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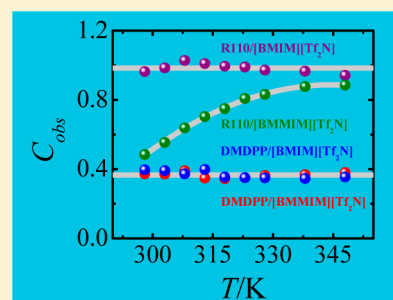
Rotational Diffusion of Nondipolar and Charged Solutes in Alkyl-Substituted Imidazolium Triflimides: Effect of C2 Methylation on Solute Rotation

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S Supporting Information

ABSTRACT: Rotational diffusion of a nondipolar solute 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) and a charged solute rhodamine 110 (R110) has been investigated in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]) and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([BMMIM][Tf₂N]) to understand the influence of the C2 methylation on solute rotation. The measured reorientation times of the nondipolar solute DMDPP are similar in both the ionic liquids and follow Stokes–Einstein–Debye hydrodynamic theory with slip hydrodynamics. In contrast, rotational diffusion of the charged solute R110 in [BMIM][Tf₂N] obeys stick hydrodynamics due to specific interactions with the anion of the ionic liquid. Nevertheless, the intriguing result of this study is that the reorientation times of R110 in [BMMIM][Tf₂N] deviate significantly from the predictions of stick hydrodynamics, especially at ambient temperatures. The solute–solvent boundary condition parameter C_{obs} , which is defined as the ratio of the measured reorientation time to the one calculated using the SED theory with stick boundary condition, for R110 is lower by a factor of 2 in [BMMIM][Tf₂N] compared to [BMIM][Tf₂N] at 298 K. Upon increasing the temperature, C_{obs} gradually increases and eventually matches with that obtained in [BMIM][Tf₂N] at 348 K. It has been well established that methylation of the C2 position in [BMMIM][Tf₂N] switches off the main hydrogen-bonding interaction between the anion and the cation, but increases the Coulombic interactions. As a consequence of the enhanced interionic interactions between the cation and anion of the ionic liquid, specific interactions between R110 and [Tf₂N] diminish leading to the faster rotation of the solute. However, such an influence is not apparent in case of DMDPP as it does not experience specific interactions with either the cation or the anion of these ionic liquids.



1. INTRODUCTION

The physicochemical properties of ionic liquids, to a large extent, are governed by interionic interactions between the constituent ions.¹ The presence of a particular atom or a small group on one of the ions can significantly alter these interactions. Thus, understanding the interactions between the cations and anions at the molecular level is essential for designing ionic liquids with desired properties. Data available in the literature indicates that the physicochemical properties of 1-alkyl-3-methylimidazolium-based ionic liquids are vastly different compared to their dimethyl counterparts in which C2 proton is replaced by a methyl group. Typically, methylation of the C2 position leads to an increase in viscosity and melting point, but a decrease in conductivity.^{2–5} Numerous theoretical and experimental studies have been carried out to rationalize the high viscosities and melting points observed in case of C2-methylated ionic liquids.^{5–11} Some of the explanations that have been put forward are mentioned below.

Results obtained by Hunt⁶ with the aid of *ab initio* molecular orbital calculations and computed vibrational spectra suggest that the presence of methyl group at the C2 position of the imidazolium ring restricts the free rotation of the butyl group due to steric hindrance, which reduces the number of low-energy configurations and also facilitates alkyl chain association.

Such a scenario results in reduced entropy or increased ordering within the fluid, thus leading to higher viscosity and melting point. Using FTIR studies, Fumino et al.,⁷ have shown that the presence of a proton in place of a methyl group at the C2 position of the imidazolium ring induces strong and directional hydrogen bonds between the cations and anions, which destroy the charge symmetry and fluidize ionic liquids. Essentially, an ordered array of charges is disrupted by the hydrogen bonding at the C2 position in 1-alkyl-3-methylimidazolium-based ionic liquids. It has also been suggested that, when the C2 position is methylated, hydrogen-bonding interactions are significantly suppressed in favor of Coulombic interactions. Somewhat similar explanation has been proposed by Noack et al.,¹⁰ based on their results from vibrational and NMR spectroscopic investigation. An altogether different explanation has been provided by Izgorodina et al.,⁵ from the potential energy surface profiles calculated using high-level *ab initio* theory. It has been proposed that the movement of the anion around the methylated cation is restricted due to high potential barriers compared to the protonated imidazolium

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cation. Thus, such a slow ion transport leads to high viscosity. In addition to the above-mentioned studies, ultrafast vibrational dynamics measurements have also been performed recently to understand the influence of the C2 methylation on the interactions between the cations and anions.^{12,13}

In view of the unusually high viscosities of 1-alkyl-2,3-dimethylimidazolium ionic liquids, it would be interesting to explore rotational diffusion of organic solutes in these systems and compare the results to ones obtained in 1-alkyl-3-methylimidazolium ionic liquids. Fluorescence anisotropy measurements involving numerous organic solutes dissolved in a wide range of ionic liquids have shed light on the role of specific interactions, nature of the anion/cation, and the influence of organized structure of the ionic liquid on solute rotation.^{14–39} In essence, these studies have enabled us to understand the interactions between ionic liquids and added solutes. However, to the best of our knowledge, influence of the C2 methylation on solute rotation has not been examined so far. Thus, the present study has been undertaken, wherein rotational diffusion of organic solutes has been examined in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]) and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([BMMIM][Tf₂N]). Figure 1

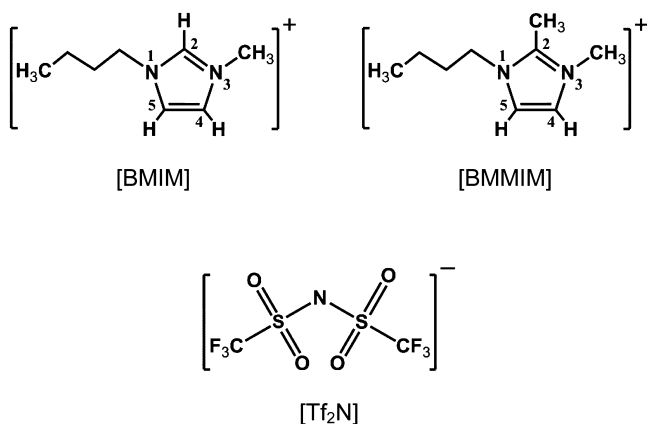


Figure 1. Molecular structures of the cations and anion of the ionic liquids.

gives the molecular structures of these ionic liquids. The organic solutes selected are 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) and rhodamine (R110) (see Figure 2 for the molecular structures of the solutes). It is evident from the figure that the former is a nondipolar solute, whereas the latter is a charged one. Rotational diffusion of DMDPP and R110 has been investigated in 1-butyl-3-methylimidazolium ionic liquids with various anions.¹⁸ It has been observed that the reorientation times of DMDPP scale with viscosities of the ionic liquids and are independent of the nature of the anion. In contrast, R110 experiences specific interactions with the anions of the ionic liquids and its rotational diffusion has been found to depend on the hydrogen bond basicities of the anions in addition to the viscosity of the medium. DMDPP and R110 have been chosen for the present study since our goal is to find out how the C2 methylation affects the rotational diffusion of solutes that are chemically distinct.

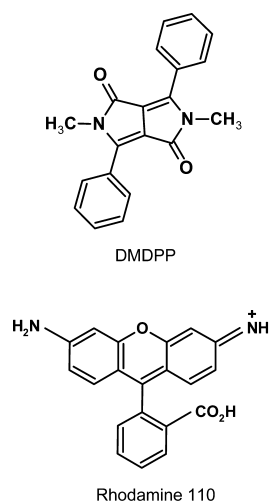


Figure 2. Molecular structures of the solutes.

2. EXPERIMENTAL SECTION

The ionic liquids [BMIM][Tf₂N] and [BMMIM][Tf₂N] were purchased from io-li-tec, Germany. 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 probes DMDPP and R110 were obtained from Ciba Specialty Chemicals, Inc., and Exciton, respectively. Concentrations of the probes in the ionic liquids were chosen such that at the wavelength of excitation the absorbance is <0.2. Viscosities of [BMIM][Tf₂N] and [BMMIM][Tf₂N] were measured over the temperature range 298–348 K using a Physica MCR 101 rheometer and the uncertainties on the measured numbers are about 5%.

Time-resolved fluorescence anisotropy decays were collected using a time-correlated single-photon-counting (TCSPC) spectrometer that was purchased from Horiba Jobin Yvon, UK. Samples containing the probes DMDPP and R110 were excited with a 451 nm DeltaDiode from Horiba Scientific whose pulse width is <100 ps and has a repetition rate of 10 MHz. The TCSPC spectrometer was operated in the inverted mode to avoid pile-up errors due to the high repetition rate of the excitation source. The fluorescence of both the probes was monitored at 550 nm using a PMT-based detection module (model TBX4). The instrument response function was measured by collecting the scattered light from a TiO₂ suspension in water, and the full width at half-maximum was found to be <200 ps. The decays were collected in 4096 channels with a time increment of 13.8 ps/channel. 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, and the temperature of the samples was controlled with a precision of 0.1 degree using a thermoelectric controller (TC 125, Quantum Northwest). Each measurement was repeated 2–3 times and the average values are reported. Reorientation times were obtained from

the analysis of anisotropy decays with the aid of the software supplied by Horiba Scientific and the details have been mentioned in our earlier publication.¹⁶

3. RESULTS AND DISCUSSION

Anisotropy decays of all the solute–ionic liquid combinations employed in this work over the temperature range 298–348 K can be adequately described by a single-exponential function with one reorientation time, τ_r . The τ_r values of DMDPP and R110 in [BMIM][Tf₂N] and [BMMIM][Tf₂N] measured at different temperatures, and the viscosities of the ionic liquids, are given in the Supporting Information. To find out how the reorientation times of DMDPP and R110 correlate with the viscosities of the ionic liquids, Stokes–Einstein–Debye (SED) hydrodynamic theory^{40,41} has been employed. According to the SED theory, τ_r of a solute molecule is proportional to the viscosity of the solvent (η) at a given temperature (T). The solute properties that govern the rotation are its size, shape, and boundary condition parameter. Size of the solute molecule is incorporated in the form of van der Waals volume (V),⁴² whereas shape factor (f) is introduced to account for the nonspherical nature of the solute.⁴³ The parameter $f > 1$ for a nonspherical solute and the solute molecules are usually treated as either symmetric or asymmetric ellipsoids. The magnitude of the boundary condition parameter, C , depends on the axial ratio of the solute molecule and the two limits are the hydrodynamic slip and stick.⁴⁴ Thus, the reorientation time of a solute molecule is given by

$$\tau_r = \frac{\eta V f C}{kT} \quad (1)$$

where k is the Boltzmann constant. In essence, the SED theory predicts that τ_r of a solute molecule is solely dependent on η/T . To test this hypothesis, anisotropy decays of DMDPP in [BMIM][Tf₂N] and [BMMIM][Tf₂N] at 298 and 318 K, respectively, are plotted in Figure 3. Although viscosities of the

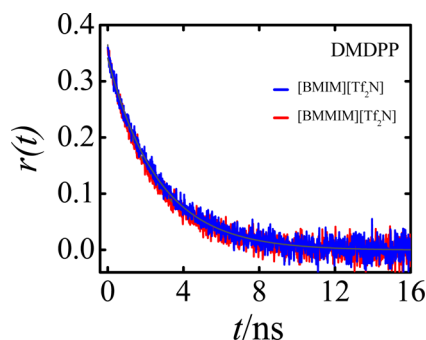


Figure 3. Anisotropy decays of DMDPP in [BMIM][Tf₂N] and [BMMIM][Tf₂N] at 298 and 318 K, respectively, along with the fitted curves. The temperatures have been chosen such that η/T values for the two ionic liquids are almost identical, which is 0.17 mPa s K^{−1}.

two ionic liquids are not identical, the temperatures have been chosen so that η/T values for the two liquids are the same. It can be noticed that the anisotropy decays of DMDPP in the two ionic liquids overlap, which suggests that the rotation of the solute in [BMIM][Tf₂N] as well as [BMMIM][Tf₂N] is essentially governed by η/T . Similarly, anisotropy decays of R110 in [BMIM][Tf₂N] and [BMMIM][Tf₂N] are plotted in Figure 4. It can be noticed from the figure that, despite η/T being the same for the two ionic liquids, the anisotropy decay

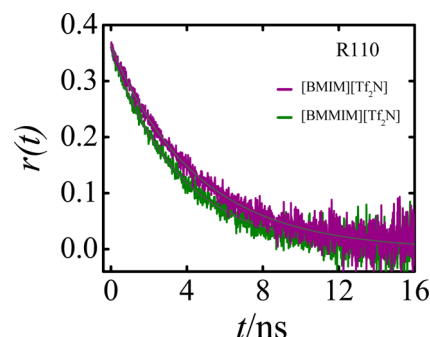


Figure 4. Anisotropy decays of R110 in [BMIM][Tf₂N] and [BMMIM][Tf₂N] at 308 and 328 K, respectively, along with the fitted curves. The temperatures have been chosen such that η/T values for the two ionic liquids are almost identical, which is 0.11 mPa s K^{−1}.

of R110 is slower in [BMIM][Tf₂N] compared to that measured in [BMMIM][Tf₂N]. To assess the applicability of SED hydrodynamic theory for the systems under investigation, reorientation times of DMDPP and R110 in the two ionic liquids are plotted as a function of η/T in Figures 5 and 6,

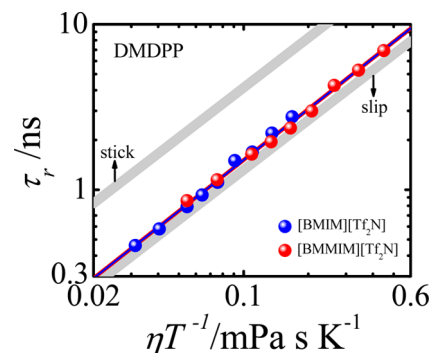


Figure 5. Plots of τ_r versus η/T for DMDPP in [BMIM][Tf₂N] and [BMMIM][Tf₂N]. The SED slip and stick lines are also shown in the figure. The reorientation times of DMDPP in the two ionic liquids are almost identical and can be represented by a common line.

respectively. The corresponding stick and slip lines are also shown in these figures. For the purpose of calculating the reorientation times of DMDPP and R110 using the SED theory, the solute molecules have been treated as asymmetric ellipsoids. The details of the modeling and the formulas used to

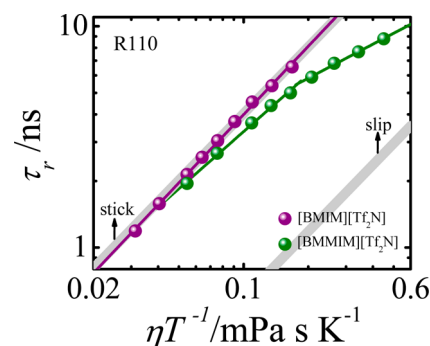


Figure 6. Plots of τ_r versus η/T for R110 in [BMIM][Tf₂N] and [BMMIM][Tf₂N]. The SED slip and stick lines are also shown in the figure. The reorientation times of R110 in [BMMIM][Tf₂N] deviate from the predictions of stick hydrodynamics especially at high η/T .

carry out these calculations have been presented in our earlier publication.¹⁶ The parameters, van der Waals volume V , shape factor f , and the boundary condition parameter C_{slip} that have been calculated for DMDPP are 281 Å³, 2.03, and 0.32, respectively, and the corresponding numbers for R110 are 275 Å³, 2.02, and 0.15.

Inspection of Figure 5 reveals that the reorientation times of the nondipolar solute DMDPP in [BMIM][Tf₂N] and [BMMIM][Tf₂N] scale linearly with the viscosities of the ionic liquids and follow slip hydrodynamics. The rotation of DMDPP in the two ionic liquids is virtually indistinguishable and can be represented by the following relationship, which has been obtained by linear least-squares fit of the data.

$$\tau_r = (15.9 \pm 0.6)(\eta/T)^{1.02 \pm 0.02} \quad (N = 18, R = 0.998)$$

In the above expression, N and R are the number of data points and regression coefficient, respectively. This result is somewhat surprising considering the fact that the hydrogen bond acidity of [BMIM][Tf₂N] is 2–3 times higher compared to [BMMIM][Tf₂N] due to the availability of the C2 proton.^{45,46} Furthermore, DMDPP is a hydrogen bond accepting solute because of the presence of two carbonyl groups. In other words, rotational diffusion of DMDPP is expected to be slower in [BMIM][Tf₂N] as the solute can readily hydrogen bond with the C2 proton of the 1-butyl-3-methylimidazolium cation. In fact, slower rotation of DMDPP has been observed in the case of other hydrogen bond donating ionic liquids such as 1-(2-hydroxyethyl)-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate and *n*-propylammonium nitrate.^{16,19} In view of our earlier results, it would be interesting to know the reason for the similar behavior observed in [BMIM][Tf₂N] and [BMMIM][Tf₂N]. The most probable explanation appears to be steric hindrance as the C2 proton is surrounded by *n*-butyl and methyl groups in 1- and 3-positions, respectively (see Figure 1), and it is likely that the bulky DMDPP cannot access the C2 proton to form hydrogen bonds. Moreover, the presence of [Tf₂N][−] anion in the vicinity of the C2 proton can also inhibit DMDPP from experiencing specific interactions. Due to these reasons the rotational diffusion of DMDPP is similar in [BMIM][Tf₂N] and [BMMIM][Tf₂N]. To further illustrate this point, solute–solvent boundary condition parameter C_{obs} (ratio of the measured reorientation time to the one calculated using the SED theory with stick boundary condition) of DMDPP in [BMIM][Tf₂N] and [BMMIM][Tf₂N] is plotted as a function of temperature in Figure 7. It can be noticed from the figure that C_{obs} is almost identical in the two ionic liquids and also independent of temperature.

In contrast to DMDPP, rotational diffusion of R110 in [BMIM][Tf₂N] follows stick hydrodynamics due to specific interactions with [Tf₂N][−] anion, which is evident from Figure 6. As mentioned earlier, such a behavior has been observed for the rotational diffusion of R110 in 1-butyl-3-methylimidazolium liquids with various types of anions such as tris(pentafluoroethyl)trifluorophosphate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide, tetrafluoroborate, trifluoromethanesulfonate, and nitrate. It has been noticed that C_{obs} values of R110 vary with the nature of the anion and this variation correlates with the hydrogen bond basicities of the ionic liquids.¹⁸ Somewhat similar result has been reported for 4-aminophthalimide in 1-ethyl-3-methylimidazolium-based ionic liquids with different anions.⁴⁷ These results suggest that rotational diffusion of hydrogen bond donating solutes is essentially governed by the hydrogen bond basicity besides the

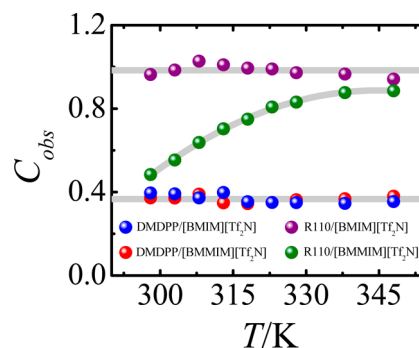


Figure 7. Plots of C_{obs} versus T for the two solutes in [BMIM][Tf₂N] and [BMMIM][Tf₂N]. The C_{obs} values are almost identical for DMDPP in the two ionic liquids and do not vary with temperature. In contrast, for R110, C_{obs} values in [BMMIM][Tf₂N] are much lower compared to [BMIM][Tf₂N] and increase with temperature. The gray-colored lines passing through the data points represent the average of the C_{obs} values, while the curve represents the variation of C_{obs} with T for R110 in [BMMIM][Tf₂N].

viscosity of the ionic liquid. If the hydrogen bond basicity is the sole parameter that controls the rotational diffusion of R110, then a similar behavior should have been observed in case of [BMMIM][Tf₂N] as well. However, a quick glance at Figure 6 indicates that the τ_r versus η/T plot for R110 in [BMMIM][Tf₂N] contains two slopes corresponding to low and high η/T and the rotational diffusion of the solute is significantly faster than stick hydrodynamic predictions, especially at high η/T . Linear least-squares fits of the data give the following relationships between τ_r and η/T for R110 in [BMIM][Tf₂N] and [BMMIM][Tf₂N].

$$\text{R110/[BMIM][Tf}_2\text{N]}$$

$$\tau_r = (42.2 \pm 1.8)(\eta/T)^{1.02 \pm 0.02} \quad (N = 9, R = 0.999)$$

$$\text{R110/[BMMIM][Tf}_2\text{N]} \quad \eta/T < 0.2$$

$$\tau_r = (24.0 \pm 1.7)(\eta/T)^{0.86 \pm 0.03} \quad (N = 5, R = 0.998)$$

$$\text{R110/[BMMIM][Tf}_2\text{N]} \quad \eta/T > 0.2$$

$$\tau_r = (13.2 \pm 0.3)(\eta/T)^{0.51 \pm 0.02} \quad (N = 4, R = 0.999)$$

These expressions provide the extent of deviations observed from the predictions of the SED hydrodynamic theory, especially for R110 in [BMMIM][Tf₂N] at high η/T . Plots of C_{obs} values of R110 versus temperature in [BMIM][Tf₂N] and [BMMIM][Tf₂N] are also presented in Figure 7. It can be noticed from the figure that C_{obs} values of R110 in [BMIM][Tf₂N] are independent of temperature and fluctuate around 1, which is the stick limit. On the other hand, the C_{obs} value of R110 in [BMMIM][Tf₂N] is lower by a factor of 2 compared to that in [BMIM][Tf₂N] at 298 K. This number gradually increases with temperature and eventually matches that obtained in [BMIM][Tf₂N] at 348 K. Here it must be mentioned that significant deviations from the SED theory have also been noticed, especially at high η/T , in the case of the rotational diffusion of R110 in 1-alkyl-3-methylimidazolium-based ionic liquids with strongly associating anions such as tetrafluoroborate ([BF₄][−]) and hexafluorophosphate ([PF₆][−]) in our earlier work.²² At ambient temperatures (high η/T), the anions of the ionic liquid are not readily accessible to the solute R110 due to the presence of the organized domains, which

leads to diminishing hydrogen-bonding interactions, thus ensuing the faster rotation of the solute. However, it may be noted that the above-mentioned study has been carried out in ionic liquids where the length of the alkyl chain on the imidazolium cation was varied from ethyl to octyl. It has been well established that imidazolium-based ionic liquids with longer alkyl chains facilitate the formation of organized structures.⁴⁸ Nevertheless, in the present study, the observed behavior does not arise as a consequence of the organized structure of the ionic liquid, which is explained in the following paragraph.

As mentioned earlier, rotational diffusion of R110 in [BMMIM][Tf₂N] is significantly faster than stick hydrodynamic predictions especially at high η/T . If the organized structure of the ionic liquid is responsible for the observed behavior, it would have affected the rotational diffusion of DMDPP as well. In our earlier paper,²¹ it had been noticed that the rotational diffusion of a nonpolar solute such as 9-phenylanthracene (9-PA) is influenced by the organized structure of 1-alkyl-3-methylimidazolium ionic liquids with [BF₄] and [PF₆] anions. Essentially, for a given η/T , faster rotation of the solute has been observed with an increase in the length of the alkyl chain on the imidazolium cation. Due to the presence of organized domains, the nonpolar solute 9-PA senses viscosity that is lower than the bulk viscosity of the ionic liquid. As the length of the alkyl chain on the imidazolium cation increases, the sizes of these domains increase, leading to the faster rotation of the solute. However, in the present work, no distinction has been noticed in the rotational diffusion of DMDPP in [BMIM][Tf₂N] and [BMMIM][Tf₂N]. Thus, it is safe to conclude that the organized structure of [BMMIM][Tf₂N] is not responsible for the observed differences in the rotational diffusion of R110 in these ionic liquids.

At this juncture, it would be prudent to discuss the reason for the unusually faster rotation of R110 observed in [BMMIM][Tf₂N]. As briefly mentioned in the Introduction, methylation of the C2 position alters electron density distribution on the imidazolium ring and as a result changes the position and strength of interionic interactions. Such a scenario leads to more stable and regularly packed molecular network with increased Coulomb interactions and decreased van der Waals interactions.¹⁰ These enhanced Coulomb interactions are the most probable reason for the observed behavior of R110. The hydrogen bond accepting ability of the anion of an ionic liquid can be visualized as two competing equilibria.⁴⁹ The anion can associate with the cation of the ionic liquid and also the cationic solute R110. An increase in the cation–anion association leads to a decrease in the R110–anion association. In other words, strength of the hydrogen-bonding interactions between R110 and [Tf₂N] diminishes due to stronger association between [BMMIM] and [Tf₂N] thus ensuing faster rotation of R110 in [BMMIM][Tf₂N] compared to [BMIM][Tf₂N]. However, at higher temperatures, the association between [BMMIM] cation and [Tf₂N] anion weakens, which leads to stronger hydrogen-bonding interactions between R110 and the anion of the ionic liquid. Due to this reason, the C_{obs} values of R110 in [BMMIM][Tf₂N] are almost identical to the ones in [BMIM][Tf₂N] at higher temperatures. The nondipolar solute DMDPP, in contrast, does not experience specific interactions with the cation or the anion of these ionic liquids and hence its rotation is essentially governed by the viscosity of the medium.

4. CONCLUSIONS

To explore the role of the C2 methylation on solute rotation, fluorescence anisotropies of nondipolar (DMDPP) and charged (R110) solutes have been measured in [BMIM][Tf₂N] and [BMMIM][Tf₂N] as a function of temperature. Rotational diffusion of DMDPP is similar in these two ionic liquids and follows SED hydrodynamic theory with slip boundary condition. The cationic solute R110 experiences specific interactions with the anion of the ionic liquid and as a consequence its reorientation times in [BMIM][Tf₂N] match with those predicted by the stick hydrodynamics. However, the rotation of R110 in [BMMIM][Tf₂N] is significantly faster than the stick limit at ambient temperatures. The enhanced Coulombic interactions resulting from the methylation of the C2 position lead to stronger association between [BMMIM] cation and [Tf₂N] anion. Such a scenario precludes the cationic solute from experiencing strong hydrogen-bonding interactions with the [Tf₂N] anion thus resulting in the faster rotation of R110. This study establishes that methylation of the C2 position in alkyl-substituted imidazolium triflimides influences the rotational diffusion of a cationic solute in addition to affecting other physicochemical properties.

■ ASSOCIATED CONTENT

Supporting Information

Reorientation times of DMDPP and R110 in the two ionic liquids and their viscosities over the temperature range 298–348 K. 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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