Influence of the Organized Structure of 1-Alkyl-3-methylimidazolium Tetrafluoroborates on the Rotational Diffusion of Structurally Similar Nondipolar Solutes

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Influence of the Organized Structure of 1-Alkyl-3-methylimidazolium Tetrafluoroborates on the Rotational Diffusion of Structurally Similar Nondipolar Solutes

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S *Supporting Information*

ABSTRACT: To understand how the organized structure of the ionic liquids influences the location and mobility of nondipolar solutes, rotational diffusion of 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DMDPP) and 1,4-dioxo-3,6-diphenylpyrrolo-[3,4-c]pyrrole (DPP) has been examined in 1-alkyl-3-methylimidazolium (alkyl = ethyl, butyl, hexyl, and octyl) tetrafluoroborates. Both the solutes are structurally similar—the sole difference being the two NCH$_3$ groups of DMDPP are replaced by two NH groups in DPP. The rotational diffusion of DPP is found to be significantly slower than DMDPP due to specific interactions between the NH groups of the solute and the anion of the ionic liquid. It has been observed that for a given viscosity and temperature, the rotational diffusion of DMDPP becomes progressively faster with an increase in the length of the alkyl chain on the imidazolium cation. DMDPP resides in the nonpolar domains of these ionic liquids whose sizes increase with an increase in the length of the alkyl chain, and as a result it experiences microviscosity that is lower than the bulk viscosity. However, an increase in the length of the alkyl chain has no apparent effect on the rotational diffusion of DPP because specific interactions with tetrafluoroborate necessitate the solute to be located in the vicinity of the anion. The results of this work exemplify that despite having similar size and shape, the rotational diffusion of DMDPP and DPP is quite contrasting as their sites of solubilization and the nature of interactions with the surroundings are vastly different owing to subtle variations in their chemical structures.
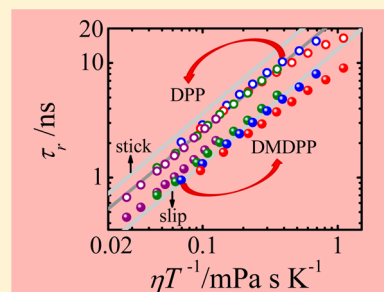
1. INTRODUCTION

The existence of organized structure in ionic liquids, which gives rise to their exotic properties, has been extensively investigated using molecular dynamics simulations and experimental techniques,[1−10] and the important findings have been summarized in a recent review.[11] Lack of strong charge ordering between the anion and cation due to asymmetry in one or both the ions and the presence of a cooperative network of hydrogen bonds between constituent ions, which induces structural directionality, are the two main features that set apart ionic liquids from molten salts.[12] Organized structure is formed in ionic liquids having long alkyl chains on one of the ions as a result of aggregation of these nonpolar tails and clustering of the anions and cations. Essentially, an optimum balance of electrostatic, hydrogen bonding, and van der Waals interactions leads to the nanostructuring in ionic liquids. Studies carried out in recent times suggest that the organized structure of the ionic liquids not only governs their physicochemical properties but also influences dynamical processes such as solvation dynamics,[13−15] photoisomerization,[15,16] and rotational diffusion.[17−23] In other words, chemical reactivity in these systems is greatly affected by the presence of organized domains.

Among the dynamical processes, rotational diffusion of organic solutes has been examined by us[21−33] and other groups[17−20,34−42] to understand the interactions between ionic liquids and added solutes. In these studies, the reorientation times (τ_r) of solute molecules are usually measured as a function of viscosity (η) and temperature (T). Nevertheless, viscosities of the ionic liquids have also been altered by increasing the length of the alkyl chain on one of the ions in quite a few studies.[17−25,39] In a majority of instances, it has been observed that the experimentally measured reorientation times did not comply with the trends predicted by the Stokes−Einstein−Debye (SED) hydrodynamic theory.[43,44] In other words, τ_r versus η/T plots displayed a significant degree of nonlinearity, and also τ_r values at a given η/T, especially for nonpolar and dipolar solutes, are found to be lower in ionic liquids with longer alkyl chains. Even the quasi-hydrodynamic theories of Gierer−Wirtz (GW)[45] and Dote−Kivelson−Schwartz (DKS)[46] have failed to explain the experimental results. Thus, to rationalize these observations, organized structure of the ionic liquids has been considered. According to the explanations provided in the literature, nonpolar and dipolar solute molecules are usually located in the nonpolar domains of the ionic liquids, and the sizes of these domains increase with an increase in the length of the alkyl chain and as a consequence the solutes experience less friction in ionic liquids with longer alkyl chains for a given η/T. However, the influence of organized structure on the rotational diffusion of charged and hydrogen bond donating solutes is not clearly
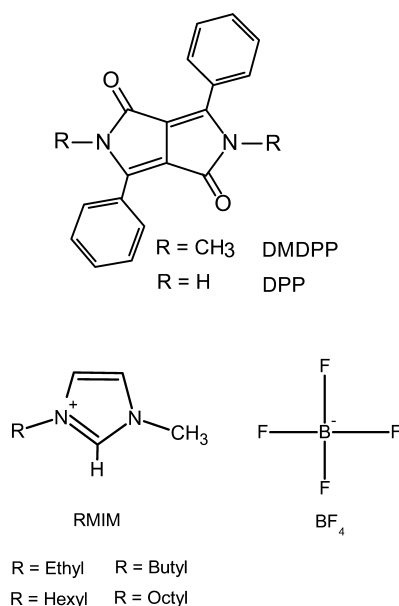
Figure 1. Molecular structures of the solutes and the ionic liquids.

discernible as they experience specific interactions and are also likely to be located in the ionic region. The sole exception being the case of rhodamine 110 (R110) in imidazolium-based ionic liquids with strongly associating anions where significant deviations from the SED theory have been noticed at higher η/T.[22]

From the discussion presented so far it is evident that the influence of organized structure of ionic liquids on the rotational diffusion of nonpolar, dipolar, and charged solutes has been investigated extensively. Among them, only a handful of studies carried out by our group deal with structurally similar solutes of comparable size such as 9-phenylanthracene (9-PA) and R110.[21−24] Such a choice of solutes enabled us to make one-to-one comparison of the measured reorientation times and glean information pertinent to the role of specific interactions, relative locations of the solutes, and other nonhydrodynamic effects. Even though 9-PA and R110 are structurally similar, they are vastly different chemically because the former is a nonpolar solute, whereas the latter is a charged one. This fact prompted us to find out how the rotational diffusion of two structurally similar nondipolar solutes with subtle variations in their chemical structures will be influenced by the organized structure of the ionic liquids. Thus, in this work, rotational diffusion of 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DMDPP) and 1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) has been investigated in 1-alkyl-3-methylimidazolium (alkyl = ethyl, butyl, hexyl, and octyl) tetrafluoroborates. Figure 1 gives molecular structures of the two solutes and the ionic liquids employed in this work. It can be noticed from the figure that the two N-methyl groups of DMDPP are replaced by two NH groups in DPP, and as a consequence, the latter is a strong hydrogen bond donor. It would be interesting to see how the rotational diffusion of the two solutes will be affected by the variation of temperature and the length of the alkyl chain on the imidazolium cation.

2. EXPERIMENTAL SECTION

The ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄], 1-hexyl-3-methylimidazolium tetrafluor-

oborate [HMIM][BF₄] and 1-methyl-3-octylimidazolium tetrafluoroborate [MOIM][BF₄] were purchased from io-li-tec, Germany, whereas the solutes DMDPP and DPP were obtained from Ciba Specialty Chemicals, Inc., Switzerland. 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 the limits specified by the manufacturers. The ionic liquids and the solutes DMDPP and DPP were used without further purification.

Fluorescence anisotropy decays were measured using a time-correlated single-photon counting spectrometer that was purchased from Horiba Jobin Yvon, UK. The instrumental details and the description concerning the measurement of anisotropy decays have been discussed in our earlier publication.[33] The ionic liquid samples containing DMDPP and DPP were excited at 451 nm, and the emission was monitored around 550 nm. The absorbance of the samples at the wavelength of excitation was maintained in the range of 0.1−0.15. The anisotropy measurements were carried out over the temperature range 298−348 K. 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. Viscosities of these ionic liquids 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%.

3. RESULTS AND DISCUSSION

Single-exponential function is adequate to describe the anisotropy decays of DMDPP and DPP in 1-alkyl-3-methylimidazolium tetrafluoroborates over the temperature range 298−348 K. To corroborate the single-exponential behavior of the two solutes in these ionic liquids, anisotropy decays of DMDPP and DPP in [EMIM][BF₄] and [MOIM]-[BF₄] measured at 298 and 348 K, respectively, along with their residual distributions are given in the Supporting Information. The reorientation times obtained from the analysis of the anisotropy decays are also listed in the Supporting Information along with the viscosities of the ionic liquids. The uncertainties on the measured reorientation times are about 5−10%. To compare the rotational diffusion of DMDPP and DPP, anisotropy decays of the two solutes in [EMIM][BF₄] and [MOIM][BF₄] are displayed in Figure 2. It can be noticed from the figure that the anisotropy decays of DPP are significantly slower compared to DMDPP, and these differences are more pronounced in [MOIM][BF₄]. To get a better appreciation of these results, the measured reorientation times of DMDPP and DPP in 1-alkyl-3-methylimidazolium tetrafluoroborates have been analyzed with the aid of SED hydrodynamic theory.[43,44] According to the SED theory, the rotation of a solute molecule occurs by small-step diffusion, and the reorientation time depends on size and shape of the solute and also on the extent of coupling between the solute and the solvent. These parameters are incorporated into the hydrodynamic theory in the form of van der Waals volume (V), shape factor (f), and the boundary condition parameter (C).[47−49] The two limits for C are the hydrodynamic slip (C_{slip}), which satisfies the inequality $0 < C_{slip} \leq 1$ and hydrodynamic stick whose value is unity. In addition to the solute properties, viscosity and temperature of
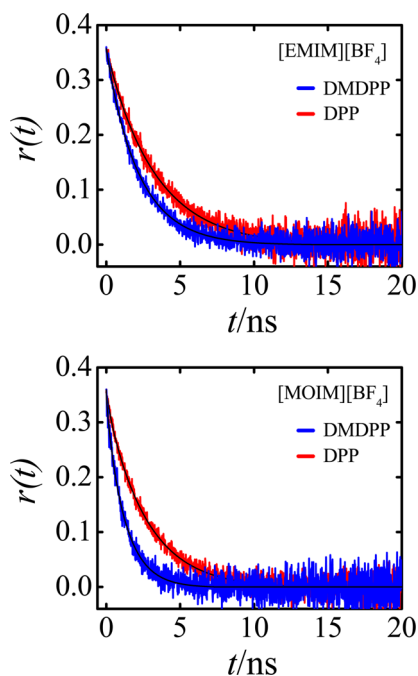
Figure 2. Anisotropy decays of the two solutes in [EMIM][BF$_4$] and [MOIM][BF$_4$] at 298 and 348 K, respectively, along with the fitted curves. It can be noticed from the figure that the anisotropy decays of DPP are significantly slower compared to DMDPP in both the ionic liquids.

Figure 3. Plots of τ_r versus η/T for DMDPP (blue) and DPP (red) in the four ionic liquids along with the least-squares fit lines. The SED slip lines for DMDPP and stick lines for DPP are also shown in the figure.

the solvent also govern the rotational diffusion. Thus, the reorientation time is given by

$$\tau_r = \frac{\eta V f C}{kT} \tag{1}$$

where k is the Boltzmann constant. To apply the SED theory to the systems under investigation, the solutes DMDPP and DPP are treated as asymmetric ellipsoids, and the reorientation times with slip and stick boundary conditions have been calculated. The details of the calculations are presented elsewhere.[50] The axial radii of DMDPP and DPP are the same ($8.2 \times 4.3 \times 1.9$ Å^3), and the corresponding van der Waals volumes are 281 and 246 Å^3. As a consequence of identical axial radii, the shape factor and the boundary condition parameter that have been calculated for the two solutes are identical, $f = 2.03$ and $C_{slip} = 0.32$. However, the calculated reorientation time of DMDPP is longer by about 14% compared to DPP due to the marginally higher van der Waals volume of the former. Conformational studies involving the two solutes suggest that the phenyl rings are out of plane with respect to the heterocyclic ring in DMDPP and DPP by 31° and 7°, respectively.[51] But the pronounced nonplanarity of DMDPP is unlikely to affect its molecular volume. Furthermore, it must also be noted that no significance can be attached to the differences obtained in the calculated reorientation times considering the limitations involved in the modeling of irregularly shaped solute molecules as asymmetric ellipsoids.

Figure 3 gives plots of τ_r versus η/T for DMDPP and DPP in 1-alkyl-3-methylimidazolium tetrafluoroborates along with the slip and stick lines. The slip and stick lines correspond to DMDPP and DPP, respectively. An important feature evident from the figure is that the reorientation times of DMDPP in [EMIM][BF$_4$] are closer to the predictions of slip hydrodynamics. The rotational diffusion of DMDPP becomes
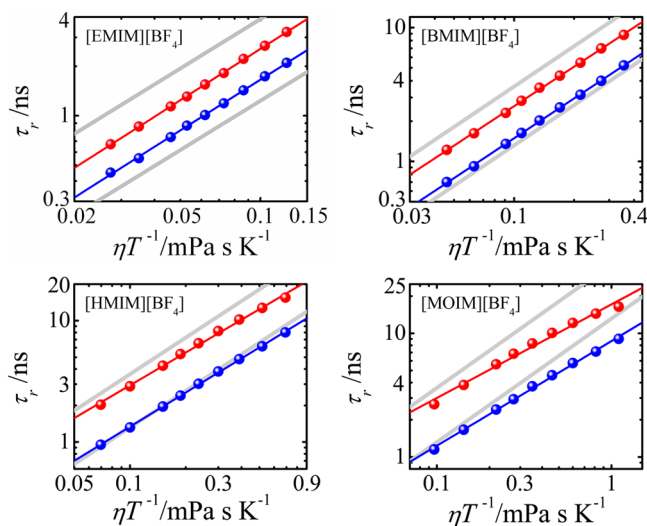
progressively faster with an increase in the length of the alkyl chain and eventually turns subslip in [MOIM][BF$_4$]. In contrast, the reorientation times of DPP are closer to the stick predictions. However, unlike DMDPP, no systematic trends can be noticed in the rotational diffusion of DPP with an increase in the length of the alkyl chain. Thus, the interplay of these factors increases the ratio of the reorientation time of DPP to DMDPP from 1.5 in [EMIM][BF$_4$] to 2.2 in [MOIM][BF$_4$]. It may be noted that the significantly slower rotation of DPP compared to DMDPP is a consequence of specific interactions between the two NH groups and [BF$_4$] anion. Thus, the reorientation time of DPP in a hydrogen bond accepting solvent depends on solute−solvent interaction strength in addition to the viscosity of the medium. In fact, these aspects have been extensively investigated in organic solvents by us,[50,52−58] and the important results are summarized.[59] In ionic liquids, however, studies involving DPP could not be performed by varying the anion as it is soluble in a limited number of imidazolium-based ionic liquids.

To get further insight into these observations, plots of τ_r versus η/T for DMDPP in the four ionic liquids are given in Figure 4. Linear least-squares fits of these log−log plots resulted in the following relationships between τ_r versus η/T with N and R being the number of data points and the regression coefficient, respectively.

DMDPP/[EMIM][BF$_4$]

$$\tau_r = (17.7 \pm 0.5)(\eta/T)^{1.03 \pm 0.01} \quad (N = 9, \ R = 0.9997)$$

DMDPP/[BMIM][BF$_4$]

$$\tau_r = (14.5 \pm 0.2)(\eta/T)^{0.99 \pm 0.01} \quad (N = 9, \ R = 0.9998)$$

DMDPP/[HMIM][BF$_4$]

$$\tau_r = (11.5 \pm 0.1)(\eta/T)^{0.93 \pm 0.01} \quad (N = 9, \ R = 0.9998)$$

DMDPP/[MOIM][BF$_4$]

$$\tau_r = (8.7 \pm 0.2)(\eta/T)^{0.85 \pm 0.01} \quad (N = 9, \ R = 0.9991)$$
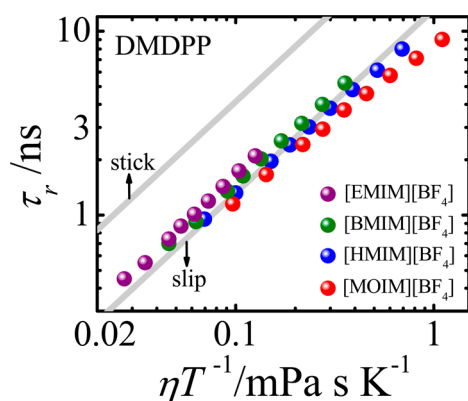
Figure 4. Plots of τ_r versus η/T for DMDPP in the four ionic liquids along with the slip and stick lines. It can be noticed from the figure that for a given η/T, the solute rotation becomes faster as the length of the alkyl chain increases from ethyl to octyl on the imidazolium cation.

It is evident from the figure and the subsequent analysis that the reorientation times of DMDPP at a given η/T decrease with an increase in the length of the alkyl chain on the imidazolium cation. It may be noted that with an increase in the length of the alkyl chain, van der Waals volume of the ionic liquid also increases, which causes the solute molecule to experience reduced friction. In fact, such a behavior has been observed for numerous nonpolar solutes in organic solvents,[60−62] which is known as the size effects. It has been noticed that even DMDPP experiences size effects in organic solvents of different sizes.[53,54,59] Calculations based on the Edward's increment method suggest that the van der Waals volume (V_s) of [EMIM][BF$_4$] is 180 Å^3, and this number increases to 282 Å^3 in the case of [MOIM][BF$_4$]. Thus, the decrease in the reorientation time of DMDPP at a given η/T from [EMIM][BF$_4$] to [MOIM][BF$_4$] could probably be due to an increase in V_s. To find out if the observed result is a consequence of size effects or not, quasi-hydrodynamic theory of Gierer−Wirtz (GW)[45] has been applied to the rotational diffusion of DMDPP in 1-alkyl-3-methylimidazolium tetrafluoroborates.

The GW theory takes into consideration the volume of the solvent as well as the solute, while calculating the boundary condition parameter, C_{GW}. It may be noted that both the solute and the solvent are treated as spheres in the GW model, and C_{GW} is given by the equation[45]

$$C_{GW} = \sigma C_0 \qquad (2)$$

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

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

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

The C_{GW}, calculated using these formulae decreases by a mere 15% from [EMIM][BF$_4$] to [MOIM][BF$_4$]. In contrast, the experimentally observed boundary condition parameter, which has been obtained from the slopes of τ_r versus η/T plots, decreases by a factor of 2 from ethyl to octyl derivative. Thus, the exercise carried out in this manner rules out the possibility that the observed result is due to variation in the volumes of the ionic liquids. The reason for the faster rotation of DMDPP with

an increase in the length of the alkyl chain at a given η/T is a result of the organized structure of the ionic liquids. It has been demonstrated that ionic liquids with longer alkyl chains segregate into polar and nonpolar domains and the sizes of the latter increase with an increase in the length of the alkyl chain on the imidazolium cation.[11] The solute DMDPP, which resides in these nonpolar domains, experiences microviscosity that is lower than the bulk viscosity of the ionic liquid. Hence, an increase in the length of the alkyl chain facilitates faster rotation of the solute at a given η/T. This result is similar to the ones observed for other nonpolar and dipolar solutes.[17−21,23]

Figure 5 gives plots of τ_r versus η/T for DPP in the four ionic liquids, and it is evident from the figure that no systematic
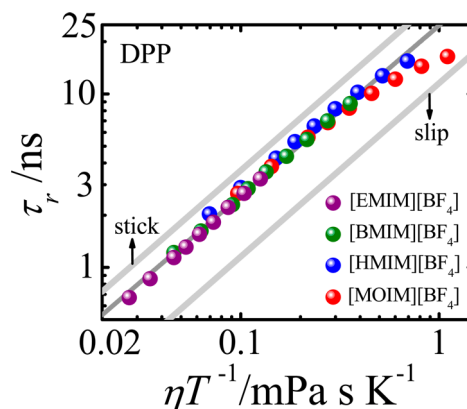

Figure 5. Plots of τ_r versus η/T for DPP in the four ionic liquids along with the slip and stick lines. It can be noticed from the figure that there is no systematic variation in the reorientation times of DPP with an increase in the length of the alkyl chain from ethyl to octyl on the imidazolium cation. The solid line passing through the data points is obtained by least-squares fit, and it may be noted that the reorientation times of DPP in [MOIM][BF$_4$] measured over the temperature range 298−308 K are not included in the fit.

influence of alkyl chain length on the reorientation times can be noticed. Only in the case of [MOIM][BF$_4$], some deviations are apparent over a limited temperature range (298−308 K). In view of this, linear least-squares fit was performed by excluding the three data points pertinent to the octyl derivative at ambient temperatures, and the following τ_r versus η/T relationship has been obtained.

$$\tau_r = (24.8 \pm 0.7)(\eta/T)^{0.98 \pm 0.01} \quad (N = 33, \ R = 0.9971)$$

This analysis clearly indicates that the reorientation times of DPP scale linearly with η/T. The result obtained here is somewhat surprising considering the fact that the rotational diffusion of another hydrogen bond donating but charged solute, R110, in the same series of ionic liquids displays a different trend altogether.[22] It has been observed that there is no alkyl chain length dependence on the reorientation times of R110 in 1-alkyl-3-methylimidazolium tetrafluoroborates. Nevertheless, the τ_r versus η/T plot exhibits two slopes corresponding to lower and higher η/T. The rotational diffusion of R110 follows stick hydrodynamics up to η/T = 0.2 mPa s K^{-1}, but significant deviations have been noticed beyond this point. This observation has been rationalized by taking into consideration the organized structure of the ionic liquids, which precludes stronger hydrogen bonding interactions between the solute and [BF$_4$] anion leading to the faster rotation. However, in the case of DPP, τ_r versus η/T plot

contains a single slope until 0.5 mPa s K^{-1}. What could be the probable reason for the observed behavior? It must be noted that even though both R110 and DPP are hydrogen bond donating solutes, some properties of the latter such as aggregation and solubility are very unique. It is a well-known fact that DPP forms various types of aggregates in the solid state due to intermolecular hydrogen bonding.[63,64] For the DPP monomer to dissolve it needs to form hydrogen bonds with the solvent so that the intermolecular hydrogen bonding between the aggregates are broken. In other words, the solubility of DPP is very much dependent on the hydrogen bond accepting ability of the solvent. DPP dissolves in 1-alkyl-3-methylimidazolium tetrafluoroborates by forming hydrogen bonds with the $[BF_4]$ anion. Thus, the unique solubility characteristics of DPP make the presence of $[BF_4]$ anion mandatory in the proximity of the solute irrespective of the existence of the organized structure. Because of these reasons, the influence of the organized structure of 1-alkyl-3-methylimidazolium tetrafluoroborates is not apparent on the rotational diffusion of DPP. Furthermore, another significant difference between DPP and R110 is that the former is a neutral solute, whereas the latter is a charged one. As a consequence, the hydrogen bond donating abilities of the two solutes will not be the same. Thus, the difference in the hydrogen bond donating abilities of R110 and DPP could also be the probable reason for the observed trends.

CONCLUSIONS

Organized structure of the ionic liquids is known to affect rotational diffusion of nonpolar, dipolar, and charged solute molecules dissolved in them. However, the influence of structural heterogeneity of the ionic liquids on the rotational diffusion of nondipolar solutes has not been examined so far. Thus, the present study has been undertaken wherein reorientation times of two structurally similar nondipolar solutes, DMDPP and DPP, have been measured in 1-alkyl-3-methylimidazolium tetrafluoroborates. Experimental results indicate that the rotational diffusion of DPP is significantly slower compared to DMDPP due to hydrogen bonding interactions between the two NH groups of the former and $[BF_4]$ anion. Furthermore, for a given η/T, rotation of DMDPP becomes faster with an increase in the length of the alkyl chain on the imidazolium cation, whereas such an alkyl chain length dependence has not been noticed in the case of DPP. Based on these observations and analysis, it can be concluded that the organized structure of the ionic liquid influences the rotational diffusion of DMDPP, which is solubilized in the nonpolar domains. In contrast, the reorientation times of DPP scale with the bulk viscosities of the ionic liquids because specific interactions with $[BF_4]$ render the solute to be in the neighborhood of the anion despite the organized structure. In essence, whether the influence of organized structure of the ionic liquid on nondipolar solute rotation manifests or not depends on the site of solubilization and nature of the interactions with the surroundings.

ASSOCIATED CONTENT

ⓢ Supporting Information

Anisotropy decays of DMDPP and DPP in $[EMIM][BF_4]$ and $[MOIM][BF_4]$ along with their residual distributions, reorientation times of DMDPP and DPP in $[EMIM][BF_4]$, $[BMIM][BF_4]$, $[HMIM][BF_4]$ and $[MOIM][BF_4]$ along with

their viscosities 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.

REFERENCES

(1) Pópolo, M. G. D.; Voth, G. A. On the Structure and Dynamics of Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 1744−1752.

(2) Wang, Y.; Voth, G. A. Unique Spatial Heterogeneity in Ionic Liquids. *J. Am. Chem. Soc.* **2005**, *127*, 12192−12193.

(3) Lopes, J. N. A. C.; Pádua, A. A. H. Nanostructural Organization in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 3330−3335.

(4) Wang, Y.; Jiang, W.; Yan, T.; Voth, G. A. Understanding Ionic Liquids through Atomistic and Coarse-Grained Molecular Dynamics Simulations. *Acc. Chem. Res.* **2007**, *40*, 1193−1199.

(5) Triolo, A.; Russina, O.; Bleif, H.-J.; Cola, E. D. Nanoscale Segregation in Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 4641−4644.

(6) Chen, S.; Kobayashi, K.; Kitaura, R.; Miyata, Y.; Shinohara, H. Direct HRTEM Observation of Ultrathin Freestanding Ionic Liquid Film on Carbon Nanotube Grid. *ACS Nano* **2011**, *5*, 4902−4908.

(7) Santos, C. S.; Murthy, N. S.; Baker, G. A.; Castner, E. W., Jr. X-Ray Scattering from Ionic Liquids with Pyrrolidinium Cations. *J. Chem. Phys.* **2011**, *134*, 121101/1−121101/4.

(8) Kashyap, H. K.; Hettige, J. J.; Annapureddy, H. V. R.; Margulis, C. J. SAXS Anti-Peaks Reveal the Length-Scales of Dual Positive−Negative and Polar−Apolar Ordering in Room- Temperature Ionic Liquids. *Chem. Commun.* **2012**, *48*, 5103−5105.

(9) Russina, O.; Triolo, A.; Gontrani, L.; Caminiti, R. Mesoscopic Structural Heterogeneities in Room-Temperature Ionic Liquids. *J. Phys. Chem. Lett.* **2012**, *3*, 27−33.

(10) Li, S.; Bañuelos, J. L.; Guo, J.; Anovitz, L.; Rother, G.; Shaw, R. W.; Hillesheim, P. C.; Dai, S.; Baker, G. A.; Cummings, P. T. Alkyl Chain Length and Temperature Effects on Structural Properties of Pyrrolidinium-Based Ionic Liquids: A Combined Atomistic Simulation and Small-Angle X-ray Scattering Study. *J. Phys. Chem. Lett.* **2012**, *3*, 125−130.

(11) Chen, S.; Zhang, S.; Liu, X.; Wang, J.; Wang, J.; Dong, K.; Sun, J.; Xu, B. Ionic Liquid Clusters: Structure, Formation Mechanism, and Effect on the Behavior of Ionic Liquids. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5893−5906.

(12) Dupont, J. From Molten Salts to Ionic Liquids: A "Nano" Journey. *Acc. Chem. Res.* **2011**, *44*, 1223−1231.

(13) Samanta, A. Dynamic Stokes Shift and Excitation Wavelength Dependent Fluorescence of Dipolar Molecules in Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 13704−13716.

(14) Samanta, A. Solvation Dynamics in Ionic Liquids: What We Have Learned from the Dynamic Fluorescence Stokes Shift Studies. *J. Phys. Chem. Lett.* **2010**, *1*, 1557−1562.

(15) Jin, H.; Xiang, L. X.; Maroncelli, M. Heterogeneous Solute Dynamics in Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 13473−13478.

(16) Castner, E. W., Jr.; Margulis, C. J.; Maroncelli, M.; Wishart, J. F. Ionic Liquids: Structure and Photochemical Reactions. *Annu. Rev. Phys. Chem.* **2011**, *62*, 85−105.

(17) Fruchey, K.; Fayer, M. D. Dynamics in Organic Ionic Liquids in Distinct Regions Using Charged and Uncharged Orientational Relaxation Probes. *J. Phys. Chem. B* **2010**, *114*, 2840−2845.

13715

dx.doi.org/10.1021/jp5104142 | *J. Phys. Chem. B* 2014, 118, 13711−13717

(18) Das, S. K.; Sarkar, M. Rotational Dynamics of Coumarin-153 and 4-Aminophthalimide in 1-Ethyl-3-methylimidazolium Alkylsulfate Ionic Liquids: Effect of Alkyl Chain Length on the Rotational Dynamics. *J. Phys. Chem. B* **2012**, *116*, 194−202.

(19) Khara, D. C.; Samanta, A. Fluorescence Response of Coumarin-153 in N-Alkyl-N- methylmorpholinium Ionic Liquids: Are These Media More Structured than the Imidazolium Ionic Liquids? *J. Phys. Chem. B* **2012**, *116*, 13430−13438.

(20) Khara, D. C.; Kumar, J. P.; Mondal, N.; Samanta, A. Effect of the Alkyl Chain Length on the Rotational Dynamics of Nonpolar and Dipolar Solutes in a Series of N-Alkyl-N-Methylmorpholinium Ionic Liquids. *J. Phys. Chem. B* **2013**, *117*, 5156−5164.

(21) Gangamallaiah, V.; Dutt, G. B. 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? *J. Phys. Chem. B* **2013**, *117*, 5050−5057.

(22) Gangamallaiah, V.; Dutt, G. B. Influence of the Organized Structure of 1-Alkyl-3-Methylimidazolium-Based Ionic Liquids on the Rotational Diffusion of an Ionic Solute. *J. Phys. Chem. B* **2013**, *117*, 9973−9979.

(23) Gangamallaiah, V.; Dutt, G. B. Effect of Alkyl Chain Length on the Rotational Diffusion of Nonpolar and Ionic Solutes in 1-Alkyl-3-Methylimidazolium Bis(trifluoromethylsulfonyl)-imides. *J. Phys. Chem. B* **2013**, *117*, 12261−12267.

(24) Gangamallaiah, V.; Dutt, G. B. 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? *J. Phys. Chem. B* **2012**, *116*, 12819−12825.

(25) Dutt, G. B. Influence of Specific Interactions on the Rotational Dynamics of Charged and Neutral Solutes in Ionic Liquids Containing Tris(pentafluoroethyl)trifluorophosphate (FAP) Anion. *J. Phys. Chem. B* **2010**, *114*, 8971−8977.

(26) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Do Organic Solutes Experience Specific Interactions with Ionic Liquids? *J. Chem. Phys.* **2005**, *123*, 174504/1−174504/7.

(27) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Rotational Diffusion of a Nonpolar and a Dipolar Solute in 1-Butyl-3-Methylimidazolium Hexafluorophosphate and Glycerol: Interplay of Size Effects and Specific Interactions. *J. Chem. Phys.* **2008**, *128*, 054504/1−054504/9.

(28) Karve, L.; Dutt, G. B. Rotational Diffusion of Neutral and Charged Solutes in Ionic Liquids: Is Solute Reorientation Influenced by Nature of Cation? *J. Phys. Chem. B* **2011**, *115*, 725−729.

(29) Karve, L.; Dutt, G. B. Rotational Diffusion of Neutral and Charged Solutes in 1-Butyl-3- Methylimidazolium Based Ionic Liquids: Influence of Nature of Anion on Solute Rotation. *J. Phys. Chem. B* **2012**, *116*, 1824−1830.

(30) Karve, L.; Dutt, G. B. Role of Specific Interactions on the Rotational Diffusion of Organic Solutes in a Protic Ionic Liquid−Propylammonium Nitrate. *J. Phys. Chem. B* **2012**, *116*, 9107−9113.

(31) Prabhu, S. R.; Dutt, G. B. Rotational Diffusion of Nonpolar and Charged Solutes in Propylammonium Nitrate−Propylene Glycol Mixtures: Does the Organized Structure of the Ionic Liquid Influence on Solute Rotation? *J. Phys. Chem. B* **2014**, *118*, 2738−2745.

(32) Prabhu, S. R.; Dutt, G. B. Rotational Diffusion of Organic Solutes in 1-Methyl-3-octylimidazolium Tetrafluoroborate−Diethylene Glycol Mixtures: Influence of Organic Solvent on the Organized Structure of the Ionic Liquid. *J. Phys. Chem. B* **2014**, *118*, 5562−5569.

(33) Prabhu, S. R.; Dutt, G. B. Rotational Diffusion of Nondipolar and Charged Solutes in Alkyl Substituted Imidazolium Triflimides: Effect of C2 Methylation on Solute Rotation. *J. Phys. Chem. B* **2014**, *118*, 9420−9426.

(34) Ingram, J. A.; Moog, R. S.; Ito, N.; Biswas, R.; Maroncelli, M. Solute Rotation and Solvation Dynamics in a Room-Temperature Ionic Liquid. *J. Phys. Chem. B* **2003**, *107*, 5926−5932.

(35) Ito, N.; Arzhantsev, S.; Heitz, M.; Maroncelli, M. Solvation Dynamics and Rotation of Coumarin 153 in Alkylphosphonium Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 5771−5777.

(36) Jin, H.; Baker, G. A.; Arzhantsev, S.; Dong, J.; Maroncelli, M. Solvation and Rotational Dynamics of Coumarin 153 in Ionic Liquids: Comparisons to Conventional Solvents. *J. Phys. Chem. B* **2007**, *111*, 7291−7302.

(37) Liang, M.; Zhang, X.-X.; Kaintz, A.; Ernsting, N. P.; Maroncelli, M. Solvation Dynamics in a Prototypical Ionic Liquid + Dipolar Aprotic Liquid Mixture: 1-Butyl-3-methylimidazolium Tetrafluoroborate + Acetonitrile. *J. Phys. Chem. B* **2014**, *118*, 1340−1352.

(38) Khara, D. C.; Samanta, A. Rotational Dynamics of Positively and Negatively Charged Solutes in Ionic Liquid and Viscous Molecular Solvent Studied by Time-Resolved Fluorescence Anisotropy Measurements. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7671−7677.

(39) Guo, J.; Mahurin, S. M.; Baker, G. A.; Hillesheim, P. C.; Dai, S.; Shaw, R. W. Influence of Solute Charge and Pyrrolidinium Ionic Liquid Alkyl Chain Length on Probe Rotational Reorientation Dynamics. *J. Phys. Chem. B* **2014**, *118*, 1088−1096.

(40) Guo, J.; Han, K. S.; Mahurin, S. M.; Baker, G. A.; Hillesheim, P. C.; Dai, S.; Hagaman, E. W.; Shaw, R. W. Rotational and Translational Dynamics of Rhodamine 6G in a Pyrrolidinium Ionic Liquid: A Combined Time-Resolved Fluorescence Anisotropy Decay and NMR Study. *J. Phys. Chem. B* **2012**, *116*, 7883−7890.

(41) Das, S. K.; Sahu, P. K.; Sarkar, M. Diffusion−Viscosity Decoupling in Solute Rotation and Solvent Relaxation of Coumarin153 in Ionic Liquids Containing Fluoroalkylphosphate (FAP) Anion: A Thermophysical and Photophysical Study. *J. Phys. Chem. B* **2013**, *117*, 636−647.

(42) Sahu, P. K.; Das, S. K.; Sarkar, M. Toward Understanding Solute−Solvent Interaction in Room-Temperature Mono- and Dicationic Ionic Liquids: A Combined Fluorescence Spectroscopy and Mass Spectrometry Analysis. *J. Phys. Chem. B* **2014**, *118*, 1907−1915.

(43) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford University Press: New York, 1986.

(44) Waldeck, D. H. The Role of Solute-Solvent Friction in Large-Amplitude Motions. In *Conformational Analysis of Molecules in the Excited States*; Waluk, J., Ed.; Wiley-VCH: New York, 2000; pp 113−176.

(45) Gierer, A.; Wirtz, K. Molekulare Theorie der Mikroreibung. *Z. Nuturforsch., A* **1953**, *8*, 532−538.

(46) Dote, J. L.; Kivelson, D.; Schwartz, R. N. A Molecular Quasi-Hydrodynamic Free-Space Model for Molecular Rotational Relaxation In Liquids. *J. Phys. Chem.* **1981**, *85*, 2169−2180.

(47) Edward, J. T. Molecular Volumes and the Stokes−Einstein Equation. *J. Chem. Educ.* **1970**, *47*, 261−270.

(48) Perrin, F. Mouvement Brownien d'un Ellipsoide. I. Dispersion Diélectrique pour des Molécules Ellipsoidales. *J. Phys. Radium* **1934**, *5*, 497−511.

(49) Hu, C. M.; Zwanzig, R. Rotational Friction Coefficients for Spheroids with the Slipping Boundary Condition. *J. Chem. Phys.* **1974**, *60*, 4354−4357.

(50) Dutt, G. B.; Srivatsavoy, V. J. P.; Sapre, A. V. Rotational Dynamics of Pyrrolopyrrole Derivatives in Alcohols: Does Solute−Solvent Hydrogen Bonding Really Hinder Molecular Rotation? *J. Chem. Phys.* **1999**, *110*, 9623−9629.

(51) Mizuguchi, J.; Grubenmann, A.; Wooden, G.; Rihs, G. *Acta. Crystallogr., Sect. B* **1992**, *48*, 696−700.

(52) Dutt, G. B.; Srivatsavoy, V. J. P.; Sapre, A. V. Rotational Dynamics of Pyrrolopyrrole Derivatives in Glycerol: A Comparative Study with Alcohols. *J. Chem. Phys.* **1999**, *111*, 9705−9710.

(53) Dutt, G. B.; Krishna, G. R. Temperature-Dependent Rotational Relaxation of Nonpolar Probes in Mono and Diols: Size Effects versus Hydrogen Bonding. *J. Chem. Phys.* **2000**, *112*, 4676−4682.

(54) Dutt, G. B. Rotational Dynamics of Nondipolar Probes in Alkane−Alkanol Mixtures: Microscopic Friction on Hydrogen Bonding and Nonhydrogen Bonding Solute Molecules. *J. Chem. Phys.* **2000**, *113*, 11154−11158.

(55) Dutt, G. B.; Ghanty, T. K. Rotational Dynamics of Nondipolar Probes in Electrolyte Solutions: Can Specific Interactions be Modeled as Dielectric Friction? *J. Chem. Phys.* **2002**, *116*, 6687−6693.

(56) Dutt, G. B.; Ghanty, T. K. Rotational Dynamics of Nondipolar Probes in Associative Solvents: Modeling of Hydrogen Bonding Interactions using the Extended Charge Distribution Theory of Dielectric Friction. *J. Chem. Phys.* **2003**, *118*, 4127−4133.

(57) Dutt, G. B.; Ghanty, T. K. Rotational Dynamics of Nondipolar Probes in Ethanols: How Does the Strength of the Solute−Solvent Hydrogen Bond Impede Molecular Rotation? *J. Chem. Phys.* **2003**, *119*, 4768−4774.

(58) Dutt, G. B.; Ghanty, T. K. Rotational Dynamics of Nondipolar Probes in Butanols: Correlation of Reorientation Times with Solute-Solvent Interaction Strengths. *J. Phys. Chem. A* **2004**, *108*, 6090−6095.

(59) Dutt, G. B. Molecular Rotation as a Tool for Exploring Specific Solute−Solvent Interactions. *ChemPhysChem* **2005**, *6*, 413−418.

(60) Ben-Amotz, D.; Scott, T. W. Microscopic Frictional Forces on Molecular Motion in Liquids: Picosecond Rotational Diffusion in Alkanes and Alcohols. *J. Chem. Phys.* **1987**, *87*, 3739−3748.

(61) Ben-Amotz, D.; Drake, J. M. The Solute Size Effect in Rotational Diffusion Experiments: A Test of Microscopic Friction Theories. *J. Chem. Phys.* **1988**, *89*, 1019−1029.

(62) Roy, M.; Doraiswamy, S. Rotational Dynamics of Nonpolar Solutes in Different Solvents: Comparative Evaluation of the Hydrodynamic and Quasi Hydrodynamic Models. *J. Chem. Phys.* **1993**, *98*, 3213−3223.

(63) Adachi, M.; Nakamura, S. Absorption Spectrum Shift in the Solid State. A MO Study of Pyrrolopyrrole Pigment. *J. Phys. Chem.* **1994**, *98*, 1796−1801.

(64) Srivatsavoy, V. J. P.; Moser, J.-E.; Grätzel, M.; Chassot, L. Surface Modification of a Hydrogen-Bonded Pigment: A Fluorescence Spectroscopy Study. *J. Colloid Interface Sci.* **1999**, *216*, 189−192.