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Rotational diffusion of a nonpolar and a dipolar solute in 1-butyl-3-methylimidazolium hexafluorophosphate and glycerol: Interplay of size effects and specific interactions

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Temperature dependent rotational diffusion of a nonpolar solute, 9-phenylanthracene (9-PA), and a dipolar solute, rhodamine 110 (R110), has been examined in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{bmim}^+][\text{PF}_6^-]$) and in a conventional solvent, glycerol. This study has been undertaken to explore how parameters such as solvent size and free volume influence solute rotation in the case of a nonpolar solute, 9-PA. To understand the role of specific solute-solvent interactions, similar measurements have been performed with a dipolar analogue, R110. It has been observed that the viscosity normalized reorientation times of 9-PA are longer by a factor of 1.4–1.6 in glycerol compared to those in $[\text{bmim}^+][\text{PF}_6^-]$. While the most commonly used Stokes-Einstein-Debye hydrodynamic theory is not successful in explaining this experimental observation, Gierer-Wirtz and Dote-Kivelson-Schwartz quasihydrodynamic theories could rationalize this trend, albeit in a qualitative manner. Rotational diffusion of R110, on the other hand, follows an exactly opposite trend compared to 9-PA. The normalized reorientation times of R110 are longer by a factor of 1.3–1.4 in $[\text{bmim}^+][\text{PF}_6^-]$ compared to glycerol, which is due to the formation of stronger solute-solvent hydrogen bonds between the positively charged R110 and the ionic liquid. © 2008 American Institute of Physics. [DOI: 10.1063/1.2827473]

I. INTRODUCTION

Numerous reports available in literature indicate that investigation of rotational diffusion of small and medium sized solute molecules in liquids is one of the convenient means of probing solute-solvent interactions.^{1–3} In these studies, the experimentally measured reorientation time of a solute molecule is compared to the one calculated using the diffusion based Stokes-Einstein-Debye (SED) hydrodynamic theory with slip or stick boundary conditions.^{4,5} Even though the SED theory is reasonably successful in predicting the reorientation times, it is the deviations that have shed light on the nature of solute-solvent interactions. Studies involving dipolar solutes in dipolar solvents have enabled us to examine the role of nonspecific interactions such as dielectric friction,^{6–22} whereas similar studies carried out with solutes possessing hydrogen-bonding functional groups explored the importance of specific interactions^{1,3,22–34} on rotational diffusion. Moreover, these studies have provided information about the influence of solvent size and free volume, also known as “size effects,” on solute rotation when the measurements were carried out with nonpolar solutes in nonpolar and/or dipolar solvents.^{7,16,35–41}

Although the influence of size effects and specific solute-solvent interactions on solute rotation has been reasonably understood in conventional solvents, these aspects have received little attention in ionic liquids. Studies dealing with ionic liquids have gained considerable interest in recent

times because of their potential utility as alternative media for carrying out synthesis and catalysis.^{42–44} Rotational diffusion of organic solutes has been examined in ionic liquids to find whether it is any different from that observed in conventional liquids.^{45–52} Baker *et al.*⁴⁵ have measured the reorientation times of a large nonpolar solute, *N,N*-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide (BTBP) in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{bmim}^+][\text{PF}_6^-]$) as a function of temperature and concluded that a single layer of $[\text{bmim}^+]$ or $[\text{PF}_6^-]$ associates with the solute. However, analysis of the same data by Ingram *et al.*⁴⁶ has revealed that the conclusion reached by Baker *et al.*⁴⁵ is a consequence of modeling BTBP as a sphere instead of an ellipsoid. Ingram *et al.*⁴⁶ have also measured the reorientation times of the solute 4-aminophthalimide (4-AP) in $[\text{bmim}^+][\text{PF}_6^-]$ and other conventional solvents and found that its rotational behavior in the ionic liquid is similar to that expected in a viscous solvent. In addition to these investigations, Ito *et al.*⁴⁸ have examined the rotational diffusion of a number of neutral and charged solutes in the above-mentioned ionic liquid and concluded that even for ionic solutes, charge-charge component of the solute-solvent interaction is not of primary importance for determining rotational friction. The most probable reason for the observed behavior is the strong association between cation and anion of the ionic liquid, which leads to the formation of ion pairs or even higher aggregates.^{53,54} Since the interactions between the cation and anion within an ionic liquid are very strong, they do not strongly interact with the added solutes so as to slow down their rotation.

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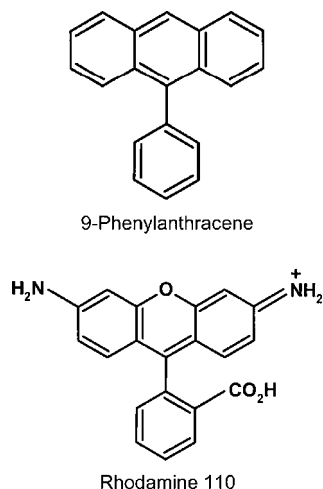


FIG. 1. Molecular structures of solutes 9-phenylanthracene and rhodamine 110.

However, exceptions to this rule do exist and recently we have confirmed it by investigating the rotational diffusion of a pair of closely related nondipolar solutes, 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), in $[\text{bmim}^+][\text{PF}_6^-]$.⁵¹ According to the results of our study, the rotation of the hydrogen bonding solute DPP is slower by a factor of 1.5 compared to DMDPP, which has been rationalized on the basis of strong specific interactions between the two secondary amino groups of the solute and the anion $[\text{PF}_6^-]$ of the ionic liquid. Paul and Samanta⁵² have measured the reorientation times of two dipolar solutes, coumarin 153 (C153) and 4-AP, in an alcohol-functionalized ionic liquid, 1-(hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl) imide, and found that the rotation of 4-AP is significantly slower than that of C153 due to specific interactions between 4-AP and the ionic liquid. These examples illustrate that the role of specific solute-solvent interactions on solute rotation has been explored to a certain extent even in ionic liquids.

However, to the best of our knowledge, the interplay of size effects and specific interactions on solute rotation has not been investigated explicitly in ionic liquids and the present work has been undertaken to address this issue. For understanding the influence of solvent size on solute rotation, investigations need to be carried out with a nonpolar solute since dipolar and charged solutes have a tendency to experience specific interactions and also nonspecific interactions such as dielectric friction. Thus, to examine the interplay of size effects and specific interactions, rotational diffusion of two structurally similar solutes of comparable size but having different functional groups needs to be studied. Such a judicious choice of the solute pair will enable us to discern the above-mentioned effects because the hydrodynamic or mechanical friction experienced by them will be similar. The solutes 9-phenylanthracene (9-PA) and rhodamine 110 (R110) fulfill the requisite criteria and hence were chosen for the present study. Figure 1 gives their molecular structures and it is evident from the figure that the two solutes are structurally similar and the differences between them are in the functional groups present on R110. The solute R110 pos-

sesses two terminal NH_2 groups and a carboxylic group and is positively charged; thus it is likely to form strong hydrogen bonds and also experience ionic interactions with select solvents. The solvents chosen for the present study are $[\text{bmim}^+][\text{PF}_6^-]$ and glycerol, which are highly associative and viscous. Besides having dissimilar functional groups, the sizes of these solvents are also different. The van der Waals volume of glycerol is nearly three times smaller than that of $[\text{bmim}^+][\text{PF}_6^-]$.⁵¹ Thus, these two solvents are well suited for exploring the interplay of size effects and specific interactions. Essentially, in this work, the reorientation times of 9-PA and R110 in $[\text{bmim}^+][\text{PF}_6^-]$ and glycerol will be measured as a function of temperature. The measured reorientation times of both the solutes in the two solvents will be compared under isoviscous conditions and also with the calculated ones obtained using hydrodynamic and quasihydrodynamic theories. It remains to be seen how the rotational diffusion of these two structurally similar solutes is going to be influenced by the interplay of size effects and specific interactions.

II. EXPERIMENT

The solutes 9-PA and R110 (chloride salt) were obtained from Aldrich and Exciton, respectively. The solvents used in this study, glycerol, ethylene glycol, and $[\text{bmim}^+][\text{PF}_6^-]$, are from S. D. Fine-Chem Ltd., Fluka, and Lancaster, respectively. The purity of the ionic liquid is 99% and the water content is less than 100 ppm. All the chemicals are of the highest available purity and were used without further purification. In these experiments, the concentration of the solutes was maintained in the range of 10^{-5} – 10^{-6} M. It has been reported in literature⁵⁵ and we have also noticed during our experiments that $[\text{bmim}^+][\text{PF}_6^-]$ displays weak emission in the wavelength region of 300–600 nm and the emission maxima shift to longer wavelengths with increase in the excitation wavelength. This kind of emission has been ascribed to various associated forms of imidazolium ions.⁵⁵ To ensure that the emission from $[\text{bmim}^+][\text{PF}_6^-]$ does not interfere with the emission of 9-PA and R110, the excitation wavelengths were chosen such that the ratio of the emission of the solute to the ionic liquid is more than 100.

The reorientation times (τ_r) of 9-PA and R110 in $[\text{bmim}^+][\text{PF}_6^-]$ and glycerol over the temperature range of 298–348 K were obtained from Eq. (1)⁵⁶ by substituting the experimentally measured parameters: steady-state anisotropy ($\langle r \rangle$), limiting anisotropy (r_0), and fluorescence lifetime (τ_f). The reasons for obtaining τ_r in an indirect manner will be discussed in due course:

$$\tau_r = \frac{\langle r \rangle}{(r_0 - \langle r \rangle)} \tau_f. \quad (1)$$

Steady-state anisotropies were measured with the aid of Hitachi F-4010 spectrofluorimeter and the experimental details have been described elsewhere.²⁷ The probe 9-PA was excited at 380 nm and emission was monitored in the range of 400–460 nm. On the other hand, R110 was excited at 480 nm and the emission was monitored from 530 to 580 nm. Fluorescence lifetimes of 9-PA were mea-

sured using time-correlated single-photon counting technique⁵⁷ with a gated hydrogen discharge lamp as the excitation source (Edinburgh Instruments, model EI-199). 9-PA was excited at 380 nm and the emission was monitored at 420 nm. Details of the experimental setup are given elsewhere.⁵⁸ For the measurement of R110 lifetimes in [bmim⁺][PF₆⁻] and glycerol and also the anisotropy decays at 348 K, frequency-doubled output of a picosecond Ti:sapphire laser (Tsunami, Spectra Physics) was used as the excitation source. The details of the single-photon counting setup and the laser system have been described in our earlier paper.²⁸ R110 was excited at 460 nm and the emission was monitored at 520 nm. The desired sample temperature in all the three instruments was attained with the help of a thermocouple based temperature controller, which is regulated by a microprocessor (Eurotherm). The viscosities of the solvents, [bmim⁺][PF₆⁻] and glycerol, as a function of temperature were measured using a Physica MCR 101 rheometer.

As mentioned earlier, steady-state anisotropies in combination with fluorescence lifetimes were used to obtain the reorientation times of both 9-PA and R110 in [bmim⁺][PF₆⁻] and glycerol, and the reasons for doing so are as follows. The single-photon counting setup used for the excitation of 9-PA employs a gated hydrogen discharge lamp as the excitation source and, as a consequence, the instrument response function has a width (full width at half maximum) of 1.2 ns. Hence, even if a short component (less than 1.2 ns) is present in the decay of the anisotropy, it cannot be resolved with this setup. In the case of R110, however, the reason for using steady-state anisotropy for obtaining τ_r is altogether different. The viscosities of [bmim⁺][PF₆⁻] and glycerol are quite high, which leads to the condition $\tau_r \gg \tau_f$. Hence, the reorientation times of R110 could not be measured using time-resolved fluorescence anisotropy decays. It must, however, be noted that use of Eq. (1) to obtain the reorientation times is valid only if the intensity and anisotropy decays follow single exponential functions. These aspects were verified by measuring the anisotropy decays of R110 in [bmim⁺][PF₆⁻] and glycerol at 348 K. To obtain the reorientation times using Eq. (1), it is also necessary to know the r_0 values of the solutes. For 9-PA, Bright and McGown⁵⁹ have determined r_0 values as a function of excitation wavelength and their study indicates that it increases when the excitation wavelength is redshifted. For excitation at 380 nm, the r_0 value of 9-PA was found to be 0.367. In the case of R110, r_0 was estimated by rearranging Eq. (1) in the following manner:

$$r_0 = \left(\frac{\tau_r + \tau_f}{\tau_r} \right) \langle r \rangle. \quad (2)$$

Steady-state anisotropies, reorientation times, and fluorescence lifetimes of the solute in ethylene glycol were measured at 298 K as well as 348 K. By substituting these parameters in Eq. (2), the value of r_0 for R110 has been evaluated, which was found to be 0.380 ± 0.005 . Alavi and Waldeck have adopted a similar procedure for the estimation of r_0 for the oxazine 118 probe.¹³

TABLE I. Steady-state anisotropies, fluorescence lifetimes, and reorientation times of 9-phenylanthracene in [bmim⁺][PF₆⁻] as a function of solvent viscosity and temperature. The maximum error in fluorescence lifetimes is less than 2%.

Temperature/K	η /mPa s	$\langle r \rangle$	τ_f /ns	τ_r /ns
298	213.2	0.079 ± 0.004	9.72	2.7 ± 0.2
303	160.6	0.066 ± 0.003	9.56	2.1 ± 0.1
308	124.3	0.056 ± 0.002	9.35	1.7 ± 0.1
313	95.7	0.047 ± 0.003	9.20	1.4 ± 0.1
318	77.3	0.039 ± 0.003	9.02	1.1 ± 0.1
323	62.7	0.033 ± 0.003	8.84	0.9 ± 0.1
328	51.6	0.028 ± 0.002	8.65	0.71 ± 0.06
338	36.5	0.022 ± 0.002	8.34	0.53 ± 0.05
348	26.3	0.017 ± 0.002	8.01	0.39 ± 0.05

III. RESULTS AND DISCUSSION

Steady-state anisotropies, fluorescence lifetimes, and reorientation times of 9-PA in [bmim⁺][PF₆⁻] and glycerol as a function of temperature and solvent viscosity are given in Tables I and II, respectively. The corresponding numbers for R110 are given in Tables III and IV. The measured viscosities of the two solvents as a function of temperature are also given in these tables. From these tables it is evident that the uncertainties on the reorientation times of 9-PA are in the range of 5%–13%, whereas for R110 this number is 8%–12%. However, for R110 at ambient temperatures, $\langle r \rangle \rightarrow r_0$, resulting in larger uncertainties on the τ_r values. Despite these limitations, steady-state anisotropy measurements are the only means of obtaining the reorientation times when $\tau_r \gg \tau_f$. In the case of R110 in [bmim⁺][PF₆⁻] and glycerol, the τ_r values measured at 348 K using time-resolved as well as steady-state methods are identical (see Tables III and IV). As mentioned earlier, the reorientation times obtained in this manner are valid only when the decay of fluorescence and anisotropy follow single exponential functions. It is evident from our experiments that the fluorescence decays of both 9-PA and R110 in [bmim⁺][PF₆⁻] and glycerol could be adequately fitted with a single exponential function throughout the temperature range studied.

However, some discretion must be applied while assuming a single exponential function for the anisotropy decay of the solutes 9-PA and R110 in [bmim⁺][PF₆⁻] due to the fol-

TABLE II. Steady-state anisotropies, fluorescence lifetimes, and reorientation times of 9-phenylanthracene in glycerol as a function of solvent viscosity and temperature. The maximum error in fluorescence lifetimes is less than 2%.

Temperature/K	η /mPa s	$\langle r \rangle$	τ_f /ns	τ_r /ns
298	802.8	0.234 ± 0.004	9.31	16.4 ± 0.8
303	513.2	0.206 ± 0.003	9.24	11.8 ± 0.4
308	372.6	0.175 ± 0.004	9.22	8.4 ± 0.4
313	256.0	0.146 ± 0.003	9.12	6.0 ± 0.2
318	185.2	0.118 ± 0.003	9.00	4.3 ± 0.2
323	136.1	0.097 ± 0.004	8.90	3.2 ± 0.2
328	102.1	0.073 ± 0.003	8.76	2.2 ± 0.1
338	62.5	0.047 ± 0.003	8.53	1.3 ± 0.1
348	38.5	0.032 ± 0.003	8.25	0.8 ± 0.1

TABLE III. Steady-state anisotropies, fluorescence lifetimes, and reorientation times of rhodamine 110 in [bmim⁺][PF₆⁻] as a function of solvent viscosity and temperature. The maximum error in fluorescence lifetimes is less than 2%.

Temperature/K	η /mPa s	$\langle r \rangle$	τ_f /ns	τ_r /ns
298	213.2	0.324 ± 0.002	3.62	20.9 ± 3.2
303	160.6	0.314 ± 0.003	3.60	17.1 ± 2.6
308	124.3	0.298 ± 0.002	3.57	13.0 ± 1.4
313	95.7	0.281 ± 0.002	3.60	10.2 ± 0.9
318	77.3	0.266 ± 0.002	3.55	8.3 ± 0.6
323	62.7	0.249 ± 0.002	3.54	6.7 ± 0.5
328	51.6	0.231 ± 0.002	3.55	5.5 ± 0.3
338	36.5	0.197 ± 0.002	3.54	3.8 ± 0.2
348	26.3	0.165 ± 0.003	3.56	2.7 ± 0.2
				$(2.74 \pm 0.04)^a$

^aMeasured using time-resolved fluorescence depolarization method.

lowing reasons. Ito *et al.*⁴⁸ have measured the anisotropy decays of a number of solutes in [bmim⁺][PF₆⁻] and found that they follow stretched exponential functions. Nevertheless, they observed that the departure from exponential behavior is only marginal. In contrast to their results, a number of groups^{45,49–51} observed single exponential anisotropy behavior for a good number of organic solutes in [bmim⁺][PF₆⁻]. Baker *et al.*⁴⁵ have observed single exponential anisotropy decay for the probe BTBP in [bmim⁺][PF₆⁻]. Chakrabarty *et al.*^{49,50} observed similar behavior for C153 in neat [bmim⁺][PF₆⁻], aqueous mixtures of [bmim⁺][PF₆⁻], and also in mixtures of organic solvents and [bmim⁺][PF₆⁻]. We have also observed single exponential behavior for medium sized nondipolar solutes DMDPP and DPP in [bmim⁺][PF₆⁻] over the temperature range of 298–363 K.⁵¹ Moreover, even for R110 at 348 K, the anisotropy decay was found to be monoexponential. However, it may be argued that the anisotropy decay at lower temperatures need not follow a single exponential function. Nevertheless, temperature dependent anisotropy decay measurements carried out by Ito *et al.*⁴⁸ in [bmim⁺][PF₆⁻] indicate that the degree of nonexponentiality is almost independent of temperature. In view of the arguments presented here and also due to the fact that a number of groups report single exponential function for the

TABLE IV. Steady-state anisotropies, fluorescence lifetimes, and reorientation times of rhodamine 110 in glycerol as a function of solvent viscosity and temperature. The maximum error in fluorescence lifetimes is less than 2%.

Temperature/K	η /mP s	$\langle r \rangle$	τ_f /ns	τ_r /ns
298	802.8	0.353 ± 0.002	3.32	43.4 ± 15.7
303	513.2	0.347 ± 0.003	3.36	35.3 ± 11.8
308	372.6	0.339 ± 0.002	3.38	27.9 ± 5.6
313	256.0	0.325 ± 0.002	3.39	20.0 ± 3.1
318	185.2	0.311 ± 0.002	3.43	15.5 ± 1.8
323	136.1	0.290 ± 0.004	3.43	11.1 ± 1.4
328	102.1	0.268 ± 0.005	3.42	8.2 ± 1.0
338	62.5	0.224 ± 0.008	3.43	4.9 ± 0.6
348	38.5	0.182 ± 0.006	3.46	3.2 ± 0.3
				$(3.2 \pm 0.2)^a$

^aMeasured using time-resolved fluorescence depolarization method.

anisotropy decay of organic solutes in [bmim⁺][PF₆⁻], it is not unreasonable to assume a similar behavior for the solutes used in the present study.

Inspection of Tables I–IV reveals that the reorientation times of 9-PA in glycerol are longer by a factor of 2–6 compared to those of [bmim⁺][PF₆⁻] and in contrast, this ratio for R110 is only in the range of 1.2–2.1. To get a better appreciation of these results and how they compare with the trend predicted by the most commonly employed model for rotational diffusion, the Stokes-Einstein-Debye hydrodynamic theory has been applied. According to this theory, the reorientation time of a solute molecule is given by^{4,5}

$$\tau_r = \frac{\eta V}{kT} (fC). \quad (3)$$

In the above equation, η is the viscosity of the solvent, and k and T are the Boltzmann constant and absolute temperature, respectively. V is the van der Waals volume of the solute, and C is the boundary condition parameter, which follows the inequality $0 < C \leq 1$. f is the shape factor and for nonspherical solutes, the value of f is greater than 1.⁶⁰ It must be noted that the reorientation time calculated using Eq. (3) essentially represents the mechanical or hydrodynamic friction experienced by the solute molecule. In other words, the intermolecular forces operating between the solute and the solvent are of repulsive nature.² To calculate the reorientation times of 9-PA and R110 using the SED theory, van der Waals volumes were obtained using Edward's increment method⁶¹ and have been found to be 236 and 275 Å³ for 9-PA and R110, respectively. For the purpose of modeling 9-PA and R110 as ellipsoids, the axial radii of the solutes were measured with the aid of Corey-Pauling-Koltun space filling models. The best ellipsoid dimensions for the two solute molecules were arrived at in the following manner. The largest dimension, the distance between the two farthest atoms, of the solute molecule was taken as the long axis ($2a$), the largest dimension perpendicular to it was considered as the short-in-plane axis ($2b$), and the thickness of the aromatic ring was considered as out-of-plane axis ($2c$). Since the phenyl ring in both the solutes is oriented orthogonal to the anthracene moiety, it is difficult to get a precise estimate of c . To circumvent this problem, the out-of-plane radius c was calculated from the relation $V = (4\pi/3)abc$ and was found to be 1.8 Å for both 9-PA and R110. Since the value of c obtained in this manner is identical for both the solutes, this method of estimation appears to be reasonable. Given that the three axial radii a , b , and c of each solute are of different lengths, 9-PA and R110 were treated as asymmetric ellipsoids even though rhodamine and fluorescein derivatives have been considered as oblate ellipsoids in literature earlier.¹ The friction coefficients ζ_i along the three principal axes of rotation with stick and slip boundary conditions were obtained from the numerical tabulations available in literature^{62,63} and the diffusion coefficients D_i were calculated from the friction coefficients using the Einstein relation,⁶⁴ which is given below:

TABLE V. Properties of the solutes.

Solute	Axial radii/Å ³	V/Å ³	<i>f</i>	<i>C</i> _{slip}
9-PA	5.7 × 5.5 × 1.8	236	1.73	0.119
R110	6.7 × 5.5 × 1.8	275	2.02	0.147

$$D_i = \frac{kT}{\zeta_i}. \quad (4)$$

Reorientation times were computed from the diffusion coefficients along the three principal axes of rotation (*D_a*, *D_b*, and *D_c*) using Eq. (5), which is valid if the transition dipole is along the long axis of the molecule,¹⁴ and for 9-PA and R110 it was assumed that this condition is fulfilled:

$$\tau_r = \frac{1}{12} \left[\frac{4D_a + D_b + D_c}{D_a D_b + D_b D_c + D_c D_a} \right]. \quad (5)$$

From the calculated reorientation times with stick and slip boundary conditions, the parameters *f* and *C*_{slip} have been obtained. The axial radii, van der Waals volumes, shape factors, and boundary condition parameters for the two solutes are given in Table V. From these calculations it is evident that for a 17% enhancement in the value of *a* from 9-PA to R110, *τ_r^{slip}* and *τ_r^{stick}* increase by 68% and 36%, respectively, and it remains to be seen whether or not this kind of increment can be observed in the experimentally measured reorientation times. However, it is not possible to experimentally verify such theoretical prediction in this particular case because R110 is insoluble in nonpolar solvents. Nevertheless, we have shown earlier that even subtle changes to the solute shape can cause significant variation in the experimentally measured reorientation times of a number of structurally similar coumarins in a nonpolar solvent, squalane.⁶⁵ Moreover, it has been demonstrated that the measured reorientation times when normalized by the respective shape factors and boundary condition parameters are almost identical. This exercise confirms that ellipsoid based hydrodynamic models are reasonably accurate in accounting for the shapes of solute molecules.

Figure 2 displays plots of *τ_r* versus *η/T* for 9-PA and R110 in [bmim⁺][PF₆⁻] and glycerol together with the theoretically calculated stick and slip lines. From the linear least-squares fits of log-log plots of *τ_r* versus *η/T* for 9-PA and R110 in the two solvents, the following nonlinear relationships have been obtained:

9-PA/[bmim⁺][PF₆⁻],

$$\tau_r = (3.72 \pm 0.08)(\eta/T)^{0.87 \pm 0.01} \quad (N = 9, R = 0.999),$$

9-PA/glycerol,

$$\tau_r = (6.9 \pm 0.2)(\eta/T)^{0.97 \pm 0.02} \quad (N = 9, R = 0.999),$$

R110/[bmim⁺][PF₆⁻],

$$\tau_r = (30.2 \pm 0.7)(\eta/T)^{0.92 \pm 0.01} \quad (N = 9, R = 0.999),$$

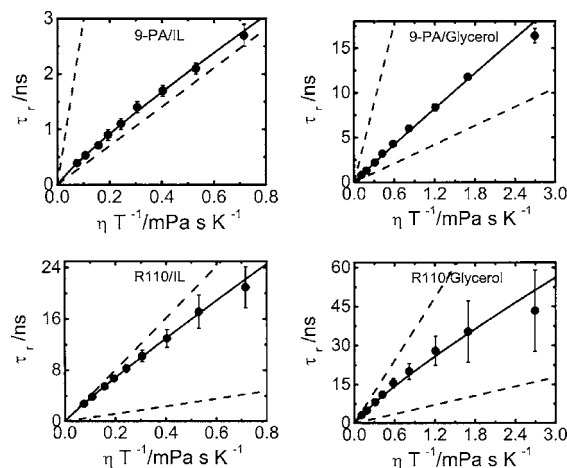


FIG. 2. Plots of *τ_r* vs *η/T* for 9-PA and R110 in [bmim⁺][PF₆⁻] and glycerol and the lines passing through the data points are the fitted ones obtained from log-log plots of *τ_r* and *η/T*. The relationships between these two parameters are given in the text. Theoretically calculated reorientation times using the SED theory with slip and stick boundary conditions are represented by the dashed lines.

R110/glycerol,

$$\tau_r = (22.1 \pm 0.8)(\eta/T)^{0.85 \pm 0.03} \quad (N = 9, R = 0.995).$$

In these expressions, *τ_r* values are in nanosecond and *η/T* in mPa s K⁻¹ and *N* and *R* are the number of data points and regression coefficients, respectively. It is evident from the above-mentioned equations that the degree of nonlinearity is not pronounced. However, it must be noted that there is no theoretical justification for these fits and they should be considered purely empirical. It is evident from Fig. 2 that the experimentally measured reorientation times of 9-PA in [bmim⁺][PF₆⁻] follow slip behavior, whereas those in glycerol are longer by a factor of 2 than predicted by slip hydrodynamics. In contrast, the reorientation times of R110 in [bmim⁺][PF₆⁻] are longer by a factor of 5–6 compared to the slip prediction and the corresponding number for glycerol is 3–5. In essence, the reorientation times of 9-PA in [bmim⁺][PF₆⁻] and glycerol are closer to the predictions of slip hydrodynamics while that of R110 are considerably longer. To get a better appreciation of the differences in the rotational diffusion of 9-PA and R110 in [bmim⁺][PF₆⁻] and glycerol, the reorientation times of both the solutes in glycerol were normalized with respect to the viscosity of the ionic liquid at each temperature by multiplying with a normalization factor, $\gamma = (\eta_{\text{ionic liquid}} / \eta_{\text{glycerol}})_T$. The reorientation times of the two solutes in glycerol normalized in this manner along with those in [bmim⁺][PF₆⁻] are plotted as a function of *η/T* in Figs. 3 and 4, respectively, for 9-PA and R110. Since the reorientation times in glycerol were normalized to that in [bmim⁺][PF₆⁻], the abscissa (*η/T*) for the two solvents is identical in these figures. Inspection of Fig. 3 reveals that the normalized reorientation times of 9-PA are longer by a factor of 1.4–1.6 in glycerol compared to those in [bmim⁺][PF₆⁻]. On the other hand, an opposite trend can be noticed in the rotational diffusion of R110 upon the inspection of Fig. 4. The remainder of the analysis and discussion is dedicated toward rationalizing these contrasting trends observed in the

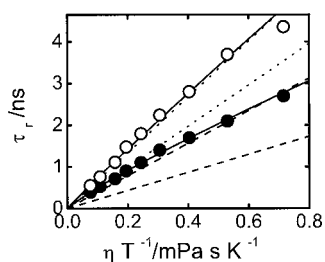


FIG. 3. Comparison of the reorientation times of 9-PA in $[bmim^+][PF_6^-]$ (●) and glycerol (○). The reorientation times in glycerol were normalized to that of $[bmim^+][PF_6^-]$ by multiplying with a normalizing factor γ as described in the text. The lines passing through the data points are the fitted ones obtained from log-log plots of τ_r and η/T . Reorientation times calculated with the GW model for 9-PA/ $[bmim^+][PF_6^-]$ and 9-PA/glycerol are represented by the dotted lines, whereas the corresponding reorientation times obtained with the DKS model are given by the dashed lines.

rotational diffusion of 9-PA and R110 in $[bmim^+][PF_6^-]$ and glycerol.

According to the SED hydrodynamic theory,⁴ rotational diffusion of a solute molecule in the absence of specific and nonspecific interactions is solely governed by solvent viscosity. Based on this perception, it is not evident as to why the viscosity normalized reorientation times of 9-PA are longer in glycerol compared to $[bmim^+][PF_6^-]$. Since 9-PA is a nonpolar solute, the only reason for the observed behavior is the disparity in the sizes of the two solvents, which leads to the prevalence of size effects. In fact, Gierer-Wirtz⁶⁶ (GW) and Dote-Kivelson-Schwartz⁶⁷ (DKS) quasihydrodynamic theories that take into consideration the relative sizes of the solute and solvent while calculating the boundary condition parameter have often been used to rationalize these kinds of experimental results.^{35–41} However, it can be argued that the applicability of the GW and DKS theories is suspect in the case of highly associative liquids such as $[bmim^+][PF_6^-]$ and glycerol, which have been used in the present study. Despite this limitation, numerous instances are available in literature where quasihydrodynamic theories have been successfully employed to rationalize the observed size effects in dealing with the rotational diffusion of nonpolar solutes in associative solvents such as alcohols,^{7,37–40} ethylene glycol,²⁹ and butanol-squalane mixtures.³⁰ Anderton and Kauffman³⁹ have

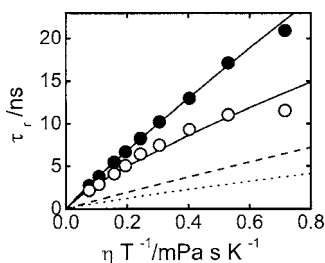


FIG. 4. Comparison of the reorientation times of R110 in $[bmim^+][PF_6^-]$ (●) and glycerol (○). The reorientation times in glycerol were normalized to that of $[bmim^+][PF_6^-]$ by multiplying with a normalizing factor γ as described in the text. The lines passing through the data points are the fitted ones obtained from log-log plots of τ_r and η/T . The dotted and dashed lines represent the mechanical friction experienced by R110 in $[bmim^+][PF_6^-]$ and glycerol, respectively. These lines were obtained from the measured reorientation times of 9-PA in the two solvents (see text for details).

even suggested an elegant method to calculate the free volume of an associative solvent, which will be discussed in due course.

Another issue that needs to be addressed here is the controversy surrounding the boundary condition experienced by nonpolar and charged solutes in highly viscous glycerol.^{28,68–71} Studies carried out with charged and hydrogen bonding solutes indicate that a faster rotation of the solutes is observed in glycerol compared to normal alcohols, which has been explained on the basis of a different boundary condition being operative in glycerol due to the formation of large polymeric network-type structures.⁶⁸ However, a recent rotational diffusion investigation²⁸ carried out with a nondipolar solute, DMDPP, which does not experience strong specific interactions with solvents containing hydroxyl groups, reveals that the hydrodynamic volumes obtained in glycerol and normal alcohols are almost identical. In contrast, it has been observed that the hydrodynamic volumes of a structurally similar hydrogen bonding analog, DPP, are more than a factor of 2 smaller in glycerol compared to that in alcohols. This result conclusively demonstrates that the boundary condition experienced by a solute molecule in the absence of specific solute-solvent interactions is identical in glycerol as well as alcohols. If the large polymeric network-type structures of glycerol are responsible for the observed faster rotation of the solutes, then the hydrodynamic volume of DMDPP should have been different in alcohols and glycerol. A more logical explanation for the observed faster rotation of the charged and hydrogen bonding solutes appears to be the relatively weaker solute-solvent hydrogen bonding in glycerol compared to alcohols. This aspect will be elaborated further while dealing with the rotational diffusion of R110 in glycerol and $[bmim^+][PF_6^-]$. In addition to the comparison with alcohols, another paradox associated with the rotational diffusion data in glycerol is the nonlinear variation of τ_r with η/T at high viscosities. Such an observation has been rationalized on the basis of the different boundary condition experienced by the solute molecules at very high viscosities.^{69–71} However, the most probable explanation appears to be the relatively long reorientation times of the solute molecules at very high viscosities, which leads to the condition $\tau_r \gg \tau_f$. Under these circumstances, the uncertainties on the measured τ_r values are very high. Hence not much can be inferred from the data obtained at very high viscosities in glycerol. Nevertheless, when the fluorescence lifetimes are comparable to the reorientation times as in the case of 9-PA in glycerol, the variation of τ_r with η/T is almost linear (see Fig. 2) even at high viscosities.

Based on the arguments presented in the preceding paragraphs, it seems logical to apply the GW and DKS theories to rationalize the rotational diffusion of 9-PA in $[bmim^+][PF_6^-]$ and glycerol. According to the Gierer-Wirtz theory,⁶⁶ the solvent is made up of concentric shells of spherical particles surrounding the spherical solute molecule at the center. The boundary condition parameter C_{GW} is calculated by considering how the angular velocity of the solvent molecules in

successive shells surrounding the solute decreases as a function of distance away from it. The expression for C_{GW} is given by

$$C_{\text{GW}} = \sigma C_0. \quad (6)$$

In the above equation, σ is the sticking factor, which is given by

$$\sigma = [1 + 6(V_s/V_p)^{1/3} C_0]^{-1} \quad (7)$$

and

$$C_0 = \left\{ \frac{6(V_s/V_p)^{1/3}}{[1 + 2(V_s/V_p)^{1/3}]^4} + \frac{1}{[1 + 4(V_s/V_p)^{1/3}]^3} \right\}^{-1}. \quad (8)$$

In these equations, V_s and V_p are the volumes of the solvent and solute, respectively. When the ratio V_s/V_p is very small, the solvent becomes continuous and C_{GW} approaches unity, which is the SED equation with stick boundary condition. To apply the GW theory, van der Waals volumes of the solvents are usually employed and for [bmim⁺][PF₆⁻] and glycerol, the V_s values are, respectively, 225 and 85.5 Å³.⁵¹ The van der Waals volume of [bmim⁺][PF₆⁻] was obtained by the addition of the volumes of the individual cation and anion. However, a recent molecular dynamics simulation study⁷² indicates that the distribution of cations and anions about a medium sized organic solute is not random. Based on this concept, the procedure adopted here to calculate the van der Waals volume of the ionic liquid is not rigorous. Moreover, because of the significant degree of order present in these systems due to ion-ion interactions, the applicability of concepts such as solvation shell and the utility of continuum models for the solvent are somewhat suspect. Nonetheless, in the absence of an alternative treatment, we have resorted to the methodology that has been applied in the case of conventional solvents. The boundary condition parameter C_{GW} calculated using Eqs. (6)–(8) was found to be 0.167 and 0.226, respectively, for 9-PA/[bmim⁺][PF₆⁻] and 9-PA/glycerol. These numbers indicate that the normalized reorientation times of 9-PA should be 35% longer in glycerol compared to those in [bmim⁺][PF₆⁻] and the experimentally observed number is in the range of 40%–60%. The reorientation times calculated with the GW model for 9-PA/[bmim⁺][PF₆⁻] and 9-PA/glycerol are also given in Fig. 3. Despite the lack of quantitative agreement between the experiment and the theory, the GW model is successful in rationalizing the observed behavior.

The quasihydrodynamic model proposed by Dote-Kivelson-Schwartz⁶⁷ on the other hand, not only considers the solvent size but also incorporates the cavities or free spaces created by the solvent around the probe molecule while calculating the boundary condition. The boundary condition parameter is assumed to depend on the ratio of the solute volume to the total volume available for solute rotation. According to this theory the solute-solvent coupling parameter C_{DKS} is given by

$$C_{\text{DKS}} = (1 + \gamma/\phi)^{-1}. \quad (9)$$

In the above equation, γ/ϕ is a measure of the ratio of the free volume of the solvent to the effective size of the solute molecule, with

$$\gamma = \frac{\Delta V}{V_p} \left[4 \left(\frac{V_p}{V_s} \right)^{2/3} + 1 \right], \quad (10)$$

and ϕ is the ratio of the rotation time predicted by slip hydrodynamics to the stick prediction for the sphere of the same volume. Alternatively ϕ is a product of fC_{slip} . ΔV is the smallest volume of free space per solvent molecule and is empirically related to viscosity, the Hilderbrand-Batschinski parameter B , and also the isothermal compressibility k_T of the solvent by the following expression:

$$\Delta V = Bk_T\eta kT. \quad (11)$$

However, Anderton and Kauffman³⁹ suggested that the Frenkel hole theory and the Hilderbrand treatment of solvent viscosity were developed for simple liquids. Thus Eq. (11) is not a valid measure of the free space per solvent molecule for highly associative solvents such as [bmim⁺][PF₆⁻] and glycerol used in the present study. For associative liquids, ΔV can be calculated by the following expression:³⁹

$$\Delta V = V_m - V_s, \quad (12)$$

where V_m is the solvent molar volume divided by the Avogadro number. Molar volumes of the two solvents used in this study were obtained from the densities of the solvents available in literature.^{43,73} C_{DKS} values calculated in this manner for 9-PA/[bmim⁺][PF₆⁻] and 9-PA/glycerol at 298 K are 0.073 and 0.132, respectively. These numbers decrease by about 8% for both the solvents as the temperature goes up from 298 to 348 K due to the decrease in the densities of [bmim⁺][PF₆⁻] and glycerol. The reorientation times of 9-PA in [bmim⁺][PF₆⁻] and glycerol calculated using the DKS model are also shown in Fig. 3. The DKS theory predicts that the differences in the reorientation times of 9-PA in [bmim⁺][PF₆⁻] and glycerol should be about 80%. The analysis carried out using these two models indicates that predictions of the GW theory are closer to the experimentally measured reorientation times. However, both these theories are successful in reproducing the experimentally observed trend in a qualitative manner. It must be noted that the highly associative nature of the two solvents is not responsible for the lack of quantitative agreement between the experimental results and the numbers obtained with the GW and DKS models. Even in the case of alcohols and alkanes, a similar pattern has been noticed for a number of nonpolar solutes.^{7,37–41}

Now, turning our attention to the rotational diffusion of R110, calculations using SED hydrodynamic theory with slip boundary condition point to the fact that the reorientation times of R110 should be longer compared to those of 9-PA by a factor of 1.7 due to its larger van der Waals volume, longer axial radius (a), and the resulting increase in the shape factor and boundary condition parameter (see Table V). However, as noticed from the results of 9-PA, the mechanical friction experienced by the solute molecule is also dependent on the size of the solvent. In an attempt to incorporate this feature and estimate the mechanical friction experienced by R110 in [bmim⁺][PF₆⁻] and glycerol, experimentally measured reorientation times of 9-PA in these two solvents were multiplied by a factor 1.36, which was ob-

tained by taking the ratio of V_{R110}/f_{R110} and V_{9-PA}/f_{9-PA} . In this estimation, the boundary condition parameter C was not used because it is a solvent dependent parameter. The mechanical friction calculated in this manner for R110 in $[bmim^+][PF_6^-]$ and glycerol is represented by dotted and dashed lines, respectively, in Fig. 4. However, the experimentally measured reorientation times of R110 in $[bmim^+][PF_6^-]$ and glycerol (normalized reorientation times) are longer than the numbers obtained in this manner by a factor of 5.5 and 2.5, respectively. This exercise firmly establishes that mechanical friction alone cannot account for the rotational diffusion of R110 in $[bmim^+][PF_6^-]$ and glycerol. The significantly longer reorientation times of R110 in the two solvents are an indication that the solute molecule is indeed experiencing strong specific interactions with $[bmim^+][PF_6^-]$ and glycerol. Since R110 has two terminal amino groups and a carboxylic group, it can form hydrogen bonds with the hydroxyl groups of glycerol. Moreover, because of its charged character, it can also experience specific interactions with the anion $[PF_6^-]$ of the ionic liquid through hydrogen bonding and ion pair formation. It has been established that specific interactions influence molecular rotation only if hydrogen bonding dynamics takes place on a time scale that is comparable to or slower than the time scale of molecular rotation, which in turn is determined by the strength of the solute-solvent hydrogen bond.¹ If there is some flexibility of the hydrogen bonds to angular motion, the small-step angular displacement occurring during the lifetime of a hydrogen bond will not cause any solvent to be dragged along; thus there will be no effect on molecular rotation.^{74,75} On the other hand, if the solute-solvent hydrogen bonds are strong enough, they will remain intact during the course of the rotation. In other words, stronger solute-solvent hydrogen bonds lead to slower rotation of the solute. In fact, this hypothesis has been verified in the case of the rotational diffusion of two structurally similar nondipolar solutes, DMDPP and DPP, in ethanol and trifluoroethanol and also in isomeric butanols by correlating the measured reorientation times with the calculated solute-solvent interaction strengths.^{33,34} In the present study, despite experiencing higher mechanical friction in glycerol, which is evident from the calculation presented earlier, the viscosity normalized reorientation times of R110 in glycerol are shorter than the ones measured in $[bmim^+][PF_6^-]$. This result clearly indicates that R110 forms stronger hydrogen bonds with $[bmim^+][PF_6^-]$ compared to glycerol.

At this juncture, it is worth mentioning a similar result that has been obtained involving the rotational diffusion of two structurally similar nondipolar solutes, DMDPP and DPP, in 1-decanol and ethylene glycol.²⁹ It has been noticed that the rotational diffusion of DMDPP, which does not experience strong specific interactions with both 1-decanol and ethylene glycol, is slower in ethylene glycol compared to those in 1-decanol. In contrast, an exactly opposite trend has been observed in the case of hydrogen bonding solute DPP. These results have been rationalized in terms of size effects and specific interactions, respectively, in the cases of DMDPP and DPP. Even though the present result is similar to the one obtained earlier, the comparison is made between the rotational diffusion of a nonpolar solute and a charged solute

in an ionic liquid and glycerol. Essentially, this study establishes the fact that when strong solute-solvent hydrogen bonding interactions are prevalent, the influence of size effects on solute rotation is not evident even in the case of ionic liquids.

IV. CONCLUSIONS

In this study an attempt has been made to understand the interplay of size effects and specific interactions on solute rotation by investigating the rotational diffusion of a pair of structurally similar nonpolar and dipolar solutes in an ionic liquid and a conventional solvent. For this purpose, reorientation times of 9-PA and R110 have been measured in $[bmim^+][PF_6^-]$ and glycerol as a function of temperature and the important conclusions are as follows. The viscosity normalized reorientation times of 9-PA in glycerol were found to be 40%–60% longer compared to those in $[bmim^+][PF_6^-]$. The observed behavior has been explained on the basis of the larger size of $[bmim^+][PF_6^-]$ compared to glycerol, which offers lower friction for the solute rotation. Quasihydrodynamic theories of Gierer and Wirtz and Dote-Kivelson-Schwartz could account for the experimental observation in a qualitative manner. It has been noticed that the rotation of R110 in both the solvents is significantly slower compared to that of 9-PA, despite both solutes being structurally similar and having comparable volumes. This behavior has been ascribed to the specific interactions between R110 and the two solvents. The viscosity normalized reorientation times of R110 are 30%–40% longer in $[bmim^+][PF_6^-]$ compared to glycerol, which is due to stronger hydrogen bonding and perhaps ionic interactions between the solute and ionic liquid. The outcome of this work essentially reveals that even in ionic liquids, apart from the viscosity of the medium, the important parameters that govern the solute rotation are the solvent size and free volume in the case of nonpolar solutes, whereas for dipolar and charged solutes, it is the solute-solvent interaction strength.

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