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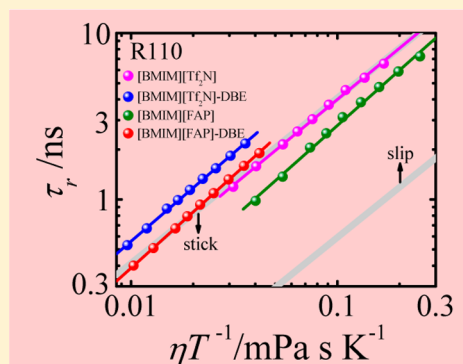
Rotational Diffusion of Charged and Nondipolar Solutes in Ionic Liquid–Organic Solvent Mixtures: Evidence for Stronger Specific Solute–Solvent Interactions in Presence of Organic Solvent

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S Supporting Information

ABSTRACT: Rotational diffusion of a charged solute, rhodamine 110 (R110), and a nondipolar solute, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]-pyrrole (DMDPP), has been investigated in ionic liquids, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]) and 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([BMIM][FAP]), with 0.8 mole fraction of dibenzyl ether (DBE). This study has been undertaken to find out how specific interactions between the solute and the ionic liquid are affected upon dilution with a nondipolar solvent. It has been observed that at a given viscosity (η) and temperature (T), the reorientation times of R110 increase by 40–60% in the ionic liquid–organic solvent mixtures compared to ones in the corresponding neat ionic liquids. In the case of DMDPP, the influence of DBE is less pronounced, and its reorientation times increase by 25–50% at a given η/T . The addition of DBE weakens the numerous interactions prevailing between the cations and the anions of the ionic liquids, which results in stronger specific interactions between the solutes and the constituent ions, consequently leading to slower rotation of the solutes.



1. INTRODUCTION

The organized nanostructure of ionic liquids and its influence on their physicochemical properties have been well-documented in literature.^{1,2} The nanostructure of ionic liquids arises as a consequence of numerous attractive interactions that prevail between the constituent cations and anions. It has also been established that dynamical processes such as photoisomerization, proton transfer, intramolecular charge transfer reactions, dynamics of solvation, and rotational diffusion carried out in these systems are often affected due to the presence of the organized structure.^{3–15} It may be noted that the rotational diffusion of solute molecules in liquids is usually described within the framework of the Stokes–Einstein–Debye (SED) hydrodynamic theory,^{16,17} which predicts a linear relationship between solute reorientation time (τ_r) and the ratio of solvent viscosity to temperature (η/T). The influence of the organized structure of the ionic liquid on solute rotation is usually manifested in the form of a significant degree of nonlinearity in the τ_r versus η/T relationship.^{7–9,11–13} Besides, an increase in the length of the alkyl chain on one of the constituent ions of the ionic liquid leads to a faster rotation of the solute at a given η/T .^{7–15} Essentially, rotational diffusion of the solute molecule is governed by the local viscosity rather than the bulk viscosity of the ionic liquid as a consequence of the organized structure of the medium.

Recent studies have addressed the role of additives on the nanostructure of ionic liquids and the dynamics of solute molecules dissolved in them.^{18–32} Results from our work

suggest that the addition of an organic solvent gradually disrupts the organized structure of the ionic liquid and turns the solvent mixture homogeneous at the microscopic level, which is evident from the trends observed in the rotational diffusion of the solute molecules.^{27,28} These studies have been carried out in 1-methyl-3-octylimidazolium tetrafluoroborate–diethylene glycol and 1-methyl-3-octylimidazolium hexafluorophosphate–dibenzyl ether mixtures. Furthermore, conclusions from our earlier work indicate that the rotational diffusion of organic solutes in neat 1-alkyl-3-methylimidazolium-based ionic liquids with strongly associating anions such as tetrafluoroborate and hexafluorophosphate is significantly influenced by the organized structure of the medium.^{7,8} However, such an influence is not apparent when similar studies were performed in 1-alkyl-3-methylimidazolium-based ionic liquids with weakly associating anions such as bis(trifluoromethylsulfonyl)imide and tris(pentafluoroethyl)trifluorophosphate.^{33,34} In other words, whether solute rotation is affected or not depends on the nature of the anion and the length of the alkyl chain on the imidazolium cation. In light of these findings, it would be pertinent to examine the rotational diffusion of organic solutes in ionic liquids with short alkyl chains and weakly associating anions that are diluted by a nondipolar solvent and compare the

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results to the ones obtained in the corresponding neat ionic liquids.

To address this issue, the present study has been undertaken, wherein the rotational diffusion of a cationic solute rhodamine 110 (R110), and a nondipolar solute, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) (see Figure 1 for

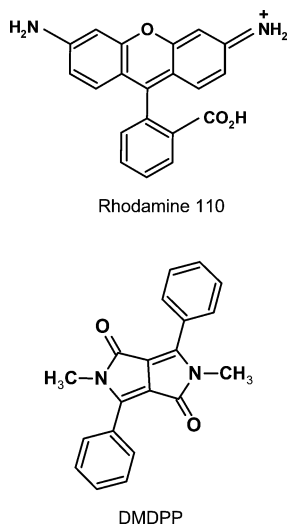


Figure 1. Molecular structures of the solutes.

the molecular structures of the solutes), will be investigated in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide–dibenzyl ether ([BMIM][Tf₂N]–DBE) and 1-butyl-3-methyl-imidazolium tris(pentafluoro-ethyl)trifluorophosphate–dibenzyl ether ([BMIM][FAP]–DBE) mixtures with 0.8 mole fraction of the organic solvent ($x_{\text{DBE}} = 0.8$). These results will be compared to the ones obtained in [BMIM][Tf₂N] and [BMIM][FAP]. DBE has been chosen in the present work due to its low polarity and miscibility with the imidazolium-based ionic liquids and because it is comparable in size to the ions and the solutes employed. A high mole fraction of the organic solvent is preferred because it has been established that the dilution of an ionic liquid with a low-dielectric-constant solvent such as DBE leads to the formation of contact ion pairs in solution.¹⁸ Thus, it would be interesting to find out how the rotational diffusion of the positively charged R110 and nondipolar DMDPP will be affected in such a system.

2. EXPERIMENTAL SECTION

The solvents used in this work, [BMIM][Tf₂N], [BMIM][FAP], and DBE, were purchased from Iolitec, Merck, and Sisco Research Laboratories Pvt. Ltd., respectively. The stated purity of the ionic liquids is >99% with <100 ppm water content and <100 ppm halide ion concentration. The water content of the ionic liquids was estimated by Karl Fischer titration with the aid of a Metrohm 831 KF coulometer and found to be within the limits specified by the manufacturer. The probes R110 (also listed as rhodamine 560) and DMDPP were obtained from Exciton and Ciba Specialty Chemicals, Inc., respectively. The samples with 0.8 mole fraction of DBE in [BMIM][Tf₂N] and [BMIM][FAP] were prepared by weighing and mixing the appropriate amounts of ionic liquid and DBE in glass bottles. Both of the ionic liquids are readily miscible with DBE upon gentle sonication.

The absorption and fluorescence spectra of the samples were recorded using a Jasco V-650 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. The concentrations of the probes were maintained in the range of 10^{-5} to 10^{-6} mol dm⁻³. Fluorescence anisotropy decays were measured using a time-correlated single-photon-counting spectrometer that was purchased from Horiba Jobin Yvon, U.K. The instrumental details and the description concerning the measurement of anisotropy decays have been discussed in our earlier publications.^{33,35} The samples were placed in quartz cells with Teflon caps and sealed with parafilm to prevent the absorption of moisture. The probes R110 and DMDPP were excited at 451 nm, and the emission was monitored around 550 nm. For samples involving R110, all the anisotropy decay measurements were carried out over the temperature range 298–348 K. The anisotropy decay measurements of DMDPP were performed from 298–348 K in neat ionic liquids, whereas for [BMIM][Tf₂N]–DBE and [BMIM][FAP]–DBE mixtures, the temperature ranges were 288–313 K and 293–318 K, respectively. 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. The viscosities of the ionic liquids and liquid mixtures were measured as a function of temperature using a Physica MCR 101 rheometer, and the uncertainties on the measured numbers are about 5%. Adequate precautions were taken to ensure that the ionic liquids do not absorb water during the viscosity measurements by covering the sample chamber of the rheometer with a Teflon plate. The effectiveness of this method was verified by checking the reproducibility of the measured values of η while increasing and decreasing the temperature of the samples.

3. RESULTS AND DISCUSSION

The anisotropy decays of R110 and DMDPP in neat ionic liquids and ionic liquid–organic solvent mixtures could be adequately described by a single-exponential function with one time constant. The reorientation times of both of the solutes obtained from the analysis of the anisotropy decays at different temperatures along with the viscosities of the neat ionic liquids and ionic liquid–organic solvent mixtures are listed in the Supporting Information. The uncertainties on these numbers are in the range of 5–10%. The reorientation times are analyzed with the aid of SED hydrodynamic theory,^{16,17} and according to this theory, τ_r is given by the following equation.

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

In the above equation, V , f , and C are the van der Waals volume of the solute, shape factor, and boundary condition parameter, respectively, and k is the Boltzmann constant. These parameters have been calculated for the solutes R110 and DMDPP by treating them as asymmetric ellipsoids, and the details of the calculation are described in an earlier publication.³³ The calculated values of V , f , and C for R110 are, respectively, 275 Å³, 2.02, and 0.15, and the corresponding numbers for DMDPP are 281 Å³, 2.03, and 0.32. It is evident from eq 1 that τ_r for a given solute should vary linearly with η/T and is independent of the solvent. To find out how well the SED theory is applicable to the solute–solvent systems considered in this study, anisotropy decays of R110 in neat ionic liquids and ionic liquid–organic solvent mixtures that were measured at identical η/T values are displayed in Figure 2,

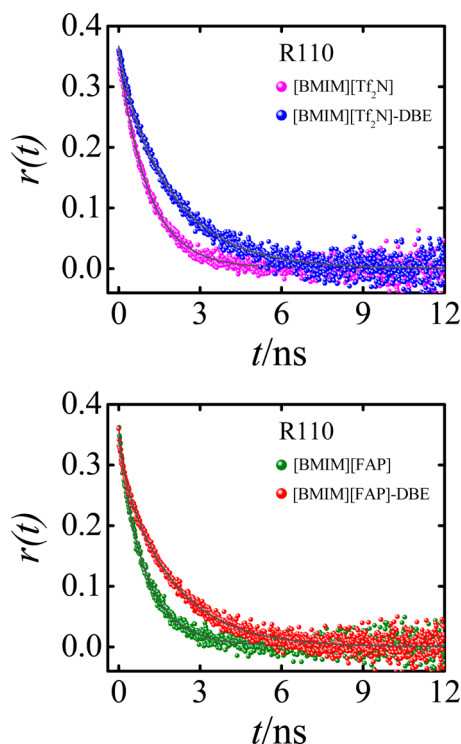


Figure 2. Comparison of anisotropy decays of R110 in neat ionic liquids and in the presence of DBE ($x_{\text{DBE}} = 0.8$), along with the fitted curves. The temperatures have been chosen such that the η/T values for ionic liquid and ionic liquid–DBE mixtures are identical. The η/T values for [BMIM][Tf₂N] and [BMIM][Tf₂N]–DBE and for [BMIM][FAP] and [BMIM][FAP]–DBE are 0.03 and 0.04 mPa s K^{−1}, respectively.

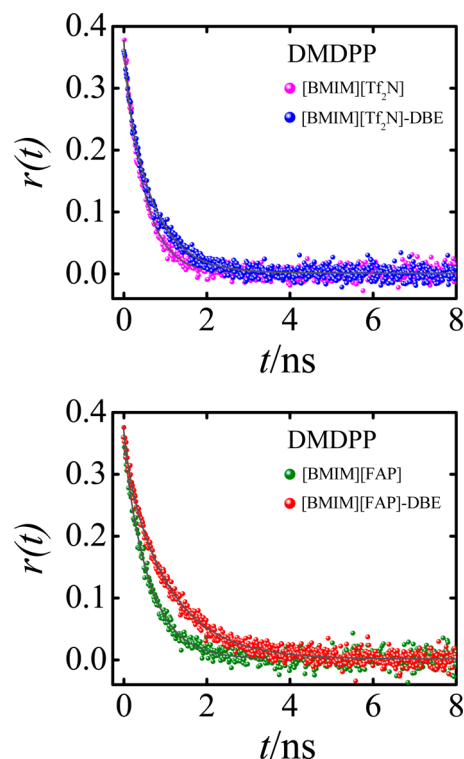


Figure 3. Comparison of anisotropy decays of DMDPP in neat ionic liquids and in the presence of DBE ($x_{\text{DBE}} = 0.8$), along with the fitted curves. The temperatures have been chosen such that the η/T values for ionic liquid and ionic liquid–DBE mixtures are identical. The η/T values for [BMIM][Tf₂N] and [BMIM][Tf₂N]–DBE and for [BMIM][FAP] and [BMIM][FAP]–DBE are 0.03 and 0.04 mPa s K^{−1}, respectively.

and the corresponding decays for DMDPP are given in Figure 3. It is evident from Figure 2 that the anisotropy decays of R110 in ionic liquid–organic solvent mixtures are considerably slower compared to the ones measured in the respective neat ionic liquids. Somewhat similar trends can be noticed for DMDPP in Figure 3, although the differences are less pronounced. To get a better appreciation of the rotational diffusion of the two solutes in these systems, the entire data has been considered by making use of τ_r versus η/T plots.

Figure 4 displays the plots of τ_r versus η/T for R110 in [BMIM][Tf₂N] and [BMIM][FAP], and the linear least-squares fits of log–log plots resulted in the following τ_r versus η/T relationships for R110 in the two ionic liquids.

R110/[BMIM][Tf₂N]

$$\tau_r = (42.2 \pm 1.7)(\eta/T)^{1.02 \pm 0.02}$$

$$(N = 9, R = 0.9992)$$

R110/[BMIM][FAP]

$$\tau_r = (35.4 \pm 2.0)(\eta/T)^{1.10 \pm 0.02}$$

$$(N = 9, R = 0.9983)$$

In these expressions, the units for τ_r and η/T are ns and mPa s K^{−1}, respectively, while N represents the number of data points and R the regression coefficient. It can be noticed from these expressions that the reorientation times of R110 in [BMIM][Tf₂N] at a given η/T are longer by about 40% compared to those observed in [BMIM][FAP]. Since the

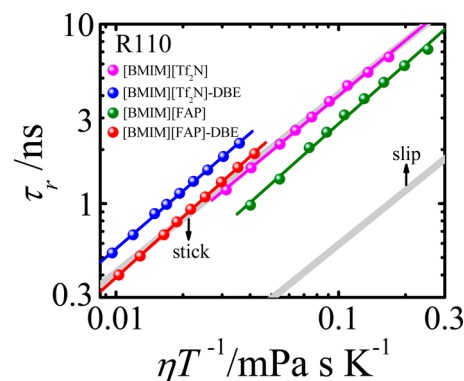


Figure 4. Plots of τ_r versus η/T for R110 in [BMIM][Tf₂N], [BMIM][Tf₂N]–DBE, [BMIM][FAP], and [BMIM][FAP]–DBE. The SED slip and stick lines are also shown in the figure. The lines passing through the data points are obtained by least-squares fits.

exponents in the above expressions are closer to unity, the variation of τ_r with η/T is more or less linear. In other words, the rotational diffusion of R110 in a given ionic liquid follows the predictions of SED hydrodynamic theory. As an alternate treatment, least-squares fits of linear plots have also been performed, which resulted in small negative intercepts that do not have any physical significance. In view of this, we have resorted to the nonlinear fits for the remaining sets of data.

In the absence of specific solute–solvent interactions, the reorientation times of medium-sized solute molecules in solvents of comparable size conform to slip hydrodynamics.³⁶

Furthermore, the friction experienced by the solute molecule decreases with an increase in the size of the solvent, which is known as the size effects.^{36–38} Thus, it is likely that R110 experiences lower friction in [BMIM][FAP] compared to [BMIM][Tf₂N] due to the larger molecular volume of the former. However, it can be noticed that the reorientation times are nowhere close to slip hydrodynamics, which rules out the possibility that the observed differences in the rotational behavior of R110 in [BMIM][FAP] and [BMIM][Tf₂N] are due to size effects. From Figure 4, it is evident that the τ_r values of R110 in [BMIM][Tf₂N] lie on the stick line, and in the case of [BMIM][FAP], they are closer to the stick than the slip line. From these observations, it can be inferred that R110 experiences specific interactions with the anions of the ionic liquids. In fact, this aspect has been extensively investigated by measuring the anisotropy decays of R110 in 1-butyl-3-methylimidazolium-based ionic liquids with various anions in an earlier publication.³⁹ On the basis of our results, it has been established that the rotational diffusion of R110 is governed by the solute–solvent interaction strength in addition to the viscosity of the medium. The strength of specific interactions between R110 and the ionic liquid, in turn, depends on the hydrogen bond basicity of the anion. Since the hydrogen bond basicity of [Tf₂N] is significantly higher than that of [FAP],^{40,41} R110 experiences stronger specific interactions with the former ensuing slower rotation in [BMIM][Tf₂N]. Somewhat similar anion dependence has been observed for nonionic hydrogen bond donating solute 4-aminophthalimide in imidazolium-based ionic liquids.⁴²

However, the main focus of the present study is to find out how the rotational diffusion of R110 will be affected when these ionic liquids are diluted with a nondipolar solvent of low dielectric constant such as DBE. To address this issue, the measured reorientation times of R110 in [BMIM][Tf₂N]–DBE and [BMIM][FAP]–DBE mixtures are also plotted as a function of η/T in Figure 4, and the following τ_r versus η/T relationships have been obtained from the least-squares fits of the data.

R110/[BMIM][Tf₂N]–DBE

$$\tau_r = (76.6 \pm 3.3)(\eta/T)^{1.07 \pm 0.01}$$

$$(N = 9, R = 0.9997)$$

R110/[BMIM][FAP]–DBE

$$\tau_r = (66.9 \pm 1.7)(\eta/T)^{1.12 \pm 0.01}$$

$$(N = 9, R = 0.9999)$$

It can be noticed from these expressions that for a given η/T , the reorientation times of R110 in ionic liquid–organic solvent mixtures are longer by about 50% compared to those obtained in the respective neat ionic liquids. Before rationalizing these results, it would be prudent to understand the nature of the species present in these ionic liquid–organic solvent mixtures. Numerous experimental and theoretical studies carried out on imidazolium ionic liquids suggest that at a high concentration of the organic solvent (usually mole fraction of 0.8 or above), constituent ions of the ionic liquids form contact ion pairs, solvent-separated ion pairs, and loose ion pairs depending on the polarity of the solvent.^{18,43–45} In the case of polar solvents, solvent-separated ion pairs and loose ion pairs are favored, whereas nonpolar solvents induce the formation of contact ion

pairs. On the basis of this premise, it can be assumed that the addition of $x_{\text{DBE}} = 0.8$ to [BMIM][Tf₂N] and [BMIM][FAP] leads to the formation of contact ion pairs where no solvent molecule interposes between the two ions. Another interesting point that must be mentioned here is that R110, being an ionic solute, is not soluble in the nondipolar solvent DBE, and it has also been noticed that at $x_{\text{DBE}} > 0.8$, the solubility of R110 decreases appreciably in the ionic liquid–organic solvent mixtures. Under these circumstances, it is highly likely that the cationic solute R110 forms contact ion pair-like structures with [Tf₂N] and [FAP] anions of the ionic liquids. In other words, the interaction strength between R110 and the anions increases in ionic liquid–organic solvent mixtures as the anions are more readily available compared to neat ionic liquids, which leads to the slower rotation of the solute at a given η/T . It may be argued that DBE forms a cage around the R110, which slows the mobility of the solute. Such a behavior has been observed in the case of the dynamics of water molecules next to hydrophobic solutes. The slowing down of water molecules has been rationalized by the excluded volume effect at the transition state in the reorientation mechanism.⁴⁶ However, fluorescence anisotropy measurements carried out with the nondipolar hydrogen-bond-donating solute 1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) in 1-butanol–squalane mixtures indicate that the rotational diffusion of the solute becomes significantly faster with an increase in the mole fraction of the alkane compared to neat alcohol.⁴⁷ Since DPP is not soluble in squalane, it is embedded in a cage-like structure formed by the butanol molecules. The faster rotation of DPP at a higher mole fraction of squalane has been attributed to DPP–butanol complex experiencing microscopic friction in the alkane-rich environment.⁴⁷ Nevertheless, in the present work, an opposite trend has been observed where the rotation of the solute becomes slower at $x_{\text{DBE}} = 0.8$. Since R110 is not soluble in DBE, it forms ion pairs with [Tf₂N] and [FAP] anions of the ionic liquids, and these ion pairs, in turn, are surrounded by the nondipolar solvent. Thus, it is logical to conclude that the slower rotation observed in ionic liquid–organic solvent mixtures is due to stronger specific interactions between the solute and the anions.

Earlier studies involving charged solutes in electrolyte solutions of organic solvents also addressed the role of ion pairs in explaining the unusually longer reorientation times observed in these systems.^{48–51} Anisotropy measurements and molecular dynamics simulations carried out by Waldeck and co-workers⁵⁰ indicate that the anionic solute resorufin forms ion pairs with Li⁺, and the ion-paired entity strongly coordinates with the solvent dimethyl sulfoxide, resulting in the slower rotation of the solute in electrolyte solutions compared to the rotation in the neat solvent. They have concluded that ion-paired species may exist as discrete entities for long enough time scales compared to the rotational time scale of the solute molecules. On the basis of their work, it is reasonable to assume that the lifetimes of the ion pairs formed between R110 and the anions of the ionic liquids are comparable to their reorientation times.

Rotational diffusion of the nondipolar solute DMDPP, in contrast, is altogether different from that in the cationic solute R110. Plots of τ_r versus η/T for DMDPP in [BMIM][Tf₂N] and [BMIM][FAP] are shown in Figure 5, and it can be noticed from the figure that the rotational diffusion of DMDPP is similar in the two ionic liquids. Since the trends in the variation of τ_r with η/T for DMDPP in [BMIM][Tf₂N] and

[BMIM][FAP] are almost identical, a combined linear least-squares fit of the two data sets was performed, and the following τ_r versus η/T relationship has been obtained.

DMDPP

$$\tau_r = (20.6 \pm 0.8)(\eta/T)^{1.12 \pm 0.02}$$

$$(N = 18, R = 0.9986)$$

It is evident from Figure 5 that the reorientation times of DMDPP in [BMIM][Tf₂N] and [BMIM][FAP] follow slip

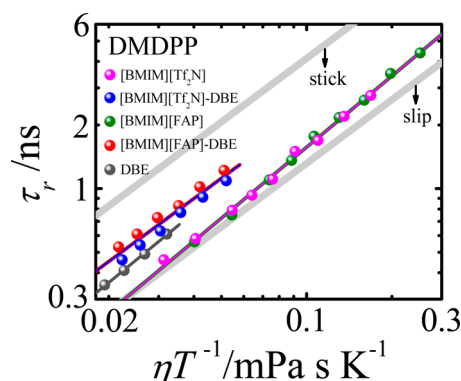


Figure 5. Plots of τ_r versus η/T for DMDPP in [BMIM][Tf₂N], [BMIM][Tf₂N]-DBE, [BMIM][FAP], [BMIM][FAP]-DBE, and DBE. The SED slip and stick lines are also shown in the figure. The lines passing through the data points are obtained by least-squares fits.

hydrodynamics, which is expected considering the fact that this nondipolar solute does not experience strong specific interactions with the 1-butyl-3-methylimidazolium cation of the ionic liquids. However, it must be noted that even DMDPP experiences strong specific interactions via the two carbonyl groups in protic ionic liquids such as 1-(2-hydroxyethyl)-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate, ethylammonium nitrate, and propylammonium nitrate, which possess strong hydrogen bond donating groups.^{32,33,52}

To compare the rotational diffusion of DMDPP in neat ionic liquids and in ionic liquid-organic solvent mixtures, the measured reorientation times of DMDPP in [BMIM][Tf₂N]-DBE and [BMIM][FAP]-DBE mixtures are also plotted as a function of η/T in Figure 5. The trends in the variation of τ_r with η/T for DMDPP in [BMIM][Tf₂N]-DBE and [BMIM][FAP]-DBE mixtures are somewhat similar. Thus, a combined linear least-squares fit of the two data sets was performed and the following τ_r versus η/T relationship has been obtained.

DMDPP

$$\tau_r = (21.7 \pm 5.1)(\eta/T)^{0.99 \pm 0.08}$$

$$(N = 12, R = 0.9701)$$

It can be noticed that the reorientation times of DMDPP in ionic liquid-organic solvent mixtures are longer by 25–50% compared to the ones in neat ionic liquids at a given η/T . The observed slower rotation of DMDPP in ionic liquid-organic solvent mixtures can be ascribed to specific interactions between the [BMIM] cation and the solute. However, unlike R110, the nondipolar solute DMDPP is soluble in the nondipolar solvent DBE. As a consequence, it is possible that DMDPP is solubilized in the DBE-rich region of the ionic liquid-organic solvent mixture. To find out if it is indeed true,

the measured reorientation times of DMDPP in DBE taken from our earlier work²⁸ are plotted in Figure 5. It is evident that the reorientation times of DMDPP in [BMIM][Tf₂N]-DBE and [BMIM][FAP]-DBE mixtures at a given η/T are longer by 15–30% compared to the ones measured in DBE. On the basis of this analysis, it is possible to infer that DMDPP experiences specific interactions with the 1-butyl-3-methylimidazolium cation in [BMIM][Tf₂N]-DBE and [BMIM][FAP]-DBE mixtures.

Alternatively, it is tempting to invoke the concept of dielectric friction to rationalize the slower rotational diffusion of R110 and DMDPP in [BMIM][Tf₂N]-DBE and [BMIM][FAP]-DBE mixtures compared to the diffusion in the corresponding neat ionic liquids. Dielectric friction is the torque on a rotating polar molecule as a result of the induced polarization of the surrounding solvent.¹⁷ It acts as additional friction on the rotating solute besides the viscous drag. According to continuum theories of dielectric friction, its magnitude is inversely proportional to the dielectric constant and directly proportional to the Debye relaxation time of the solvent.^{53,54} The solute properties that contribute to the dielectric friction are its dipole moment or the charge distribution, depending on the model used. Since the dilution of an ionic liquid with a nondipolar solvent makes the system less polar (the dielectric constant as well as the Debye relaxation time decrease), it is unlikely that dielectric friction effects are responsible for the observed slower rotation of the solutes in ionic liquid-DBE mixtures.

CONCLUSIONS

It has been well-established that imidazolium-based ionic liquids at high concentrations of organic solvents form different types of ion pairs depending on the polarity of the latter. In an attempt to find out how such systems influence the rotational diffusion of organic solutes dissolved in them, the present study has been undertaken, and the important conclusions are as follows. According to our findings, the rotational diffusion of cationic R110 as well as nondipolar DMDPP has been affected by the addition of 0.8 mole fraction of nondipolar solvent DBE to [BMIM][Tf₂N] and [BMIM][FAP]. Both solutes undergo slower rotation in ionic liquid-organic solvent mixtures compared to the corresponding neat ionic liquids. Dilution of the ionic liquids with DBE weakens the attractive interactions prevailing between the constituent ions, which allows them to experience stronger specific interactions with the added solute molecules, resulting in slower rotation. Since these results deal with molecular motions in ionic liquid-organic solvent mixtures, they have potential implications toward understanding the rates of chemical reactions in such systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b06297.

Tables showing the reorientation times of R110 and DMDPP in the two ionic liquids and the corresponding ionic liquid-organic solvent mixtures ($x_{\text{DBE}} = 0.8$), along with their viscosities, as a function of temperature.

(PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- Dupont, J. From Molten Salts to Ionic Liquids: A "Nano" Journey. *Acc. Chem. Res.* **2011**, *44*, 1223–1231.
- Hayes, R.; Warr, G. G.; Atkin, R. Structure and Nanostructure in Ionic Liquids. *Chem. Rev.* **2015**, *115*, 6357–6426.
- 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.
- 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.
- Jin, H.; Li, X.; Maroncelli, M. Heterogeneous Solute Dynamics in Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 13473–13478.
- Kimura, Y.; Fukuda, M.; Suda, K.; Terazima, M. Excited State Intramolecular Proton Transfer Reaction of 4'-N,N-Diethylamino-3-hydroxyflavone and Solvation Dynamics in Room Temperature Ionic Liquids Studied by Optical Kerr Gate Fluorescence Measurement. *J. Phys. Chem. B* **2010**, *114*, 11847–11858.
- Gangamallaiiah, 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.
- Gangamallaiiah, 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.
- Gangamallaiiah, 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.
- 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.
- 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.
- 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.
- 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.
- Das, D. K.; Sarkar, M. Solvation and Rotational Relaxation of Coumarin 153 in a New Hydrophobic Ionic Liquid: An Excitation Wavelength Dependence Study. *J. Lumin.* **2012**, *132*, 368–374.
- Das, S. K.; Sahu, P. K.; Sarkar, M. Diffusion–Viscosity Decoupling in Solute Rotation and Solvent Relaxation of Coumarin-153 in Ionic Liquids Containing Fluoroalkylphosphate (FAP) Anion: A Thermophysical and Photophysical Study. *J. Phys. Chem. B* **2013**, *117*, 636–647.
- Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford University Press: New York, 1986.
- 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.
- Stassen, H. K.; Ludwig, R.; Wulf, A.; Dupont, J. Imidazolium Salt Ion Pairs in Solution. *Chem. - Eur. J.* **2015**, *21*, 8324–8335 and references therein..
- Paul, A.; Samanta, A. Effect of Nonpolar Solvents on the Solute Rotation and Solvation Dynamics in an Imidazolium Ionic Liquid. *J. Phys. Chem. B* **2008**, *112*, 947–953.
- Makowska, A.; Dyoniziak, E.; Siporska, A.; Szydlowski, J. Miscibility of Ionic Liquids with Polyhydric Alcohols. *J. Phys. Chem. B* **2010**, *114*, 2504–2508.
- Trivedi, S.; Pandey, S. Interactions within a [Ionic Liquid + Poly(ethylene glycol)] Mixture Revealed by Temperature-Dependent Synergistic Dynamic Viscosity and Probe-Reported Microviscosity. *J. Phys. Chem. B* **2011**, *115*, 7405–7416.
- Li, B.; Wang, Y.; Wang, X.; Vdovic, S.; Guo, Q.; Xia, A. Spectroscopic Evidence for Unusual Microviscosity in Imidazolium Ionic Liquid and Tetraethylene Glycol Dimethyl Ether Cosolvent Mixtures. *J. Phys. Chem. B* **2012**, *116*, 13272–13281.
- Das, D. K.; Sarkar, M. Steady-State and Time-Resolved Fluorescence Behavior of Coumarin-153 in a Hydrophobic Ionic Liquid and Ionic Liquid–Toluene Mixture. *J. Mol. Liq.* **2012**, *165*, 38–43.
- Zhang, X.-X.; Liang, M.; Hunger, J.; Buchner, R.; Maroncelli, M. Dielectric Relaxation and Solvation Dynamics in a Prototypical Ionic Liquid + Dipolar Protic Liquid Mixture: 1-Butyl-3-Methylimidazolium Tetrafluoroborate + Water. *J. Phys. Chem. B* **2013**, *117*, 15356–15368.
- 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.
- 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 Solute Rotation? *J. Phys. Chem. B* **2014**, *118*, 2738–2745.
- 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.
- Prabhu, S. R.; Dutt, G. B. Effect of Low Viscous Nondipolar Solvent on the Rotational Diffusion of Structurally Similar Nondipolar Solutes in an Ionic Liquid. *J. Phys. Chem. B* **2015**, *119*, 2019–2025.
- Jiang, H. J.; FitzGerald, P. A.; Dolan, A.; Atkin, R.; Warr, G. G. Amphiphilic Self-Assembly of Alkanols in Protic Ionic Liquids. *J. Phys. Chem. B* **2014**, *118*, 9983–9990.
- Barra, K. M.; Sabatini, R. P.; Zachery, P.; McAtee, Z. P.; Heitz, M. P. Solvation and Rotation Dynamics in the Trihexyl(tetradecyl)-phosphonium Chloride Ionic Liquid/Methanol Cosolvent System. *J. Phys. Chem. B* **2014**, *118*, 12979–12992.
- Lawler, C.; Fayer, M. D. The Influence of Lithium Cations on Dynamics and Structure of Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2013**, *117*, 9768–9774.
- Prabhu, S. R.; Dutt, G. B. Does Addition of an Electrolyte Influence the Rotational Diffusion of Nondipolar Solutes in a Protic Ionic Liquid? *J. Phys. Chem. B* **2015**, *119*, 6311–6316.
- 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.
- Gangamallaiiah, 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.

- (35) Prabhu, S. R.; Dutt, G. B. Rotational Diffusion of Nondipolar and Charged Solutes in Alkyl Substituted Imidazolium Triflimides: Effect of C2Methylation on Solute Rotation. *J. Phys. Chem. B* **2014**, *118*, 9420–9426.
- (36) Dutt, G. B. Molecular Rotation as a Tool for Exploring Specific Solute–Solvent Interactions. *ChemPhysChem* **2005**, *6*, 413–418.
- (37) Gierer, A.; Wirtz, K. Molekulare Theorie der Mikrorreibung. *Z. Naturforsch., A: Phys. Sci.* **1953**, *8*, 532–538.
- (38) 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.
- (39) 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.
- (40) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. Characterizing Ionic Liquids on the Basis of Multiple Solvation Interactions. *J. Am. Chem. Soc.* **2002**, *124*, 14247.
- (41) Zhao, Q.; Eichhorn, J.; Pitner, W. R.; Anderson, J. L. Using the Solvation Parameter Model to Characterize Functionalized Ionic Liquids Containing the tris(pentafluoroethyl) trifluorophosphate (FAP) Anion. *Anal. Bioanal. Chem.* **2009**, 395, 225.
- (42) Das, D. K.; Sarkar, M. Probing Solute–Solvent Interaction in 1-Ethyl-3-methylimidazolium-Based Room Temperature Ionic Liquids: A Time-Resolved Fluorescence Anisotropy Study. *J. Fluoresc.* **2014**, *24*, 455–463.
- (43) Köddermann, T.; Ludwig, R.; Paschek, D. On the Validity of Stokes–Einstein and Stokes–Einstein–Debye Relations in Ionic Liquids and Ionic-Liquid Mixtures. *ChemPhysChem* **2008**, *9*, 1851–1858.
- (44) Fumino, K.; Fossog, V.; Stange, P.; Wittler, K.; Polet, W.; Hempelmann, R.; Ludwig, R. Ion Pairing in Protic Ionic Liquids Probed by Far-Infrared Spectroscopy: Effects of Solvent Polarity and Temperature. *ChemPhysChem* **2014**, *15*, 2604–2609.
- (45) Herold, E.; Strauch, M.; Michalik, D.; Appelhagen, A.; Ludwig, R. Dynamics of Methanol in Ionic Liquids: Validity of the Stokes–Einstein and Stokes–Einstein–Debye Relations. *ChemPhysChem* **2014**, *15*, 3040–3048.
- (46) Laage, D.; Stirnemann, G.; Hynes, J. T. Why Water Reorientation Slows without Iceberg Formation around Hydrophobic Solutes. *J. Phys. Chem. B* **2009**, *113*, 2428–2435.
- (47) 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.
- (48) Hartman, R. S.; Konitsky, W. M.; Waldeck, D. H. Rotational Diffusion in Electrolyte Solutions. *J. Am. Chem. Soc.* **1993**, *115*, 9692–9700.
- (49) Balabai, N.; Waldeck, D. H. Solute–Solvent Frictional Coupling in Electrolyte Solutions. Role of Ion Pairs. *J. Phys. Chem. B* **1997**, *101*, 2339–2347.
- (50) Balabai, N.; Kurnikova, M. G.; Coalson, R. D.; Waldeck, D. H. Rotational Relaxation of Ionic Molecules in Electrolyte Solutions. Anisotropy Relaxation and Molecular Dynamics Study. *J. Am. Chem. Soc.* **1998**, *120*, 7944–7951.
- (51) Dutt, G. B.; Ghanty, T. K. Rotational Diffusion of Coumarins in Electrolyte Solutions: The Role of Ion Pairs. *J. Phys. Chem. B* **2003**, *107*, 3257–3264.
- (52) 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.
- (53) Nee, T. W.; Zwanzig, R. Theory of Dielectric Relaxation in Polar Liquids. *J. Chem. Phys.* **1970**, *52*, 6353–6363.
- (54) Alavi, D. S.; Waldeck, D. H. Rotational Dielectric Friction on a Generalized Charge Distribution. *J. Chem. Phys.* **1991**, *94*, 6196–6202.