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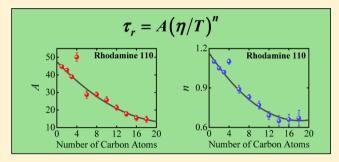
Effect of Alkyl Chain Length on the Rotational Diffusion of Nonpolar and Ionic Solutes in 1-Alkyl-3-Methylimidazoliumbis(trifluoromethylsulfonyl)imides

V. Gangamallaiah and G. B. Dutt*

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Supporting Information

ABSTRACT: Rotational diffusion of a nonpolar solute 9phenylanthracene (9-PA) and a cationic solute rhodamine 110 (R110) has been examined in a series of 1-alkyl-3methylimidazolium (alkyl = octyl, decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl) bis(trifluoromethylsulfonyl)imides to understand the influence of alkyl chain length on solute rotation. In this study, reorientation times (τ_r) have been measured as a function of viscosity (η) by varying the temperature (T) of the solvents. These results have been analyzed using the Stokes-Einstein-Debye (SED) hydrodynamic theory along with the ones obtained for the same



solutes in 1-alkyl-3-methylimidazolium (alkyl = methyl, ethyl, propyl, butyl, and hexyl) bis(trifluoromethylsulfonyl)imides (Gangamallaiah and Dutt, J. Phys. Chem. B 2012, 116, 12819-12825). It has been noticed that the data for 9-PA and R110 follows the relation $\tau_r = A(\eta/T)^n$ with A being the ratio of hydrodynamic volume of the solute to the Boltzmann constant and n = 11 as envisaged by the SED theory. However, upon increasing the alkyl chain length from methyl to octadecyl significant deviations from the SED theory have been observed especially from the octyl derivative onward. From methyl to octadecyl derivatives, the value of A decreases by a factor of 3 for both the solutes and n by a factor of 1.4 and 1.6 for 9-PA and R110, respectively. These observations have been rationalized by taking into consideration the organized structure of the ionic liquids, whose influence appears to be pronounced when the number of carbon atoms in the alkyl chain attached to the imidazolium cation exceeds eight.

1. INTRODUCTION

Ionic liquids, an important class of solvents that are entirely composed of ions, have emerged as alternative reaction media for synthesis, catalysis, and in many other fields of science and technology due to their novel physicochemical properties and unique structure. 1–5 The properties of these ionic liquids can be tailored by varying the constituent ions as well as the substituents present on either of the ions.^{6,7} Physicochemical and structural properties of the imidazolium-based ionic liquids, the most studied ones to date, have been explored by carrying out theoretical as well as experimental investigations.⁸⁻²¹ The observed results indicate that the properties and structure of the ionic liquids are influenced by the nonpolar alkyl chains attached to the constituent ions of the ionic liquids. These alkyl side chains on the imidazolium cation undergo aggregation, and this behavior, in particular, depends on the length of the alkyl chain and also on the nature of the anion present in the ionic liquid.¹⁷⁻²¹ Thus, the aggregation behavior of the alkyl chains and numerous interactions prevailing between the constituent ions lead to a complex organized structure of the ionic liquids. 22-30 The complex structure of these ionic liquids results in physicochemical properties, which are vastly different compared to the conventional solvents. Therefore, to get a better appreciation of the influence of the organized structure

on chemical reactivity, various chemical processes need to be carried out in different classes of ionic liquids.

To understand the influence of specific interactions and organized structure of the ionic liquids on solute rotation, we have extensively investigated rotational diffusion, a fundamental dynamical process that gives the information about solutesolvent interactions, of various organic solutes in a variety of ionic liquids. In these studies, the reorientation time (τ_r) of a solute molecule has been measured as a function of viscosity (η) by changing the temperature (T) of the medium and also varying the length of the alkyl chain on the imidazolium cation. The experimental data has been analyzed with the aid of Stokes-Einstein-Debye (SED) hydrodynamic theory, 40,41 and the deviations from this theory have enabled us to assimilate the role of specific interactions and the organized structure of these liquids on solute rotation. Somewhat similar studies have been performed by other groups. 42-53 Of late, our efforts have been directed toward understanding the role of organized structure of ionic liquids on solute rotation. Rotational diffusion studies carried out using a pair of

Received: August 5, 2013 Revised: September 12, 2013 Published: September 16, 2013 structurally similar nonpolar (9-phenylanthracene, 9-PA) and cationic (rhodamine 110, R110) solutes in 1-alkyl-3-methylimidazolium ([Rmim $^+$]) based ionic liquids with anions such as tetrafluoroborate ([BF $_4$ $^-$]) and hexafluorophosphate ([PF $_6$ $^-$]) indicate that organized structure of the ionic liquids affects the solute rotation. 38,39

Samanta and co-workers^{47,48} have investigated rotational diffusion of nonpolar and dipolar solutes in morpholiniumbased bis(trifluoromethylsulfonyl)imides ($\lceil Tf_2N^- \rceil$), and on the basis of the results they have inferred that these ionic liquids are more structured compared to their imidazolium counterparts. Essentially, for a given n/T, a decrease in τ , has been noticed upon increasing the alkyl chain length on the morpholinium cation for three of the four solutes examined. However, similar studies carried out by us with nonpolar and charged solutes in the ionic liquid series comprising the cations 1,3-dimethylimidazolium ([mmim⁺]), 1-ethyl-3-methylimidazolium ([emim⁺]), 1-methyl-3-propylimidazolium ([mpim⁺]), 1-butyl-3-methylimidazolium ([bmim+]), 1-hexyl-3-methylimidazolium ([hmim $^+$]), and the anion [Tf $_2$ N $^-$] did not display any systematic decrease in τ_r with an increase in the alkyl chain length for a given η/T . In other words, the influence of organized structure of the medium on solute rotation is not apparent in the case of 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imides. It appears that either the weakly associating nature of the $[Tf_2N^-]$ anion or the low viscosity of the solvents employed is responsible for the observed behavior. As mentioned earlier, the formation of the organized structure in ionic liquids depends on how strongly the constituent cations and anions associate with each other and also on the length of the alkyl chain on one of the ions. Thus, to find out how these factors influence solute rotation in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, the present study has been undertaken. In this work, rotational diffusion of the nonpolar solute 9-PA and the cationic solute R110 (see Figure 1 for their molecular

Figure 1. Molecular structures of the solutes.

structures) has been examined in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides with longer alkyl chains. The ionic liquids having the longer alkyl chains on the imidazolium cation such as 1-methyl-3-octylimidazolium ([moim $^+$]), 1-decyl-3-methylimidazolium ([ddmim $^+$]), 1-methyl-3-tetradecylimidazolium ([mtdim $^+$]), 1-hexadecyl-3-methylimidazolium ([hdmim $^+$]), and 1-methyl-3-octadecylimidazolium ([modim $^+$]) in combination with the [Tf $_2$ N $^-$] anion have been employed for this purpose. We hope that the results

Rhodamine 110

obtained in this study in conjunction with our earlier work³⁷ will provide conclusive information about how the alkyl chain length influences solute rotation in case of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides.

2. EXPERIMENTAL SECTION

All the ionic liquids used in this study were purchased from ioli-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 Metrohm 831 KF Coulometer and found to be within limits specified by the manufacturer. The fluorophores 9-phenylanthracene and rhodamine 110 chloride were obtained from Aldrich and Exciton, respectively. All 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. 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%.

Time-resolved fluorescence measurements were carried out with a setup that works on the principle of time-correlated single-photon counting.⁵⁴ The setup used in the present study was purchased from IBH, UK and employs a diode laser as the excitation source. The instrumental details have been described in our earlier publication.³³ 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 probe 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 13.8 ps/channel. The instrument response function of the setup was measured by collecting the scattered light from a TiO₂ 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. The anisotropy measurements were carried out over the temperature range 298-348 K in case of $[\text{moim}^+][\text{Tf}_2\text{N}^-]$, $[\text{dmim}^+][\text{Tf}_2\text{N}^-]$, and $[\text{ddmim}^+][\text{Tf}_2\text{N}^-]$. However, for [mtdim⁺][Tf₂N⁻], [hdmim⁺][Tf₂N⁻], and [modim⁺][Tf₂N⁻], the measurements were performed over the temperature ranges 308-348, 323-358, and 338-358 K, respectively, as these are solids at ambient temperatures. 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.

3. RESULTS AND DISCUSSION

The experimentally measured anisotropy decays of 9-PA and R 1 1 0 in 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imides can be fit with a single-exponential function over the temperature range employed in this study. Typical anisotropy decays of the two solutes in $[mmim^+][Tf_2N^-]$, $[moim^+][Tf_2N^-]$ and $[modim^+][Tf_2N^-]$ measured at 348 K along with the fitted curves are shown in the Figure 2, and it can be noticed from the figure that the

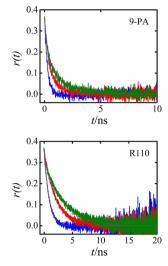


Figure 2. Anisotropy decays of 9-PA and R110 in $[mmim^+][Tf_2N^-]$ (blue), $[moim^+][Tf_2N^-]$ (red), and $[modim^+][Tf_2N^-]$ (olive) at 348 K together with the fitted curves. It can be noticed that the anisotropy decays of the solutes become progressively slower with an increase in the length of the alkyl chain on the imidazolium cation.

decays of both the solutes become progressively slower from methyl to octadecyl derivatives as a consequence of increase in the viscosity upon increasing the alkyl chain length on the imidazolium cation. The measured reorientation times of 9-PA and R110 in [Rmim⁺][Tf₂N⁻] (from methyl to octadecyl) along with the solvent viscosities at different temperatures are listed in the Supporting Information, and the uncertainties on the τ_r values are about 5 to 10%. It may be noted that reorientation times of the two solutes from methyl to hexyl derivatives and their viscosities have been taken from our earlier work.³⁷ The experimentally measured data has been analyzed by means of SED hydrodynamic theory. According to this theory, the rotational diffusion of a solute molecule in a solvent continuum is assumed to occur by small-step diffusion and the reorientation time is related to the macroscopic viscosity of the solvent by the following relation.

$$\tau_{\rm r} = A(\eta/T)^n \tag{1}$$

In the above equation, A is the ratio of hydrodynamic volume (V_h) of the solute to Boltzmann constant (k) and n=1 as predicted by the SED theory. V_h is a product of van der Waals volume (V), shape factor (f), and boundary condition parameter (C). The shape factor takes into consideration the nonspherical nature of the solute molecule, 55 while the boundary condition parameter determines the extent of solute—solvent coupling and the two limiting cases are the hydrodynamic stick and slip. 56 The methodology used to obtain these parameters with the aid of SED hydrodynamic theory has been discussed in our earlier publication. 37 The calculated

values of the parameters V, f, and C are 236 Å³, 1.73, and 0.12, respectively, for 9-PA and the corresponding numbers for R110 are 275 Å³, 2.02, and 0.15.

To find out if the SED hydrodynamic theory is able to explain the experimental data, reorientation times of 9-PA and R110 are plotted as a function of η/T in Figure 3. The SED slip

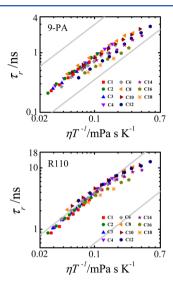


Figure 3. Plots of τ_r versus η/T for 9-PA and R110 in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides of varying alkyl chain lengths (C_1 to C_{18}). The SED slip and stick lines for the two solutes are also shown in the figure.

and stick lines for the two solutes are also shown in the figure. Inspection of the figure indicates that the rotational diffusion of 9-PA is closer to the predictions of slip hydrodynamics, whereas reorientation times of R110 obey stick hydrodynamics due to specific interactions prevailing between R110 and the [Tf₂N⁻] anion of the ionic liquids. The parameters A and n (given in eq 1) have been obtained for both the solutes in $[Rmim^+][Tf_2N^-]$ from the linear least-squares fits of log-log plots (fitted lines not shown in the figure). It has been observed that both A and n decrease with an increase in the alkyl chain length on the imidazolium cation and these trends have been depicted in Figures 4 and 5 for 9-PA and R110, respectively. From methyl to octadecyl derivatives, the parameter A decreases by a factor of 3 for both the solutes and n by a factor of 1.4 and 1.6 for 9-PA and R110, respectively. However, it may be noted that in case of $\lceil ddmim^+ \rceil \lceil Tf_2N^- \rceil$ there is an increase in *n* for 9-PA, while for the cationic solute R110, there is an increase in both Aand n in $[bmim^+][Tf_2N^-]$. To verify this anomaly, experiments have been repeated with fresh sets of samples for 9-PA in $[ddmim^+][Tf_2N^-]$ and R110 in $[bmim^+][Tf_2N^-]$. Such a repetition did not alter the earlier result, and at this moment we do not have an explanation for this observation. Nevertheless, the results obtained from the analysis reveal that the value of the parameter A decreases with an increase in the alkyl chain length on the imidazolium cation, which is an indication that the boundary condition parameter C is not constant but varies in each member of the homologous series. Furthermore, the value of n deviates from unity, notably from the octyl derivative onward, and this observation suggests that failure of the SED hydrodynamic theory in explaining the experimental results especially in case of ionic liquids having longer alkyl chains on the imidazolium cation. It may be possible that the value of A

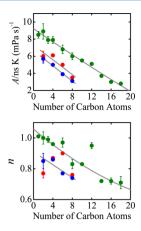


Figure 4. Plots of *A* and *n* versus number of carbon atoms present in the alkyl chain on the imidazolium cation with $[Tf_2N^-]$ (olive), $[BF_4^-]$ (red), and $[PF_6^-]$ (blue) anions for the solute 9-PA. The lines passing through the data points are drawn as visual aids and it can be noticed that barring a few exceptions, both *A* and *n* decrease with an increase in the number of carbon atoms. Data for 9-PA in $[Rmim^+][BF_4^-]$ and $[Rmim^+][PF_6^-]$ has been taken from ref 38.

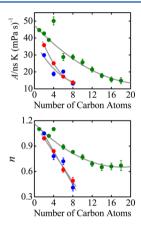


Figure 5. Plots of A and n versus number of carbon atoms present in the alkyl chain on the imidazolium cation with $[Tf_2N^-]$ (olive), $[BF_4^-]$ (red), and $[PF_6^-]$ (blue) anions for the solute R110. The lines passing through the data points are drawn as visual aids, and it can be noticed that barring a few exceptions, both A and n decrease with an increase in the number of carbon atoms. Data for R110 in $[Rmim^+][BF_4^-]$ and $[Rmim^+][PF_6^-]$ has been taken from ref 39.

decreases with alkyl chain length because the volume of the solvent molecule increases, which in turn leads to a decrease in the boundary condition parameter. Quasihydrodynamic theory of Gierer-Wirtz $(GW)^{57}$ has been considered to account for the changes associated with the A values and this model incorporates the size of the solute as well as the solvent (V_s) while calculating the boundary condition parameter.

The boundary condition parameter, C_{GW} , according to GW quasihydrodynamic theory is given by the following equation:⁵⁷

$$C_{\rm GW} = \sigma C_0 \tag{2}$$

where the parameters σ and C_0 are given by eqs 3 and 4, respectively.

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

$$C_0 = \left[\frac{6(V_{\rm s}/V)^{1/3}}{\left[1 + 2(V_{\rm s}/V)^{1/3}\right]^4} + \frac{1}{\left[1 + 4(V_{\rm s}/V)^{1/3}\right]^3} \right]^{-1} \tag{4}$$

The volumes of the ionic liquids used in this study have been calculated using Edward increment method,58 and the limitations involved in this procedure have been discussed in our earlier publication.³⁸ It has been noticed that from $[mmim^+][Tf_2N^-]$ to $[modim^+][Tf_2N^-]$, V_s increases by a factor of 2, nevertheless, $C_{\rm GW}$ decreases by a mere 26% for both 9-PA and R110. Thus, the value of A calculated using $C_{\rm GW}$ for 9-PA in $[mmim^+][Tf_2N^-]$ is 4.6 ns K $(mPa\ s)^{-1}$ and it decreases to 3.7 ns K (mPa s)⁻¹ in [modim⁺][Tf₂N⁻] and the corresponding decrease in case of R110 is from 6.6 to 5.3 ns K (mPa s)⁻¹. In other words, a factor of 3 decrease observed in the value of A from methyl to octadecyl derivatives of the ionic liquids could not be mimicked by the quasihydrodynamic theory of Gierer-Wirtz. Thus, the analyses carried out in this manner suggest that both hydrodynamic and quasihydrodynamic theories are unable to explain the observed trends.

The results presented here clearly indicate that the influence of alkyl chain length on the rotational diffusion of both 9-PA and R110 in 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imides is similar although both the solutes are chemically distinct. The only difference is the significantly slower rotation of the ionic solute R110 as a consequence of its specific interactions with the $\lceil Tf_2N^- \rceil$ anion of the ionic liquids. Furthermore, the nonlinear dependence of τ_r on η/T could not be accounted by either hydrodynamic or qusihydrodynamic theories. Somewhat similar behavior has been noticed for the same solutes in 1-alkyl-3-methylimidazolium-based ionic liquids with $[BF_4^{}]$ and $[PF_6^{}]$ anions. 38,39 It may be noted that in these studies, significant deviations from the SED hydrodynamic theory have been noticed even though the length of the alkyl chain on the imidazolium cation was varied only from ethyl to octyl and these results have also been presented in Figures 4 and 5 for 9-PA and R110, respectively. The observed results have been ascribed to the organized structure of the ionic liquids. The high charge to size ratio of [BF₄⁻] and [PF₆⁻] anions enables them to associate strongly with the imidazolium cation leading to the formation of organized structures even in the presence of shorter alkyl chains. Neutron diffraction studies carried out with [mmim⁺]-[Tf₂N⁻] suggest that charge ordering is substantially less compared to [mmim⁺][PF₆⁻] as result of delocalization of the charge over the anion and this has a major influence on the properties of [Tf₂N⁻]-based ionic liquids.¹⁷ For example, viscosities of these ionic liquids are, in general, lower than those found for the corresponding ionic liquids with [BF₄⁻] and [PF₆] anions due to the much softer ionic structure, which allows the ions to move more freely with respect to one another. Moreover, the weaker Coulombic interactions reduce the ability of long alkyl chain [Tf₂N⁻]-based ionic liquids to form liquid crystals. 18 Due to these reasons influence of alkyl chain length on solute rotation has not been observed in our earlier work involving methyl to hexyl derivatives of 1-alkyl-3methylimidazolium bis(trifluoromethylsulfonyl)imides.³⁷

In the present work, the alkyl chain length on the imidazolium cation was varied from methyl to octadecyl, and to the best of our knowledge this is the first instance where the rotational diffusion studies have been performed in ionic liquids having extremely short to very long alkyl chains. It can be noticed that there is no change in the rotational diffusion of 9-PA and R110 with an increase in the length of the alkyl chain from the methyl to hexyl on the imidazolium cation, which is in contrast to the results observed in case of ionic liquids with $\left[BF_4^-\right]$ and $\left[PF_6^-\right]$ anions. 38,39 This observation clearly

indicates that the length of the alkyl chain has no bearing on solute rotation in ionic liquids when a weakly coordinating anion such as $[Tf_2N^-]$ is present in combination with the imidazolium cation having shorter alkyl chains. However, a pronounced influence has been noticed on the rotation of 9-PA and R110 in the case of ionic liquids with longer alkyl chains, especially, from octyl derivative onward. This behavior can be ascribed to the organized structure of the ionic liquids. In other words, even [Tf₂N⁻]-based ionic liquids form organized structures in the presence of longer alkyl chains on the imidazolium cation, which influence solute rotation. Essentially, ionic liquids with [Tf₂N⁻] anions form softer ionic structures due to the less charge ordering, which is a result of delocalization of charge over the bulky anion.¹⁷ Therefore, in case of [Rmim⁺][Tf₂N⁻] ionic liquids with shorter alkyl chains, the combination of ineffective Coulombic interactions and weaker van der Waals interactions cannot form the extensive organized structure. However, longer alkyl chains present on the imidazolium cation undergo aggregation due to the stronger van der Waals interactions between them, which results in organized domain structure of the ionic liquids even in the case of weakly associating anions.²⁵ The size of the domain structure increases with an increase in the length of the alkyl chain on the imidazolium cation. Thus, solute rotation is significantly influenced by the length of the alkyl chain attached to the imidazolium cation from octyl derivative onward.

At this juncture, it is pertinent to discuss the somewhat similar alkyl chain length dependence observed on the rotational diffusion of 9-PA and R110 in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides. Because of their distinct chemical nature, 9-PA and R110 are probably located in different regions of the ionic liquids. The nonpolar solute resides in the nonpolar domains, while the location of the charged solute is somewhat circumstantial. Considering the size and also the larger fraction being nonpolar, it likely that R110 will be located at the boundary between the nonpolar domains and the ionic group region comprising [Tf₂N⁻] anions and imidazolium rings. Such a location would allow R110 to access [Tf₂N⁻] anions through its ionic groups and the nonpolar domains of the ionic liquid via the nonpolar fraction. As the length of the alkyl chain increases on the imidazolium cation, the nonpolar domains become larger in size and therefore the nonpolar solute, 9-PA, which resides in these domains, experiences lower friction. In other words, at a particular η/T , the observed faster rotation of 9-PA upon increasing the alkyl chain length is due to an increase in the size of the organized domains. In case of cationic solute, however, larger organized domain structures probably shield [Tf₂N⁻] anions from the solute and hence lead to weaker hydrogen bonding interactions between R110 and the anion of the ionic liquid. Thus, at a given η/T , rotation of the cationic solute becomes faster with an increase in the length of the alkyl chain on the imidazolium cation. In essence, an increase in the length of the alkyl chain on the imidazolium cation facilitates rotation of nonpolar as well as charged solutes via different mechanisms.

4. CONCLUSIONS

Rotational diffusion studies carried out with a pair of structurally similar nonpolar and charged solutes in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides indicate that the alkyl chain length on the imidazolium cation has a bearing on solute rotation only when the number of carbon atoms in the alkyl chain exceeds eight. Both hydrodynamic and

quasihydrodynamic theories fail to rationalize the experimental results. Organized structures arising as a consequence of alkyl chain aggregation is responsible for the observed behavior. These results are somewhat different compared to the ones observed in the case of 1-alkyl-3-methylimidazolium-based ionic liquids with tetrafluoroborate and hexafluorophosphate anions, where alkyl chain length dependence has been observed even from ethyl to octyl derivatives. Weakly associating nature of bis(trifluoromethylsulfonyl)imide, which results from the delocalization of charge over the bulky anion is responsible for the observed behavior. However, with an increase in the length of the alkyl chain on the imidazolium cation, stronger van der Waals interactions prevail between the alkyl chains leading to the formation of organized domains and ensuing faster rotation of the solutes.

ASSOCIATED CONTENT

S Supporting Information

Tables listing reorientation times of 9-PA and R110 in the eleven 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.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gbdutt@barc.gov.in. Phone: (91) 22-2559-0302.

Notes

The authors declare no competing financial interest.

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