]$ anions were purchased from io-li-tec, whereas ionic liquids containing $[\text{FAP}^-]$ anions were obtained from Merck. The stated purity of the ionic liquids is >99% with <100 ppm water content and <100 ppm halide ion concentration. The 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. The ionic liquids and 9-PA are of the highest available purity and were used without further purification. Concentrations of 9-PA in ionic liquids were chosen such that the absorbance is in the range 0.1–0.2 at the wavelength of excitation. Viscosities of the ionic liquids were measured as a function of temperature using a Physica MCR 101 rheometer, and the uncertainties on the measured numbers are about 5%. Appropriate precautions have been taken to ensure the prevention of absorption of water during sample preparation, fluorescence

experiments, and viscosity measurements by the ionic liquids with $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ anions, which are hygroscopic by nature.

Time-resolved fluorescence measurements were carried out with a setup that works on the principle of time-correlated single-photon counting.²⁹ The setup used in the present study was purchased from IBH, U.K., and employs a diode laser as the excitation source. The instrumental details have been described in our earlier publication.¹² 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. The decays were collected in 4096 channels with a time increment of 13.8 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 150 ps. For lifetime measurements, decays were collected by keeping the emission polarizer at magic angle (54.7°) with respect to the polarization of the excitation laser to ensure the 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; only in the case of $[\text{emim}^+][\text{PF}_6^-]$ the decays were measured in the range 338–358 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. The analyses of fluorescence and anisotropy decays were performed using the software supplied by IBH.

RESULTS AND DISCUSSION

The reorientation times (τ_r) of 9-PA in all the ionic liquids investigated in this work have been obtained by fitting the measured anisotropy decays to a single exponential function of the form described by the following equation.

$$r(t) = r_0 \exp(-t/\tau_r) \quad (1)$$

where r_0 is the limiting anisotropy, whose magnitude is determined by the angle between absorption and emission transition dipoles of the solute molecule. The reorientation times of 9-PA in 1-alkyl-3-methylimidazolium-based ionic liquids having $[\text{Tf}_2\text{N}^-]$, $[\text{FAP}^-]$, $[\text{BF}_4^-]$, and $[\text{PF}_6^-]$ anions at various temperatures along with their viscosities are reported in the Supporting Information. Only in the case of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, data has been taken from our earlier work.¹⁶ The uncertainties on the reorientation times are in the range 5–10%. Stokes–Einstein–Debye (SED) hydrodynamic theory^{30,31} has been employed to analyze the experimental results. The SED theory is based on the presumption that the rotation of a solute molecule dissolved in a solvent continuum takes place by a small-step diffusion, and its reorientation time is proportional to the viscosity of the fluid at a given temperature. The solute properties that govern the rotation are its size and shape, which are expressed in terms of van der Waals volume, V , and shape factor, f . These parameters are incorporated into the SED model by

treating the solute as a symmetric or an asymmetric ellipsoid.³² In addition to the above-mentioned parameters, the coupling between the solute and the solvent also plays an important role in controlling the rotational diffusion of a solute molecule. In the SED model, the magnitude of the solute–solvent coupling parameter or the boundary condition parameter, which is usually denoted by C , depends on the axial ratio of the solute molecule and the two limiting cases are the hydrodynamic stick and slip.³³ Thus, the expression for τ_r is given by

$$\tau_r = \frac{VfC}{k} \left(\frac{\eta}{T} \right) \quad (2)$$

where k is the Boltzmann constant. According to SED theory, τ_r for a particular solute molecule is proportional to η/T . To apply the SED theory, the solute molecule used in the present study, 9-PA, has been treated as an asymmetric ellipsoid. Its shape factor and boundary condition parameter were calculated, and the details have been described in our earlier publication.¹¹ The calculated values for f and C_{slip} are 1.73 and 0.12, respectively.

Typical anisotropy decays of 9-PA in [hmim⁺][BF₄[−]] and [moim⁺][BF₄[−]] and also in [hmim⁺][PF₆[−]] and [moim⁺][PF₆[−]] at 298 K are displayed in Figure 2. It can be noticed

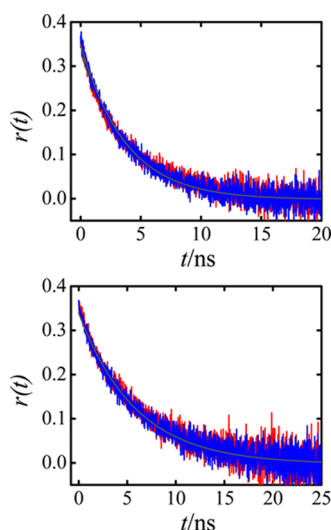


Figure 2. Anisotropy decays of 9-PA in [hmim⁺][BF₄[−]] (blue) and [moim⁺][BF₄[−]] (red) (top) and [hmim⁺][PF₆[−]] (blue) and [moim⁺][PF₆[−]] (red) (bottom) at 298 K together with the fitted curves. The anisotropy decays of 9-PA are almost identical in hexyl and octyl derivatives of the ionic liquids despite the octyl derivatives having significantly higher viscosities compared to the hexyl derivatives in both the cases.

from the figure that the anisotropy decays of 9-PA in [hmim⁺][BF₄[−]] and [moim⁺][BF₄[−]] are identical despite the octyl derivative having significantly higher viscosity compared to the hexyl derivative and a similar result has been obtained in the case of ionic liquids with [PF₆[−]] anion. Thus, these results are in conflict with the predictions of the SED theory. To understand these results in totality, τ_r is plotted as a function of η/T in Figure 3 for ionic liquids with [Tf₂N[−]] and [FAP[−]] anions and Figure 4 depicts similar plots for ionic liquids having [BF₄[−]] and [PF₆[−]] anions. It is evident from Figure 3 that there

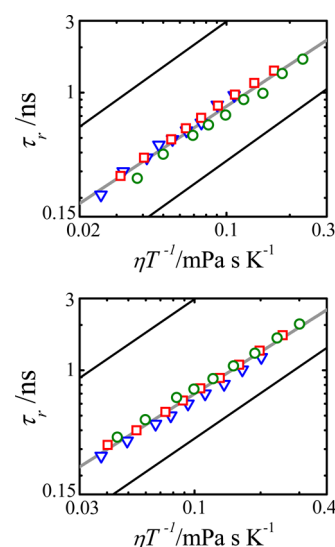


Figure 3. Plots of τ_r versus η/T for 9-PA in [emim⁺][Tf₂N[−]] (▽), [bmim⁺][Tf₂N[−]] (□), and [hmim⁺][Tf₂N[−]] (○) (top) and [emim⁺][FAP[−]] (▽), [bmim⁺][FAP[−]] (□), and [hmim⁺][FAP[−]] (○) (bottom). The lines passing through data points were obtained by fitting the data to nonlinear η/T relationships as described in the text. It can be noticed from these plots that the rotation of 9-PA is not influenced by the length of the alkyl chain on the imidazolium cation for [Tf₂N[−]] as well as [FAP[−]] series. The SED slip and stick lines for 9-PA are also shown in the plots.

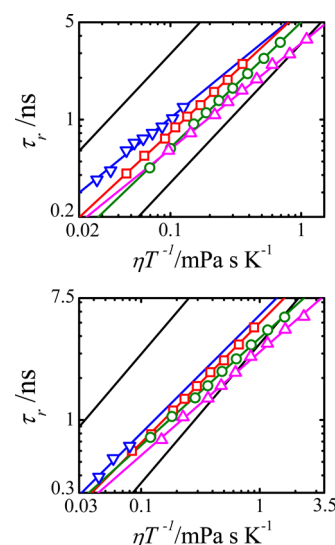


Figure 4. Plots of τ_r versus η/T for 9-PA in [emim⁺][BF₄[−]] (▽), [bmim⁺][BF₄[−]] (□), [hmim⁺][BF₄[−]] (○), and [moim⁺][BF₄[−]] (△) (top) and [emim⁺][PF₆[−]] (▽), [bmim⁺][PF₆[−]] (□), [hmim⁺][PF₆[−]] (○), and [moim⁺][PF₆[−]] (△) (bottom). The lines passing through data points were obtained by fitting the data to nonlinear η/T relationships as described in the text. It can be noticed from these plots that the rotation of 9-PA at a given η/T becomes progressively faster with an increase in the length of the alkyl chain on the imidazolium cation for [BF₄[−]] as well as [PF₆[−]] series. The SED slip and stick lines for 9-PA are also shown in the plots.

is no discernible variation in the rotational diffusion of 9-PA from ethyl to hexyl derivatives of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides. A similar result has

been obtained in the case of ionic liquids with [FAP[−]] anion. Linear least-squares fits of log–log plots give the following

$$9\text{-PA}/[\text{Rmim}^+][\text{TF}_2\text{N}^-] \quad \tau_r = (6.8 \pm 0.6)(\eta/T)^{0.92 \pm 0.03} \quad (N = 27, R = 0.986)$$

$$9\text{-PA}/[\text{Rmim}^+][\text{FAP}^-] \quad \tau_r = (5.9 \pm 0.3)(\eta/T)^{0.93 \pm 0.02} \quad (N = 27, R = 0.992)$$

In these 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 regression coefficient, respectively. To get a better appreciation of these results, solute–solvent coupling constants (C_{obs}) have been obtained from the measured reorientation times using eq 2 and they are listed in Tables 1 and 2, respectively, for

Table 1. van der Waals Volumes of 1-Alkyl-3-Methylimidazolium Bis(trifluoromethylsulfonyl)imides Together with C_{obs} and the Boundary Condition Parameters Calculated Using Quasihydrodynamic Theories for 9-PA

ionic liquid	$V_s/\text{\AA}^3$	C_{obs}	C_{GW}	C_{DKS}^a
[emim ⁺][TF ₂ N [−]]	292	0.30 ± 0.01	0.154	0.074
[bmim ⁺][TF ₂ N [−]]	326	0.30 ± 0.01	0.148	0.068
[hmim ⁺][TF ₂ N [−]]	360	0.25 ± 0.01	0.143	0.063

^aCalculated at 298 K.

[Rmim⁺][TF₂N[−]] and [Rmim⁺][FAP[−]]. It can be noticed from the tables that C_{obs} decreases by 20% from [emim⁺][TF₂N[−]] to [hmim⁺][TF₂N[−]] and increases by a meager 14% from [emim⁺][FAP[−]] to [hmim⁺][FAP[−]]. These observations essentially indicate that there is no significant variation in the

relationships between τ_r and η/T for 9-PA in [Rmim⁺][TF₂N[−]] and [Rmim⁺][FAP[−]].

Table 2. van der Waals Volumes of 1-Alkyl-3-Methylimidazolium Tris(pentafluoroethyl)trifluorophosphates Together with C_{obs} and the Boundary Condition Parameters Calculated Using Quasihydrodynamic Theories for 9-PA

ionic liquid	$V_s/\text{\AA}^3$	C_{obs}	C_{GW}	C_{DKS}^a
[emim ⁺][FAP [−]]	376	0.22 ± 0.01	0.141	0.070
[bmim ⁺][FAP [−]]	410	0.24 ± 0.01	0.138	0.065
[hmim ⁺][FAP [−]]	444	0.25 ± 0.02	0.134	0.061

^aCalculated at 298 K.

environment experienced by the solute 9-PA from ethyl to hexyl derivatives of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as well as tris(pentafluoroethyl)-trifluorophosphate.

In contrast, inspection of Figure 4 reveals that, for a given η/T , rotational diffusion of 9-PA becomes progressively faster from ethyl to octyl derivatives of 1-alkyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate. Linear least-squares fits of log–log plots give the following relationships between τ_r and η/T for 9-PA in [Rmim⁺][BF₄[−]] and [Rmim⁺][PF₆[−]].

$$9\text{-PA}/[\text{emim}^+][\text{BF}_4^-] \quad \tau_r = (6.0 \pm 0.6)(\eta/T)^{0.77 \pm 0.03} \quad (N = 9, R = 0.993)$$

$$9\text{-PA}/[\text{bmim}^+][\text{BF}_4^-] \quad \tau_r = (6.1 \pm 0.1)(\eta/T)^{0.87 \pm 0.01} \quad (N = 9, R = 0.999)$$

$$9\text{-PA}/[\text{hmim}^+][\text{BF}_4^-] \quad \tau_r = (5.0 \pm 0.1)(\eta/T)^{0.90 \pm 0.01} \quad (N = 9, R = 0.999)$$

$$9\text{-PA}/[\text{moim}^+][\text{BF}_4^-] \quad \tau_r = (3.5 \pm 0.1)(\eta/T)^{0.76 \pm 0.01} \quad (N = 9, R = 0.999)$$

$$9\text{-PA}/[\text{emim}^+][\text{PF}_6^-] \quad \tau_r = (5.7 \pm 1.8)(\eta/T)^{0.85 \pm 0.13} \quad (N = 3, R = 0.988)$$

$$9\text{-PA}/[\text{bmim}^+][\text{PF}_6^-] \quad \tau_r = (4.98 \pm 0.06)(\eta/T)^{0.86 \pm 0.01} \quad (N = 9, R = 0.999)$$

$$9\text{-PA}/[\text{hmim}^+][\text{PF}_6^-] \quad \tau_r = (3.87 \pm 0.03)(\eta/T)^{0.77 \pm 0.01} \quad (N = 9, R = 0.999)$$

$$9\text{-PA}/[\text{moim}^+][\text{PF}_6^-] \quad \tau_r = (3.08 \pm 0.04)(\eta/T)^{0.74 \pm 0.01} \quad (N = 9, R = 0.999)$$

It can be noticed that the relationships between τ_r and η/T are nonlinear and such a behavior has been attributed to heterogeneity of the ionic liquids, which leads to the viscosity–diffusion decoupling especially in highly viscous ionic liquids. These aspects have been extensively discussed in the literature.^{24,28} However, a systematic analysis of the data needs to be carried out before the observed behavior can be attributed to the heterogeneity of the medium in the present case. Tables 3 and 4 list the C_{obs} values for 9-PA in the two series of ionic liquids, and it can be noticed from the tables that C_{obs} decreases by a factor of 2.4 from ethyl to octyl derivatives of [Rmim⁺][BF₄[−]] as well as [Rmim⁺][PF₆[−]]. These results indicate that, unlike in [Rmim⁺][TF₂N[−]] and [Rmim⁺][FAP[−]], the

Table 3. van der Waals Volumes of 1-Alkyl-3-Methylimidazolium Tetrafluoroborates Together with C_{obs} and the Boundary Condition Parameters Calculated Using Quasihydrodynamic Theories for 9-PA

ionic liquid	$V_s/\text{\AA}^3$	C_{obs}	C_{GW}	C_{DKS}^a
[emim ⁺][BF ₄ [−]]	180	0.39 ± 0.05	0.179	0.100
[bmim ⁺][BF ₄ [−]]	214	0.26 ± 0.02	0.170	0.086
[hmim ⁺][BF ₄ [−]]	248	0.20 ± 0.01	0.162	0.077
[moim ⁺][BF ₄ [−]]	282	0.16 ± 0.03	0.155	0.070

^aCalculated at 298 K.

Table 4. van der Waals Volumes of 1-Alkyl-3-Methylimidazolium Hexafluorophosphates Together with C_{obs} and the Boundary Condition Parameters Calculated Using Quasihydrodynamic Theories for 9-PA

ionic liquid	$V_s/\text{\AA}^3$	C_{obs}	C_{GW}	C_{DKS}^a
[emim ⁺][PF ₆ [−]]	214	0.29 ± 0.02	0.170	0.110
[bmim ⁺][PF ₆ [−]]	248	0.20 ± 0.02	0.162	0.091
[hmim ⁺][PF ₆ [−]]	282	0.16 ± 0.03	0.155	0.082
[moim ⁺][PF ₆ [−]]	316	0.12 ± 0.03	0.150	0.073

^aCalculated at 298 K and only in the case of [emim⁺][PF₆[−]] it is at 338 K.

environment experienced by 9-PA is altered substantially upon increasing the length of the alkyl chain on the imidazolium cation for [Rmim⁺][BF₄[−]] and [Rmim⁺][PF₆[−]]. It may be argued that, in the case of bis(trifluoromethylsulfonyl)-imides and tris(pentafluoroethyl)trifluorophosphates, only ethyl to hexyl derivatives were employed, whereas, for tetrafluoroborates and hexafluorophosphates, ethyl to octyl derivatives have been used. However, a close scrutiny of Tables 3 and 4 indicates that, even from ethyl to hexyl derivatives, C_{obs} decreases by a factor of 2.0 and 1.8 in the case of tetrafluoroborates and hexafluorophosphates, respectively. Figure 5 gives plots of C_{obs} versus number of carbon atoms in

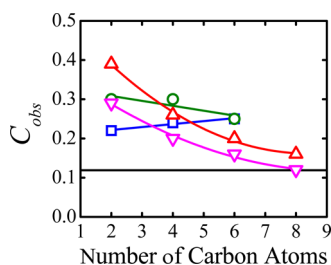


Figure 5. Plots of C_{obs} for 9-PA versus number of carbon atoms in the alkyl chain attached to the imidazolium cation of the ionic liquid. The symbols ○, □, △, and ▽ are for [Tf₂N[−]], [FAP[−]], [BF₄[−]], and [PF₆[−]] series, respectively, and the lines connecting the points represent the trends in their variation. The slip line is also shown in the figure for comparison.

the alkyl chain attached to the imidazolium cation of the ionic liquid, and it can be noticed that the variation is negligible in the case of [Rmim⁺][Tf₂N[−]] and [Rmim⁺][FAP[−]], while it is sizable for [Rmim⁺][BF₄[−]] and [Rmim⁺][PF₆[−]].

It may be noted that an increase in the length of the alkyl chain on the imidazolium cation leads to an enhancement in the van der Waals volume of the ionic liquid. Tables 1–4 list the van der Waals volumes (V_s) of the ionic liquids employed in this study. The van der Waals volumes of ionic liquids were obtained by the addition of the volumes of the individual cations and anions. The procedure adopted here to calculate the van der Waals volumes of the ionic liquids is not rigorous, since the distribution of cations and anions about a medium sized organic solute is not random.³⁴ 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. It must further be noted that the van der Waals volumes obtained in this manner especially for molecules

with long alkyl chains may not be very accurate. Nonetheless, in the absence of an alternative treatment, the methodology employed here is reasonably satisfactory. It can be noticed from the tables that V_s increases by 20% from ethyl to hexyl derivatives in the case of [Rmim⁺][Tf₂N[−]] and [Rmim⁺][FAP[−]], whereas it increases by about 50% from ethyl to octyl derivatives of [Rmim⁺][BF₄[−]] and [Rmim⁺][PF₆[−]]. Even though the solute–solvent boundary condition parameter depends solely on the axial ratio of the solute molecule according to the SED theory, some of the experimental results obtained in this work do not conform to this trend. Thus, quasihydrodynamic theories of Gierer–Wirtz (GW)³⁵ and Dote–Kivelson–Schwartz (DKS)³⁶ which incorporate the size of the solute as well as the solvents to calculate the boundary condition parameters have been considered. These theories have been successful in explaining the influence of solvent size on solute rotation in the case of conventional solvents qualitatively.^{37–42} For the 9-PA/ionic liquid combinations employed in the present study, the boundary condition parameters have been calculated with the aid of GW and DKS theories.

The boundary condition parameter C_{GW} according to Gierer–Wirtz quasihydrodynamic theory is given by the following equation³⁵

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

where the parameters σ and C_0 are given by eqs 4 and 5, respectively.

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

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

Tables 1–4 list the C_{GW} values calculated using eqs 3–5 for the systems used in this work. It can be noticed from Tables 3 and 4 that a decrease of 15 and 13% has been noticed in the C_{GW} values from ethyl to octyl derivatives of [Rmim⁺][BF₄[−]] and [Rmim⁺][PF₆[−]], respectively. Thus, the GW theory fails to account for the significant decrease in the C_{obs} values obtained from ethyl to octyl derivatives of [Rmim⁺][BF₄[−]] and [Rmim⁺][PF₆[−]].

In an attempt to find out if the experimentally observed trends can at least be mimicked in a qualitative manner, Dote–Kivelson–Schwartz quasihydrodynamic theory has also been applied. The boundary condition parameter C_{DKS} has been calculated using the following equations.³⁶

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

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

with $\phi = fC_{\text{slip}}$ and ΔV , the free volume. For associative liquids, ΔV is given by³⁹

$$\Delta V = V_m - V_s \quad (8)$$

where V_m is the ratio of solvent molar volume and the Avogadro number. It may be noted that C_{DKS} is a temperature-dependent parameter, since molar volume depends on density, which in turn decreases with temperature. C_{DKS} values calculated using eqs 6–8 at 298 K are given in Tables 1–4. It is evident from Tables 3 and 4 that a decrease of 44 and 50%

has been noticed in the C_{DKS} values from ethyl to octyl derivatives of $[\text{Rmim}^+][\text{BF}_4^-]$ and $[\text{Rmim}^+][\text{PF}_6^-]$, respectively. Thus, DKS theory mimics the experimental trends in a superior manner compared to the GW model, especially the large decrease in the C_{obs} values obtained from ethyl to octyl derivatives of $[\text{Rmim}^+][\text{BF}_4^-]$ and $[\text{Rmim}^+][\text{PF}_6^-]$. However, even the DKS theory fails to account for the factor of 2.4 decrease noticed in the C_{obs} values of 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates.

From the analysis carried out so far, it is evident that neither the hydrodynamic nor the quasihydrodynamic theories are able to explain the rotational diffusion of 9-PA in 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates. What is the reason for the observed behavior? As mentioned in the Introduction, ionic liquids are known to form organized structures and the solute molecule 9-PA is experiencing an environment that cannot be characterized by the bulk viscosity of the ionic liquid. In other words, the friction sensed by 9-PA decreases with an increase in the length of the alkyl chain on the imidazolium cation, which is predominantly due to the organized domains formed by the ionic liquids. The present study has been carried out in 1-alkyl-3-methylimidazolium-based ionic liquids with four different anions ($[\text{Tf}_2\text{N}^-]$, $[\text{FAP}^-]$, $[\text{BF}_4^-]$, and $[\text{PF}_6^-]$). However, only in the case of ionic liquids having $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ anions, rotational diffusion of 9-PA for a given η/T becomes progressively faster upon increasing the alkyl chain length. This observation clearly indicates that the anion of the ionic liquid also plays an important role in the formation of the organized structure. Since $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ anions are relatively smaller compared to $[\text{Tf}_2\text{N}^-]$ and $[\text{FAP}^-]$, they possess a higher charge-to-size ratio. It is this high charge-to-size ratio of $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ ions that facilitates stronger association with the cation of the ionic liquid and thus leads to the formation of organized domain structure. It may be noted that cation tails of pyrrolidinium-based ionic liquids with long alkyl chains also exhibit aggregation behavior similar to imidazolium-based ionic liquids. The alkyl chain segregation is attributed to electrostatic interactions between polar groups and van der Waals forces of the nonpolar alkyl chains.⁴³ Another point that needs some attention is the systematically higher C_{obs} values obtained in the case of $[\text{Rmim}^+][\text{BF}_4^-]$ compared to $[\text{Rmim}^+][\text{PF}_6^-]$ (see Tables 3 and 4). When organized domains are formed as in the case of ionic liquids with $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ ions, solute rotation is no longer governed by the bulk viscosity of the medium. Instead, the domain size and the packing of the polar and nonpolar groups in these organized structures are probably responsible for the friction experienced by the solute molecule. However, in the absence of these structural details, it is difficult to pinpoint the reasons for the observed behavior.

At this juncture, it is worth discussing these observations in the context of similar results available in the literature. As mentioned earlier, Fruchey and Fayer²¹ observed nearly 50% decrease in the C_{obs} values of a nonpolar solute, perylene in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, whereas such a dramatic decrease has not been noticed in the case of 9-PA. However, a close inspection of both the data sets reveals that, from ethyl to hexyl derivatives, C_{obs} decreases by 17 and 20% for perylene and 9-PA, respectively, but from hexyl to octyl derivatives, the decrease is more than 25% for perylene. Thus, the results presented in this work are in tune with those obtained by Fruchey and Fayer,²¹ and the influence of organized structure on solute rotation is apparent in the case

of bis(trifluoromethylsulfonyl)imides only when longer alkyl chains are present on the imidazolium cation. This has also been substantiated from the ESR studies of Strehmel et al.⁴⁴ Another issue that needs to be addressed is whether the organized structure of the ionic liquid or the increasingly nonpolar environment, which is responsible for the decrease in C_{obs} values upon increasing the alkyl chain length on the imidazolium cation. Since an increase in the alkyl chain length has led to a decrease in the C_{obs} values only in two of the four systems investigated, it is reasonable to conclude that the organized structure of the ionic liquids is responsible for the observed behavior. In another recent study, Khara and Samanta²⁴ have observed more than 80% decrease in the C_{obs} values of C153 in a series of *N*-alkyl-*N*-methylmorpholinium bis(trifluoromethylsulfonyl)imides and concluded that these ionic liquids are more structured compared to imidazolium-based ionic liquids. However, results from the present work indicate that the organized structure of the ionic liquid depends not only on the cation but is also governed by the anion associated with it.

CONCLUSIONS

As a consequence of their highly associative nature, ionic liquids are known to form organized structures, which in turn can have a profound influence on rates of dynamical processes. In an attempt to find out whether the organized structure of an ionic liquid affects rotational diffusion of a nonpolar solute molecule, the present study has been undertaken and the important findings are summarized in this section. The significantly faster rotation of 9-PA observed in octyl derivatives of 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates compared to their ethyl counterparts for a given η/T could not be rationalized using the hydrodynamic and quasihydrodynamic theories. This behavior could only be explained by taking into consideration the organized structure of the ionic liquids. Another important observation from this study is that, in the case of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides and tris(pentafluoroethyl)-trifluorophosphates, there is no significant influence of the alkyl chain length on the rotational diffusion of 9-PA. Thus, it can be concluded that whether the organized structure of an ionic liquid influences dynamical processes or not also depends on the nature of the anion and how strongly it can associate with the cation. The high charge-to-size ratio of $[\text{BF}_4^-]$ and $[\text{PF}_6^-]$ anions, which arises as a consequence of their smaller size compared to $[\text{Tf}_2\text{N}^-]$ and $[\text{FAP}^-]$, is responsible for the observed behavior.

ASSOCIATED CONTENT

Supporting Information

Four tables listing reorientation times of 9-PA in the four ionic liquid series 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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