

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/262494219>

Rotational Diffusion of Organic Solutes in 1-Methyl-3-octylimidazolium Tetrafluoroborate–Diethylene Glycol Mixtures: Influence of Organic Solvent on the Organized Structure of the...

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · MAY 2014

Impact Factor: 3.3 · DOI: 10.1021/jp5032459

CITATIONS

8

READS

27

2 AUTHORS:



Sugosh Prabhu

Bhabha Atomic Research Centre

10 PUBLICATIONS 22 CITATIONS

SEE PROFILE



GB Dutt

Bhabha Atomic Research Centre

75 PUBLICATIONS 1,636 CITATIONS

SEE PROFILE

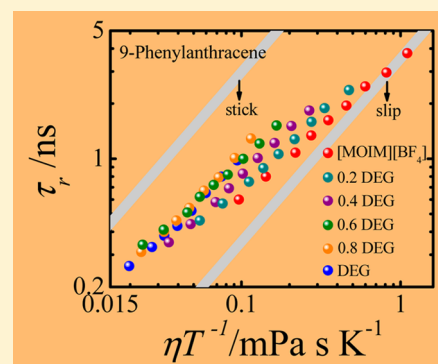
Rotational Diffusion of Organic Solutes in 1-Methyl-3-octylimidazolium Tetrafluoroborate–Diethylene Glycol Mixtures: Influence of Organic Solvent on the Organized Structure of the Ionic Liquid

Sugosh R. Prabhu and G. B. Dutt*

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

Supporting Information

ABSTRACT: Rotational diffusion of two structurally similar organic solutes, 9-phenylanthracene (9-PA) and rhodamine 110 (R110), has been investigated in 1-methyl-3-octylimidazolium tetrafluoroborate–diethylene glycol ([MOIM][BF₄]–DEG) mixtures to understand the influence of organic solvent on the organized structure of the ionic liquid. The reorientation times (τ_r) of nonpolar and charged solutes have been measured as a function of viscosity (η) by changing the temperature (T) as well as the composition of the ionic liquid–organic solvent mixture. These results when analyzed using the Stokes–Einstein–Debye (SED) hydrodynamic theory follow the relationship $\tau_r = A(\eta/T)^n$, where A is the ratio of hydrodynamic volume of the solute to Boltzmann constant. However, in neat [MOIM][BF₄] and up to 0.4 mole fraction of DEG (x_{DEG}), significant deviations from the SED hydrodynamic theory have been noticed with n being much less than unity. As x_{DEG} is increased further, the parameters A and n increase considerably for both solutes, and their rotational diffusion follows the predictions of the SED hydrodynamic theory. It has also been observed that the trends in the variation of τ_r with η/T for 9-PA and R110 are not similar. These observations have been rationalized by taking into consideration the organized structure of the ionic liquid, which gradually becomes homogeneous at the microscopic level with the addition of the organic solvent.



INTRODUCTION

Ionic liquids are known for their distinct physical properties such as nonvolatility, thermal stability, and large liquidus range.¹ Even though ionic liquids can no longer be perceived as nonvolatile,² their applicability in diverse areas of science has been proven adequately.^{3–6} From a fundamental perspective, it has become evident that numerous interactions prevail between the anions and cations of the ionic liquids, which lead to the formation of organized structure.⁷ A thorough grasp on the structure and intermolecular interactions is essential to get a better appreciation of chemical reactivity in ionic liquids. The structural features of ionic liquids have been assimilated with the aid of experimental^{8–13} as well as molecular dynamics simulation studies.^{13–21} To explore molecular motions and solute–solvent interactions, solvation dynamics^{22–31} and rotational diffusion^{27–46} measurements have been performed. The outcome of some of these investigations suggests that the organized structure of the ionic liquids has a significant bearing on the above-mentioned dynamical processes.

Of late, numerous studies have addressed the role of the organized structure of the ionic liquids on solute rotation.^{27–29,38–43} In a majority of these studies, it has been observed that the rotational diffusion of solute molecules did not conform to the predictions of Stokes–Einstein–Debye (SED) hydrodynamic theory.^{47,48} The breakdown of the SED

theory manifested in nonlinear relationships between the reorientation time (τ_r) and η/T , where η and T are the viscosity of the solvent and temperature, respectively. Besides, a faster rotation of the solute has been observed for a given η/T with an increase in the length of the alkyl chain on one of the constituent ions of the ionic liquid. In a few instances, the measured reorientation times of the solutes in ionic liquids have been found to depend on the choice of the excitation wavelength.^{29,42} The breakdown of the SED theory and the excitation wavelength-dependent reorientation times result because of the microheterogeneous nature of the ionic liquids. It has been well-established that ionic liquids, especially ones with long alkyl chains on one of the ions, are prone to aggregate due to van der Waals interactions. 1-Alkyl-3-methylimidazolium-based ionic liquids belong to this category, and recently we have observed the influence of the organized structure of these ionic liquids on solute rotation.^{38–40}

Rotational diffusion studies carried out with a pair of structurally similar nonpolar (9-phenylanthracene, 9-PA) and charged (rhodamine 110, R110) solutes in 1-alkyl-3-methylimidazolium-based ionic liquids with strongly associating anions

Received: April 2, 2014

Revised: April 22, 2014

Published: May 6, 2014

such as tetrafluoroborate ($[\text{BF}_4]$) and hexafluorophosphate ($[\text{PF}_6]$) reveal that the influence of organized structure is not similar for the two solutes.^{38,39} In the case of 9-PA, a faster rotation has been observed for a given η/T with an increase in the length of the alkyl chain from ethyl to octyl on the imidazolium cation. In the presence of organized domains, solute rotation is essentially governed by the local viscosity instead of the bulk viscosity of the ionic liquid. It is likely that the domain sizes increase with an increase in the length of the alkyl chain, and as a consequence the solute 9-PA, which resides in these nonpolar domains, experiences lower friction, leading to the faster rotation. In contrast, for R110, two slopes have been obtained in τ_r versus η/T plots. At low η/T , the rotational diffusion of R110 follows stick hydrodynamics due to specific interactions. However, at high η/T , the organized structure of the ionic liquids precludes stronger hydrogen bonding interactions between the solute and the anions $[\text{BF}_4]$ and $[\text{PF}_6]$, resulting in the faster rotation of the solute than predicted by the SED theory. It may be noted that the effect of the organized structure of ionic liquids on solute rotation has also been observed in the case of *N*-alkyl-*N*-methylmorpholinium bis(trifluoromethylsulfonyl)imides,^{27,42} 1-(2-methoxyethyl)-1-methylmorpholinium tris(pentafluoroethyl)-trifluorophosphate,²⁹ and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides.⁴⁰ In view of these results, it would be pertinent to find out how solute rotation is going to be affected if the organized structure of the ionic liquid is “ruptured” by the addition of an organic solvent.

To address this issue, the present study has been undertaken wherein temperature-dependent fluorescence anisotropies of 9-PA and R110 have been measured in 1-methyl-3-octylimidazolium tetrafluoroborate–diethylene glycol ($[\text{MOIM}][\text{BF}_4]$ –DEG) mixtures. Figure 1 gives the molecular structures of the

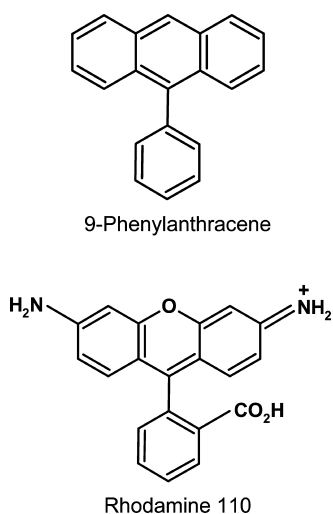


Figure 1. Molecular structures of the solutes.

two solutes employed in this study. $[\text{MOIM}][\text{BF}_4]$ is chosen for this purpose because the rotational diffusion of the solutes 9-PA and R110 in this ionic liquid has been investigated by us earlier.^{38,39} Moreover, it is completely miscible with the moderately viscous organic solvent DEG in all proportions. Essentially, our goal is to find out how the addition of DEG alters the organized structure of $[\text{MOIM}][\text{BF}_4]$ and the subsequent influence on the rotational diffusion of nonpolar and charged solutes in the resulting ionic liquid–organic

solvent mixtures. It may be noted that rotational diffusion studies have been carried out in ionic liquid–organic solvent mixtures before;^{31,41,49–52} however, all of these studies deal with ionic liquids having short alkyl chains.

EXPERIMENTAL SECTION

The ionic liquid 1-methyl-3-octylimidazolium tetrafluoroborate was purchased from io-li-tec, Germany. The stated purity of $[\text{MOIM}][\text{BF}_4]$ is >99% with <100 ppm water content and <100 ppm halide ion concentration. The water content of the ionic liquid was estimated by Karl Fischer titration with the aid of a Metrohm 831 KF coulometer and found to be within limits specified by the manufacturer. The organic solvent diethylene glycol was obtained from Loba Chemie, India, whereas the fluorophores 9-phenylanthracene and rhodamine 110 were from Aldrich and Exciton, respectively. The organic solvent and the fluorophores are of the highest available purity and were used without further purification. The samples with desired mole fractions of DEG in $[\text{MOIM}][\text{BF}_4]$ were prepared by weighing and mixing appropriate amounts of the two liquids in glass bottles. These two liquids are readily miscible upon gentle sonication. Concentrations of the fluorophores in these liquid mixtures were chosen such that the absorbance is in the range of 0.1–0.2 at the wavelength of excitation. The viscosities of the $[\text{MOIM}][\text{BF}_4]$, DEG, and $[\text{MOIM}][\text{BF}_4]$ –DEG mixtures were measured as a function of temperature using a Physica MCR 101 rheometer, and the uncertainties on the measured numbers are about 5%.

Time-resolved fluorescence measurements were carried out with a setup that works on the principle of time-correlated single-photon counting.⁵³ The setup used in the present study was purchased from IBH, UK, and employs a diode laser as the excitation source. The instrumental details have been described in our earlier publication.³³ Samples containing the probe 9-PA were excited with a 374 nm diode laser, and the emission from the samples was collected at 420 nm. On the other hand, samples with the probe R110 were excited with a 445 nm diode laser, and the emission was monitored at 550 nm. The decays were collected in 4096 channels with a time increment of 13.8 ps/channel. The instrument response function of the setup was measured by collecting the scattered light from a TiO_2 suspension in water, and the full width at half-maximum was found to be around 150 ps. 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 values of the *G*-factor at the detection wavelengths of 420 and 550 nm are 0.7 and 0.5, respectively. The anisotropy measurements were carried out over the temperature range 298–348 K, and the temperature of the samples was controlled with the aid of a thermoelectric controller (model DS) from IBH. Each measurement was repeated two to three times, and the average values are reported. The analysis of anisotropy decays was performed using software supplied by IBH, and the details of the analysis have been described in our earlier publication.³³

RESULTS AND DISCUSSION

Figure 2 displays variation of viscosities of [MOIM][BF₄]-DEG mixtures with x_{DEG} over the temperature range of 298–

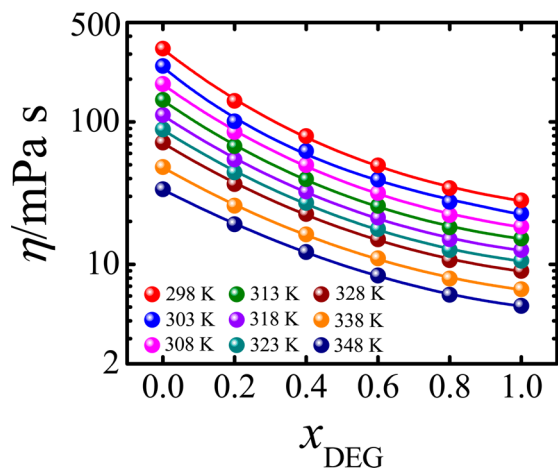


Figure 2. Plots of viscosities of [MOIM][BF₄]-DEG mixtures versus mole fraction of DEG from 298 to 348 K. The curves passing through the data points represent the variation of η with x_{DEG} .

348 K. The viscosities of neat DEG and [MOIM][BF₄] at 298 K are 28.1 and 328 mPa s, respectively, which implies that the viscosity of the ionic liquid is nearly a factor of 12 higher compared to that of the organic solvent. It is evident from the figure that an increase in temperature and x_{DEG} leads to a decrease in the viscosities of the solvent mixtures. To examine the nonideal nature of these liquid mixtures, excess viscosities (η^E) at different temperatures have been calculated with the aid of eq 1.⁵⁴

$$\eta^E = \eta - [x_{\text{DEG}}\eta_{\text{DEG}} + (1 - x_{\text{DEG}})\eta_{[\text{MOIM}][\text{BF}_4]}] \quad (1)$$

In the above equation, η is the viscosity of the [MOIM][BF₄]-DEG mixture at a given x_{DEG} , whereas η_{DEG} and $\eta_{[\text{MOIM}][\text{BF}_4]}$ are the viscosities of neat DEG and [MOIM][BF₄], respectively. The excess viscosities calculated using eq 1 at various temperatures are plotted as a function of x_{DEG} in Figure 3.

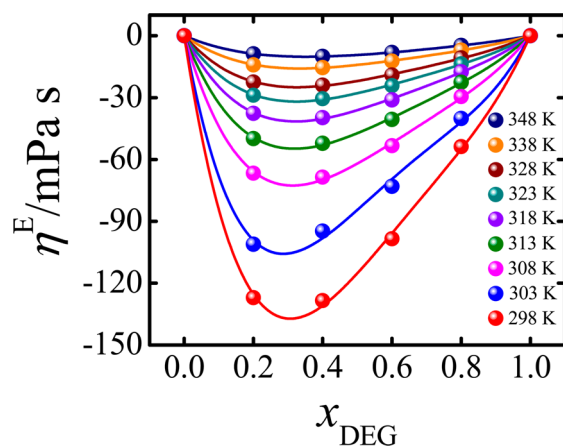


Figure 3. Plots of excess viscosities of [MOIM][BF₄]-DEG mixtures versus mole fraction of DEG from 298 to 348 K. The curves passing through the data points represent the variation of η^E with x_{DEG} , and these curves are obtained by fitting the data to fourth-order polynomial functions.

Inspection of the figure reveals that [MOIM][BF₄]-DEG mixtures exhibit negative η^E at all temperatures with minima centered around $x_{\text{DEG}} = 0.3$, and the excess viscosities become less negative with an increase in temperature. Negative η^E usually arises due to Coulombic interactions within the ionic liquid being replaced by specific interactions between the ionic liquid and the organic solvent in the liquid mixture. Such negative excess viscosities have been observed for numerous ionic liquid-organic solvent mixtures as well.^{41,55–59} It remains to be seen how the loss of Coulombic interactions and the rupture of the organized structure of [MOIM][BF₄] that result from the addition of DEG affect the rotational diffusion of nonpolar and charged solutes.

To obtain the reorientation times, the measured anisotropy decays of 9-PA and R110 in [MOIM][BF₄]-DEG mixtures over the temperature range of 298–348 K have been analyzed, and in all cases a single-exponential function was found to be adequate. The reorientation times of the two solutes along with the viscosities of the solvent mixtures are given in the Supporting Information. The uncertainties on the reorientation times are in the range of 5 to 10%. To understand these results, SED hydrodynamic theory has been employed.^{47,48} According to this theory, the reorientation time of a solute molecule in a solvent continuum is proportional to η/T , which can be expressed as

$$\tau_r = A(\eta/T) \quad (2)$$

In the above equation, $A = (V_h/k)$, where V_h and k are the hydrodynamic volume of the solute and the Boltzmann constant, respectively. The SED theory assumes that V_h depends only on the solute parameters and is given by $V_h = VfC$, where V , f , and C are the van der Waals volume, shape factor, and boundary condition parameter, respectively. The parameter f takes into consideration the nonspherical nature of the solute molecule, and it is >1 for nonspherical solutes.⁶⁰ The extent of coupling between the solute and the solvent is determined by C ; the two boundary condition parameters are hydrodynamic stick with $C = 1$ and hydrodynamic slip, where it follows the inequality $0 < C \leq 1$, and the exact value is a function of the axial ratio of the solute molecule.⁶¹ To apply the SED theory, the solutes employed in this study have been treated as asymmetric ellipsoids, and the details of the calculation have been described in our earlier publication.⁶² The parameters V , f , and C_{slip} that have been calculated for 9-PA are 236 Å³, 1.73, and 0.12, respectively, and the corresponding numbers for R110 are 275 Å³, 2.02, and 0.15.

It has been well-established that rotational diffusion of medium-sized solute molecules such as the ones used in the present study follow SED hydrodynamic theory with slip boundary condition if they experience only viscous friction.^{47,48} Furthermore, because the solutes 9-PA and R110 are structurally similar and comparable in size, their rotational diffusion is expected to be similar according to the predictions of the SED theory. However, the experimentally measured reorientation times of R110 are longer by a factor of 3–6.5 compared to those of 9-PA in [MOIM][BF₄]-DEG mixtures. Charged solutes such as R110 are known to experience specific interactions and also dielectric friction effects in addition to the viscous drag.⁴⁸ It has been shown in our earlier publications that the slower rotational diffusion of R110 is due to the specific interactions it experiences with the medium.^{33,35,36,62} Because R110 is a hydrogen bond donating solute, it forms hydrogen bonds with the anions of the ionic liquid, and the

strength of these hydrogen bonds depends on the hydrogen bond accepting ability or the basicity of the anion.^{35,36} In contrast, 9-PA, being a nonpolar solute, experiences only viscous friction, and as a consequence its rotation is significantly faster compared to that of R110. Moreover, the location of the two solutes in ionic liquids is probably different owing to their distinct chemical nature. Thus, despite their structural similarity, rotational diffusion of 9-PA and R110 is vastly different.

Anisotropy decays of 9-PA and R110 in $x_{\text{DEG}} = 0.4$ at 298 K and in neat $[\text{MOIM}][\text{BF}_4]$ at 323 K are plotted in Figure 4 to

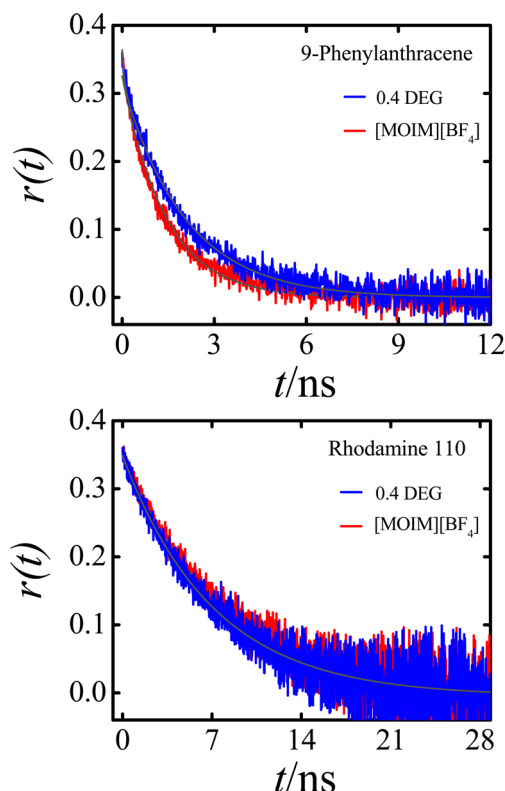


Figure 4. Anisotropy decays of 9-PA and R110 in $x_{\text{DEG}} = 0.4$ and neat $[\text{MOIM}][\text{BF}_4]$ at 298 and 323 K, respectively, along with the fitted curves. These specific composition–temperature combinations have been chosen such that the η/T values for the two systems are almost identical, which is $0.27 \text{ mPa s K}^{-1}$. It can be noticed that the anisotropy decay of 9-PA in $x_{\text{DEG}} = 0.4$ is slower compared to that in neat $[\text{MOIM}][\text{BF}_4]$. In contrast, the anisotropy decays of R110 are almost identical in $x_{\text{DEG}} = 0.4$ and neat $[\text{MOIM}][\text{BF}_4]$.

test the predictions of the SED theory for the systems under investigation. These specific composition–temperature combinations have been chosen such that the η/T values for the two systems are almost identical, which is $0.27 \text{ mPa s K}^{-1}$. It is evident from the figure that the anisotropy decay of 9-PA in $x_{\text{DEG}} = 0.4$ at 298 K is slower compared to that in neat $[\text{MOIM}][\text{BF}_4]$ at 323 K despite both solvent systems having identical η/T . On the contrary, the anisotropy decays overlap in the case of R110. These examples merely illustrate that the SED theory is not valid for some of the solute–solvent combinations employed in this work. To get a complete perspective of the results collated in this work, reorientation times of 9-PA and R110 are plotted as a function of η/T in Figures 5 and 6, respectively. A careful inspection of these figures reveals the following features.

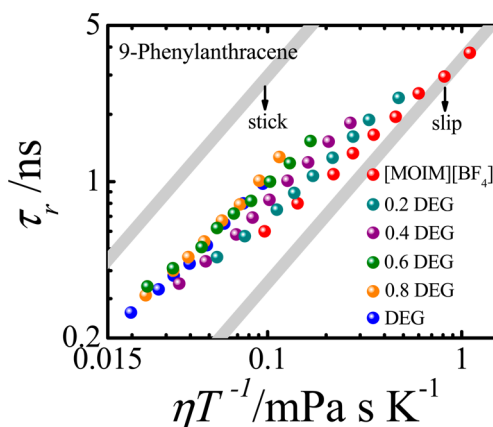


Figure 5. Plots of τ_r versus η/T for 9-PA in $[\text{MOIM}][\text{BF}_4]$ –DEG mixtures. The SED slip and stick lines are also shown. It can be noticed from the figure that the rotation of 9-PA at a given η/T becomes progressively slower with an increase in x_{DEG} .

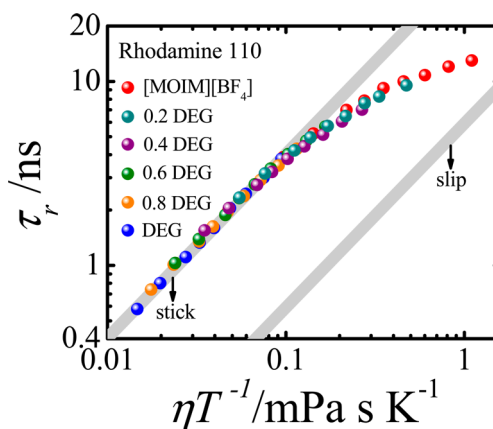


Figure 6. Plots of τ_r versus η/T for R110 in $[\text{MOIM}][\text{BF}_4]$ –DEG mixtures. The SED slip and stick lines are also shown. It can be noticed from the figure that the reorientation times of R110 begin to deviate from the stick line at $\eta/T = 0.1 \text{ mPa s K}^{-1}$.

In neat $[\text{MOIM}][\text{BF}_4]$, the rotational diffusion of 9-PA is closer to the predictions of slip hydrodynamics, whereas in neat DEG, the reorientation times are between the slip and stick limits (see Figure 5). For a given η/T , an increase in the mole fraction of DEG leads to a slower rotation of the solute 9-PA. In the case of R110, the scenario is somewhat different, up to $0.10 \text{ mPa s K}^{-1}$, the reorientation times obey stick hydrodynamics as a consequence of specific interactions between the solute and the solvent mixtures. However, beyond $0.10 \text{ mPa s K}^{-1}$, deviations from the SED stick line can be noticed (see Figure 6). Thus, the data presented in Figures 5 and 6 suggest that for 9-PA there appears to be a change in the boundary condition with an increase in x_{DEG} , whereas in case of R110, the deviations observed at high η/T appear to be as a consequence of decoupling of rotational diffusion from the viscosity of the medium. These aspects have been discussed at length in our earlier publications.^{38,39} Even though the trends in the variation of τ_r with η/T appear to be different for 9-PA and R110, linear least-squares fits of the data provide intriguing information. The reorientation times of the two solutes follow the relationship $\tau_r = A(\eta/T)^n$ instead of eq 2, where both A and n increase with x_{DEG} and the results of the analysis are depicted in Figure 7. It may be noted that there is little or no theoretical justification

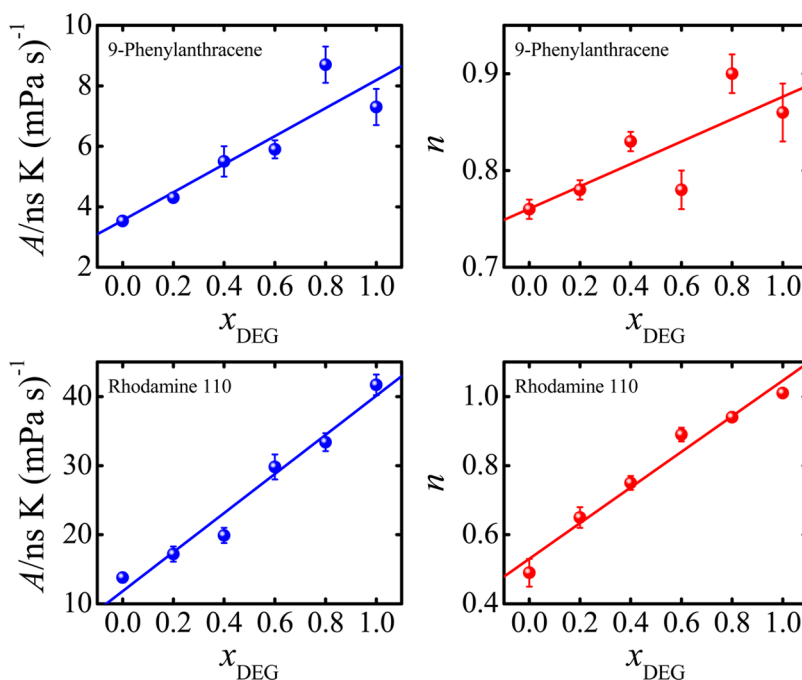


Figure 7. Plots of A and n versus x_{DEG} for the solutes 9-PA and R110 in $[\text{MOIM}][\text{BF}_4]$ –DEG mixtures. The lines passing through the data points have been obtained by linear least-squares fits, and it can be noticed from these plots that both A and n increase with an increase in x_{DEG} .

for these fits, and they should be considered purely empirical by nature. Nevertheless, the departure of n from unity and also the variation of A with solvent composition can be considered as a measure of deviation of the data from the SED model. It can be noticed that the parameter A increases by a factor of 2 and 3, respectively, for 9-PA and R110 with an increase in the mole fraction of DEG. Likewise, n also increases, but marginally for 9-PA and by a factor of 2 for R110 with x_{DEG} . The value of n approaches 1 for both the solutes as the mole fraction of DEG increases, which is in agreement with the predictions of the SED theory. Thus, the analysis carried out so far indicates that the rotational diffusion of nonpolar as well as charged solutes in the DEG-rich region follows SED theory, whereas in the $[\text{MOIM}][\text{BF}_4]$ -rich region, significant deviations have been noticed. It would be interesting to find out the reasons for the observed behavior.

As mentioned earlier, the SED theory assumes that the parameter A depends solely on the properties of the solute. In other words, the hydrodynamic volume of the solute is independent of the solvent in which it is immersed. However, the results obtained in this study suggest that for both solutes, A varies with the composition of the $[\text{MOIM}][\text{BF}_4]$ –DEG mixtures, which is an indication that the boundary condition parameter is not unique in the solvent mixtures employed. This is probable considering the fact that the sizes of organic solvent and ionic liquid used in this study are different. The quasihydrodynamic theory proposed by Gierer–Wirtz (GW) takes these aspects into consideration while calculating the boundary condition parameter.⁶³ According to GW quasihydrodynamic theory, the boundary condition parameter, C_{GW} , is given by the following equation:

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

The parameters σ and C_0 are given by the following equations:

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

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

In these equations, V_s is the volume of the solvent. For the purpose of calculating C_{GW} , van der Waals volumes of the solute and the solvent are usually employed. The V_s values obtained using Edward's increment method⁶⁴ for DEG and $[\text{MOIM}][\text{BF}_4]$ are 101 and 282 Å³, respectively. V_s of the solvent mixture at a particular composition has been calculated using eq 6.⁵⁴

$$V_s = x_{\text{DEG}}V_{\text{DEG}} + (1 - x_{\text{DEG}})V_{[\text{MOIM}][\text{BF}_4]} \quad (6)$$

In the above equation, V_{DEG} and $V_{[\text{MOIM}][\text{BF}_4]}$ are the van der Waals volumes of DEG and $[\text{MOIM}][\text{BF}_4]$, respectively. The C_{GW} values of 9-PA and R110 in DEG are about 40% higher compared to that in $[\text{MOIM}][\text{BF}_4]$. From the calculated C_{GW} values, the parameter A has been obtained, which is 6.4 ns K (mPa s)^{−1} for 9-PA in $[\text{MOIM}][\text{BF}_4]$ and increases to 8.8 ns K (mPa s)^{−1} in DEG, and the corresponding increase in the case of R110 is from 9.1 to 12.5 ns K (mPa s)^{−1}. Thus, the significant increase observed in the values of A for 9-PA and R110 with an increase in the mole fraction of DEG could not be mimicked by the GW quasihydrodynamic theory.

The analysis carried out so far establishes that neither the hydrodynamic nor the quasihydrodynamic theories are able to rationalize the experimental trends noticed in the rotational diffusion of 9-PA and R110 in $[\text{MOIM}][\text{BF}_4]$ –DEG mixtures, especially at low x_{DEG} . As mentioned in the Introduction, somewhat similar results have been obtained when the rotational diffusion of these solutes was investigated by varying the length of the alkyl chain from ethyl to octyl in 1-alkyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphates.^{38,39} The observed results have been explained by taking into consideration the organized structure of the ionic liquids, especially the ones with long alkyl chains. In the present work, however, the influence of organic solvent on the

organized structure of the ionic liquid is examined by investigating the rotational diffusion of 9-PA and R110 in [MOIM][BF₄]-DEG mixtures. It can be noticed from Figure 5 that the reorientation times of 9-PA for a given η/T become progressively longer with an increase in the mole fraction of DEG. The explanation for such an observation is that solute rotation in organized domains, which exist at low mole fraction of the organic solvent in [MOIM][BF₄]-DEG mixtures, is essentially governed by the microviscosity rather than the bulk viscosity of the liquid. Nevertheless, beyond $x_{\text{DEG}} = 0.4$, the reorientation times of 9-PA, for a given η/T , are almost independent of the mole fraction of DEG, which is an indication that there is no change in the organized structure of the medium.

In the case of R110, the trends in the variation of τ_r with η/T are different compared to 9-PA. At low η/T , the reorientation times of R110 follow stick hydrodynamics as it experiences specific interactions with hydroxyl groups of DEG and [BF₄] anion of the ionic liquid. In contrast, at high η/T , deviations from the stick predictions have been noticed. When a solute molecule experiences specific interactions with the surroundings, its reorientation time depends on the solute-solvent interaction strength.^{65,66} On the basis of this premise, at low η/T , the strengths of the specific interactions experienced by R110 with OH groups and [BF₄] anion are probably identical. However, at high η/T , which corresponds to ambient temperatures, the [MOIM][BF₄]-DEG mixtures are likely to be more structured and hence do not facilitate stronger specific interactions with R110. Such an explanation is consistent with results obtained from molecular dynamics simulations that have been carried out using multiscale coarse-graining models for neat imidazolium-based ionic liquids. At ambient temperature with enough attractive interactions between the nonpolar groups on the cationic side chain, the tail groups form relatively stable spatially heterogeneous tail domains. However, at high enough temperatures, the tail groups are expected to have sufficient thermal energy so that they no longer aggregate.¹⁸ Thus, at ambient temperatures (high η/T), hydrogen-bonding groups of the liquid mixtures are not readily accessible to R110 due to the organized structure, which leads to weaker specific interactions and hence the faster rotation of the solute. The results from this work conclusively demonstrate that the organized structure of [MOIM][BF₄] gets ruptured with the addition of DEG and eventually the mixture turns homogeneous at the microscopic level.

CONCLUSIONS

To explore the influence of an organic solvent on the organized structure of an ionic liquid and find out how solute rotation is affected in the resulting ionic liquid-organic solvent mixtures, the present study has been undertaken, and the important findings are summarized in this section. Fluorescence anisotropy measurements performed with a pair of structurally similar nonpolar and charged solutes in [MOIM][BF₄]-DEG mixtures reveal that hydrodynamic and quasihydrodynamic theories fail to rationalize the variation of τ_r with η/T for both 9-PA and R110, especially at low concentrations of the organic solvent. This behavior has been explained by considering the organized structure of the medium. However, with an increase in the mole fraction of DEG, rotational diffusion of both solutes follows the predictions of the SED hydrodynamic theory as the [MOIM][BF₄]-DEG mixtures attain homogeneity at the microscopic level. These results assume importance in view

of the fact that the nanostructural organization of an ionic liquid can be ruptured by mixing it with an appropriate organic solvent, which in turn affects the dynamical process-solute rotation.

ASSOCIATED CONTENT

Supporting Information

Reorientation times of 9-PA and R110 in [MOIM][BF₄]-DEG mixtures and their viscosities as a function of temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

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

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by financial assistance from the Department of Atomic Energy for the Project 2008/38/04-BRNS. S.R.P. acknowledges the University Grants Commission for the award of a Senior Research Fellowship.

REFERENCES

- (1) Rogers, R. D. Reflections on ionic liquids. *Nature* **2007**, *447*, 917–918.
- (2) Earle, E. J.; Esperança, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831–834.
- (3) Cooper, E. R.; Andrews, C. D.; Wheatley, P. S.; Webb, P. B.; Wormald, P.; Morris, R. E. Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues. *Nature* **2004**, *430*, 1012–1016.
- (4) Hallett, J. P.; Welton, T. Room-temperature ionic liquids: solvents for synthesis and catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508–3576.
- (5) Rosen, B. A.; Salehi-Khojin, A.; Thorson, M. R.; Zhu, W.; Whipple, D. T.; Kenis, P. J. A.; Masel, R. I. Ionic liquid-mediated selective conversion of CO₂ to CO at low overpotentials. *Science* **2011**, *334*, 643–644.
- (6) Borra, E. F.; Seddiki, O.; Angel, R.; Eisenstein, D.; Hickson, P.; Seddon, K. R.; Worden, S. P. Deposition of metal films on an ionic liquid as a basis for a lunar telescope. *Nature* **2007**, *447*, 979–981.
- (7) Dupont, J. From molten salts to ionic liquids: a “nano” journey. *Acc. Chem. Res.* **2011**, *44*, 1223–1231.
- (8) Xiao, D.; Rajian, J. R.; Li, S.; Bartsch, R. A.; Quitevis, E. L. Additivity in the optical Kerr effect spectra of binary ionic liquid mixtures: implications for nanostructural organization. *J. Phys. Chem. B* **2006**, *110*, 16174–16178.
- (9) Iwata, K.; Okajima, H.; Saha, S.; Hamaguchi, H. Local structure formation in alkyl-imidazolium-based ionic liquids as revealed by linear and nonlinear Raman spectroscopy. *Acc. Chem. Res.* **2007**, *40*, 1174–1181.
- (10) Atkin, R.; Warr, G. G. The smallest amphiphiles: nanostructure in protic room-temperature ionic liquids with short alkyl groups. *J. Phys. Chem. B* **2008**, *112*, 4164–4166.
- (11) Hardacre, C.; Holbrey, J. D.; Mullan, C. L.; Youngs, T. G. A.; Bowron, D. T. Small angle neutron scattering from 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids ([C_nmim][PF₆], *n* = 4, 6, and 8). *J. Chem. Phys.* **2010**, *133*, 074510/1–074510/7.
- (12) Russina, O.; Triolo, A.; Gontrani, L.; Caminiti, R. Mesoscopic structural heterogeneities in room-temperature ionic liquids. *J. Phys. Chem. Lett.* **2012**, *3*, 27–33.

- (13) 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.
- (14) Pópolo, M. G. D.; Voth, G. A. On the structure and dynamics of ionic liquids. *J. Phys. Chem. B* **2004**, *108*, 1744–1752.
- (15) Wang, Y.; Voth, G. A. Unique spatial heterogeneity in ionic liquids. *J. Am. Chem. Soc.* **2005**, *127*, 12192–12193.
- (16) Hu, Z.; Margulis, C. J. Heterogeneity in a room-temperature ionic liquid: persistent local environments and the red-edge effect. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 831–836.
- (17) Lopes, J. N. A. C.; Pádua, A. A. H. Nanostructural organization in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 3330–3335.
- (18) Wang, Y.; Voth, G. A. Tail aggregation and domain diffusion in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 18601–18608.
- (19) 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.
- (20) 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.
- (21) Hettige, J. J.; Kashyap, H. K.; Margulis, C. J. Anomalous temperature dependence of the intermediate range order in phosphonium ionic liquids. *J. Chem. Phys.* **2014**, *140*, 111102/1–111102/4.
- (22) 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.
- (23) Jin, H.; Li, X.; Maroncelli, M. Heterogeneous solute dynamics in room temperature ionic liquids. *J. Phys. Chem. B* **2007**, *111*, 13473–13478.
- (24) 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.
- (25) Zhang, X.-X.; Liang, M.; Ernsting, N. P.; Maroncelli, M. Conductivity and solvation dynamics in ionic liquids. *J. Phys. Chem. Lett.* **2013**, *4*, 1205–1210.
- (26) 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.
- (27) 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.
- (28) Das, S. K.; Sarkar, M. Studies on the solvation dynamics of coumarin 153 in 1-ethyl-3-methylimidazolium alkylsulfate ionic liquids: dependence on alkyl chain length. *ChemPhysChem* **2012**, *13*, 2761–2768.
- (29) 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.
- (30) Sahu, P. K.; Das, S. K.; Sarkar, M. Fluorescence response of a dipolar organic solute in a dicationic ionic liquid (IL): is the behavior of dicationic IL different from that of usual monocationic IL? *Phys. Chem. Chem. Phys.* **2014**, DOI: 10.1039/C4CP01053A.
- (31) 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.
- (32) 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.
- (33) 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.
- (34) 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.
- (35) 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.
- (36) 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.
- (37) Gangamallai, 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.
- (38) Gangamallai, 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.
- (39) Gangamallai, 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.
- (40) Gangamallai, 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.
- (41) 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.
- (42) 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.
- (43) 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.
- (44) 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.
- (45) 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.
- (46) 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.
- (47) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford University Press: New York, 1986.
- (48) 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.
- (49) 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.

- (50) Sarkar, S.; Pramanik, R.; Ghatak, C.; Setua, P.; Sarkar, N. Probing the interaction of 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][EtSO₄]) with alcohols and water by solvent and rotational relaxation. *J. Phys. Chem. B* **2010**, *114*, 2779–2789.
- (51) 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.
- (52) Das, S. K.; Sahu, P. K.; Sarkar, M. Probing the microscopic aspects of 1-butyl-3-methylimidazolium trifluoroacetate ionic liquid and its mixture with water and methanol: a photophysical and theoretical (DFT) study. *J. Fluoresc.* **2013**, *23*, 1217–1227.
- (53) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: London, 1984.
- (54) Atkins, P.; de Paula, J. *Atkins' Physical Chemistry*, 8th ed.; Oxford University Press: New York, 2006.
- (55) Tian, Y.; Wang, X.; Wang, J. Densities and viscosities of 1-butyl-3-methylimidazolium tetrafluoroborate + molecular solvent binary mixtures. *J. Chem. Eng. Data* **2008**, *53*, 2056–2059.
- (56) Mokhtarani, B.; Sharifi, A.; Mortaheb, H. R.; Mirzaei, M.; Mafi, M.; Sadeghian, F. Density and viscosity of 1-butyl-3-methylimidazolium nitrate with ethanol, 1-propanol, or 1-butanol at several temperatures. *J. Chem. Thermodyn.* **2009**, *41*, 1432–1438.
- (57) Mokhtarani, B.; Sharifi, A.; Mortaheb, H. R.; Mirzaei, M.; Mafi, M.; Sadeghian, F. Densities and viscosities of pure 1-methyl-3-octylimidazolium nitrate and its binary mixtures with alcohols at several temperatures. *J. Chem. Eng. Data* **2010**, *55*, 3901–3908.
- (58) Mokhtarani, B.; Sharifi, A.; Mortaheb, H. R.; Mirzaei, M.; Mafi, M.; Sadeghian, F. Density and viscosity of pyridinium-based ionic liquids and their binary mixtures with water at several temperatures. *J. Chem. Thermodyn.* **2009**, *41*, 323–329.
- (59) Anouti, M.; Vigeant, A.; Jacquemin, J.; Brigouleix, C.; Lemordant, D. Volumetric properties, viscosity and refractive index of the protic ionic liquid, pyrrolidinium octanoate, in molecular solvents. *J. Chem. Thermodyn.* **2010**, *42*, 834–845.
- (60) Perrin, F. Mouvement Brownien d'un ellipsoïde—I. Dispersion diélectrique pour des molécules ellipsoïdales. *J. Phys. Radium* **1934**, *5*, 497–511.
- (61) Hu, C. M.; Zwanzig, R. Rotational friction coefficients for spheroids with the slipping boundary condition. *J. Chem. Phys.* **1974**, *60*, 4354–4357.
- (62) 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.
- (63) Gierer, A.; Wirtz, K. Molekulare Theorie der Mikrorreibung. *Z. Naturforsch. A* **1953**, *8*, 532–538.
- (64) Edward, J. T. Molecular volumes and the Stokes–Einstein equation. *J. Chem. Educ.* **1970**, *47*, 261–270.
- (65) Dutt, G. B.; Ghanty, T. K. Rotational dynamics of nondipolar probes in ethanols: how does the strength of solvent–solute hydrogen bond impede molecular rotation? *J. Chem. Phys.* **2003**, *119*, 4768–4774.
- (66) Dutt, G. B. Molecular rotation as a tool for exploring specific solute–solvent interactions. *ChemPhysChem* **2005**, *6*, 413–418.