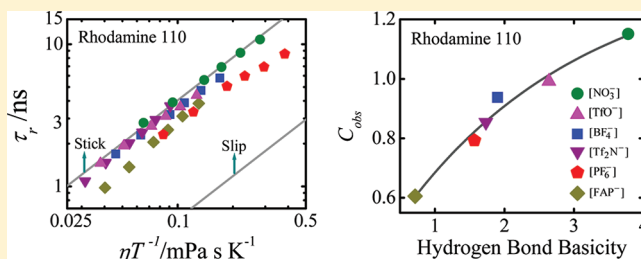Article

Rotational Diffusion of Neutral and Charged Solutes in 1-Butyl-3-Methylimidazolium-Based Ionic Liquids: Influence of the Nature of the Anion on Solute Rotation

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Ⓢ *Supporting Information*

ABSTRACT: Temperature-dependent fluorescence anisotropies of two organic solutes, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DMDPP) and rhodamine 110 (R110), have been measured in 1-butyl-3-methylimidazolium ([bmim$^+$])-based ionic liquids containing the anions hexafluorophosphate ([PF$_6^-$]), bis(trifluoromethylsulfonyl)imide ([Tf$_2$N$^-$]), tetrafluoroborate ([BF$_4^-$]), trifluoromethanesulfonate ([TfO$^-$]), and nitrate ([NO$_3^-$]). This data has been used in conjunction with the recently published results (Dutt, G. B. *J. Phys. Chem. B* **2010**, *114*, 8971) for the same solutes in [bmim$^+$] tris(pentafluoroethyl)trifluorophosphate ([FAP$^-$]) to understand the influence of various anions on solute rotation. The boundary condition parameter C_{obs}, which has been obtained from the analysis of the data using Stokes−Einstein−Debye hydrodynamic theory, for the neutral solute DMDPP is more or less the same in all the ionic liquids. Moreover, C_{obs} values are close to the predictions of slip boundary condition, which indicates that solvent viscosity alone governs the rotation of DMDPP. In contrast, for R110, which experiences specific interactions with the anions of the ionic liquids, the C_{obs} values are close to stick hydrodynamics. It has also been noticed that the C_{obs} values vary with the nature of the anion and this variation correlates with the hydrogen bond basicities of the anions of the ionic liquids.

1. INTRODUCTION

Research dealing with ionic liquids has received a tremendous impetus due to their utility and novelty. The use of ionic liquids in synthesis, catalysis, and electrochemistry and in the formation of metal nanoparticles has been well-documented.[1,2] In addition to the utilitarian aspects of ionic liquids, efforts have also been directed toward exploring reaction rates,[3−9] dynamics of solvation,[10−16] and rotation[12−27] in these media and assimilating the measured parameters in terms of their physicochemical properties and structure. Among the processes mentioned, rotational diffusion of solute molecules has been employed to comprehend the interactions prevailing between the solute and the constituents of the ionic liquids. The results obtained to date can be broadly divided into two categories. In the first category, solute rotation is solely governed by the viscosity of the medium,[13−15] whereas, in the second category, specific interactions between the solute and the ions of the medium need to be invoked to explain the observed trends.[7,17−25] It must be noted that our endeavor belongs to the latter category, wherein solute rotation has been investigated in ionic liquids with an emphasis on understanding hydrogen bonding interactions.[17−21]

Recently, we have examined the rotational diffusion of neutral and cationic solutes in a new class of ionic liquids containing tris(pentafluoroethyl)trifluorophosphate ([FAP$^-$]) anion.[20,21] The purpose behind these studies is to understand how a weakly coordinating anion such as [FAP$^-$] influences the

solute rotation. The ionic liquids have been chosen in such a manner that the nature of the cation constituting ionic liquid was varied but the anion remained the same. It has been noticed that rotational diffusion of the neutral solute 1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DMDPP) in 1-alkyl-3-methylimidazolium [FAP$^-$] follows slip hydrodynamics and there is no influence of alkyl chain length on its rotation. These observations indicate that the rotational diffusion of DMDPP is essentially controlled by the viscosity of the ionic liquid. In contrast, rotational diffusion of the cationic solute rhodamine 110 (R110) is close to the predictions of stick hydrodynamics, which is due to specific interactions between the solute and the [FAP$^-$] anion. A small but discernible influence has been noticed on the rotational diffusion of R110 upon increasing the alkyl chain length on the imidazolium cation, and the observed behavior has been rationalized by taking into consideration the solventberg model. Only in the case of 1-(2-hydroxyethyl)-3-methylimidazolium [FAP$^-$], rotational diffusion of the neutral solute DMDPP was found to be marginally slower compared to its ethyl counterpart due to hydrogen bonding interactions between the carbonyl groups of the solute and the hydroxyl group of the imidazolium cation.[20]

Apart from the imidazolium-based tris(pentafluoroethyl)-trifluorophosphates, rotational diffusion studies have also been performed in other FAP-based ionic liquids with cations such as 1-butyl-1-methylpyrrolidinium, 1-(2-methoxyethyl)-1-methyl-pyrrolidinium, 1-(2-methoxyethyl)-1-methylpiperidinium, and N-(2-methoxyethyl)-N-methylmorpholinium.[21] While the results for DMDPP are more or less similar to those obtained in imidazolium-based ionic liquids, R110 displayed somewhat different trends. Rotational diffusion of R110 in the ionic liquid having morpholinium cation was found to be faster by a factor of 1.5 compared to others. The faster rotation of the solute has been rationalized on the basis of the highly associative nature of the N-(2-methoxyethyl)-N-methylmorpholinium cation, which precludes R110 from experiencing strong specific interactions with the [FAP⁻]. This result establishes that, even though specific interactions transpire between the solute and the anion of the ionic liquid, the cation can indeed modulate the strength of these interactions and thus influence its rotation. In essence, the results summarized here illustrate how the cation of the ionic liquid affects solute rotation.

Thus, as a subsequent stride, it would be interesting to investigate the influence of various anions of the ionic liquids on the rotational diffusion of the solutes DMDPP and R110, whose molecular structures are given in Figure 1. To this effect,
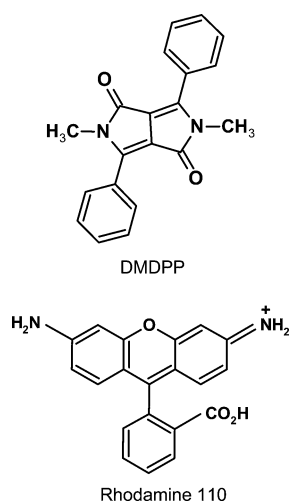

Figure 1. Molecular structures of the solutes used in the study.

the most commonly used cation 1-butyl-3-methylimidazolium ([bmim⁺]) has been considered in conjunction with anions such as hexafluorophosphate ([PF_6^-]), bis-(trifluoromethylsulfonyl)imide ([Tf_2N^-]), tetrafluoroborate ([BF_4^-]), trifluoromethanesulfonate ([TfO⁻]), and nitrate ([NO_3^-]). These results will be analyzed together with the ones obtained in [bmim⁺][FAP⁻]. Therefore, the main objective of the present study is to find out how these different anions affect the rotational diffusion of neutral and charged solutes and whether the observed trends can be correlated with any known physicochemical property of the anions.

2. EXPERIMENTAL SECTION

The probes DMDPP and R110 were obtained from Exciton and Ciba Specialty Chemicals, Inc., respectively. Concentrations of the probes in the ionic liquids were chosen such that, at the wavelength of excitation, which is 445 nm for both DMDPP and R110, the absorbance is less than 0.2. All the ionic

liquids were purchased from io-li-tec, and the purity of the liquids is >99% with <100 ppm halide ion concentration. The stated water contents of the ionic liquids, 1-ethyl-3-methyl-imidazolium hexafluorophosphate ([emim⁺][PF_6^-]), [bmim⁺]-[PF_6^-], and 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim⁺][PF_6^-]), are 140, 240, and 250 ppm, respectively. In the case of 1-butyl-3-methylimidazolium ionic liquids having [BF_4^-], [TfO⁻], and [NO_3^-] anions, the stated water content is 240 ppm, whereas for [bmim⁺][Tf_2N^-] it is 90 ppm. To find out if the amount of water present in these ionic liquids adheres to the values mentioned by the manufacturer, it was estimated by Karl Fischer titration with the aid of a Metrohm 831 KF Coulometer and found to be within the specified limits. The viscosities (η) of the ionic liquids were measured as a function of temperature using a Physica MCR 101 rheometer, and the uncertainties on the measured numbers are about 5%. To find out whether the small amount of water present in these ionic liquids alters their viscosity in a significant manner, the measured viscosities were compared with the data available in the literature.[28,29] It has been found that the discrepancy between the viscosity values measured by us and the reported numbers is in the range 5−10%.

Time-resolved fluorescence measurements were carried out with a setup that works on the principle of time-correlated single-photon counting.[30] The setup used in the present study was purchased from IBH, U.K., and employs a diode laser as the excitation source. The instrumental details have been described in our earlier publication.[20] Samples containing the probes DMDPP and R110 in ionic liquids were excited with a 445 nm diode laser, and the emission from the samples was collected at 550 nm. The decays were collected in 4096 channels with a time increment of 14.4 ps/channel. The instrument response function (IRF) of the setup was measured by collecting the scattered light from a TiO_2 suspension in water, and the full width at half-maximum (FWHM) was found to be around 100 ps. For lifetime measurements, decays were collected by keeping the emission polarizer at a magic angle (54.7°) with respect to the polarization of the excitation laser to ensure the complete depolarization of the fluorescence. 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. All the anisotropy measurements were carried out over the temperature range 313−348 K. Only in the case of [emim⁺][PF_6^-] anisotropy decays were measured in the temperature range 338−358 K, as it melts only at 335 K. The temperature of the sample was controlled with the aid of a thermoelectric controller (model DS) from IBH. Each measurement was repeated 2−3 times, and the average values are reported. The analyses of fluorescence and anisotropy decays were performed using the software supplied by IBH. The anisotropy decays were analyzed using the impulse reconvolution method as well as tail fit of the anisotropy data (without reconvolution). Both of the methods of analysis yielded identical numbers for the anisotropy decay constants, since the smallest time constant measured in the present study is 460 ps, which is 4 times longer than the FWHM of the IRF.

3. RESULTS AND DISCUSSION

The reorientation times (τ_r) of the solutes DMDPP and R110 over the temperature range 313−348 K have been obtained from the analysis of the measured anisotropy decays. A single exponential function with one τ_r is adequate to fit the anisotropy decays of both of the solutes in all the ionic liquids used in the present study. The reorientation times obtained in this manner are given in the Supporting Information, and the uncertainties on these numbers are about 5−10%. The Stoke−Einstein−Debye (SED) hydrodynamic theory[31,32] has been employed to assimilate these results obtained in 1-butyl-3-methylimidazolium-based ionic liquids with various anions. The SED theory is based on the presumption that the rotation of a solute dissolved in a solvent takes place by small-step diffusion and its reorientation time is proportional to the viscosity of the fluid at a given temperature, T. The solute properties that govern the rotation are its size and shape, which are expressed in terms of van der Waals volume, V, and shape factor, f. These parameters are incorporated into the SED model by treating the solute as a symmetric or an asymmetric ellipsoid.[33] In addition to the above-mentioned parameters, the coupling between the solute and the solvent also plays an important role in controlling the rotational diffusion of a solute molecule. In the SED model, the magnitude of the solute−solvent coupling parameter, which is usually denoted by C, depends on the axial ratio of the solute molecule and the two limiting cases are the hydrodynamic stick and slip.[34] Thus, the expression for the reorientation time is given by

$$\tau_r = \frac{VfC}{k}\left(\frac{\eta}{T}\right) \tag{1}$$

where k is the Boltzmann constant. The SED theory predicts a linear relationship between τ_r and η/T with $\tau_r \to 0$ when $\eta/T \to 0$. Even though a vast majority of experimental data satisfies the first criteria, the latter condition is seldom fulfilled, as extrapolation of τ_r vs η/T plots leads to nonzero intercepts. As an alternate treatment of the data, when the fits were performed by considering the log−log scale, a slight degree of nonlinearity was noticed in these plots. Despite numerous studies, a suitable explanation for such a behavior was found to be elusive.

Figure 2 displays variation of η as a function of temperature for the six 1-butyl-3-methylimidazolium-based ionic liquids, and
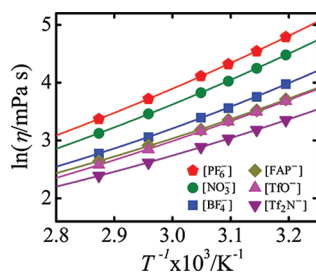
Figure 2. Plots of $\ln(\eta)$ versus $1/T$ for 1-butyl-3-methylimidazolium-based ionic liquids with various anions. The lines passing through the data points are drawn as a visual aid.

this data is also given in the Supporting Information. It can be noticed from the figure that $[bmim^+][PF_6^-]$ and $[bmim^+]$-$[Tf_2N^-]$ have the highest and lowest viscosities, respectively, and at 313 K these numbers differ by more than a factor of 4. Another interesting feature to be noted from Figure 2 is that the viscosities of $[bmim^+][TfO^-]$ and $[bmim^+][FAP^-]$ are

almost identical. Thus, it would be interesting to compare the anisotropy decays of DMDPP and R110 in these ionic liquids, since the viscosity of the medium is the sole parameter responsible for the rotational diffusion according to the SED theory. Anisotropy decays of DMDPP and R110 are displayed in Figure 3, and inspection of the figure reveals that the
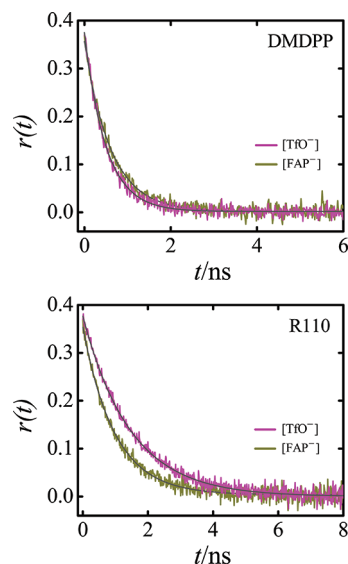
Figure 3. Anisotropy decays of DMDPP and R110 in $[bmim^+][FAP^-]$ and $[bmim^+][TfO^-]$ at 348 K. The fitted curves are also shown in the figure. It can be noticed from the figure that the anisotropy decays of DMDPP almost overlap in the two ionic liquids, since its rotational diffusion is essentially governed by the viscosity, which is more or less similar for these two ionic liquids. In contrast, the anisotropy decay of R110 is significantly slower in $[bmim^+][TfO^-]$ compared to that observed in $[bmim^+][FAP^-]$.

anisotropy decays of DMDPP are almost identical in the two ionic liquids, whereas the anisotropy decay of R110 is significantly slower in $[bmim^+][TfO^-]$ compared to that observed in $[bmim^+][FAP^-]$. The reasons for the observed behavior will be discussed in due course.

Apart from the viscosities of the ionic liquids, solute parameters such as van der Waals volume, shape factor, and boundary condition parameter, C_{slip}, also need to be calculated for applying the SED theory. The details concerning the calculation of these parameters for DMDPP and R110 have been described in our earlier publication.[20] The parameters V, f, and C_{slip} for DMDPP are 281 Å^3, 2.03, and 0.32, respectively, and the corresponding numbers for R110 are 275 Å^3, 2.02, and 0.15. Plots of τ_r vs η/T for DMDPP and R110 along with the slip and stick lines are displayed in Figure 4. It can be noticed from the figure that the reorientation times of DMDPP follow the predictions of slip boundary condition, while for R110 they are close to stick hydrodynamics. Besides these general features, it is not possible to gauge the influence of various anions on solute rotation from the figure due to a large disparity in the viscosities of the ionic liquids employed, which in turn leads to a considerable variation in the measured reorientation times. To circumvent this limitation, the observed boundary condition parameter C_{obs} for a given solute−ionic liquid combination, which is expected to be independent of viscosity and temperature, has been calculated from the measured reorientation times using eq 1.
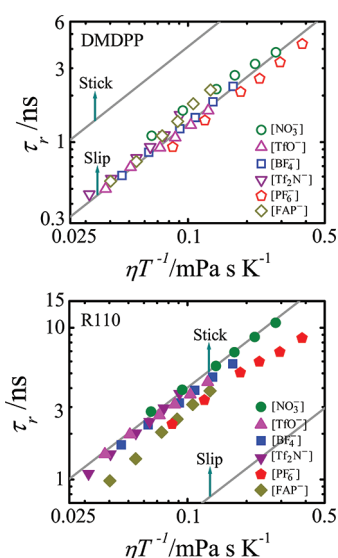
Figure 4. Plots of τ_r versus η/T for DMDPP and R110 in 1-butyl-3-methylimidazolium-based ionic liquids with various anions. Calculated reorientation times using SED theory with slip and stick boundary conditions are also shown in the figures.

However, to our surprise, a small increase or decrease has been noticed in the C_{obs} values with an increase in temperature. A careful scrutiny of the numbers revealed that these trends are a consequence of noncompliance of eq 1. In other words, as mentioned earlier, τ_r versus η/T plots do not pass through the origin and the resulting intercepts have either small positive or negative values. When the intercepts are positive, an increase in the C_{obs} values is observed upon increasing the temperature and vice versa. Alternatively, least-squares analysis of the log–log plots results in a slight degree of nonlinearity in τ_r versus η/T plots. A decrease or an increase in the C_{obs} values with temperature depends on whether the exponent is greater than 1 or less than 1, respectively. Thus, temperature-independent C_{obs} values can be obtained by taking into consideration either the "intercept correction" or the nonlinear dependence of τ_r on η/T. In the present scenario, however, the latter option was preferred, as nonzero intercepts, especially the ones with negative values, do not have any physical significance. Therefore, a modified SED equation as given by eq 2 has been employed.

$$\tau_r = \frac{VfC}{k}\left(\frac{\eta}{T}\right)^n \tag{2}$$

For each solute–ionic liquid combination, n values have been obtained by linear least-squares fits of logarithmic plots of τ_r versus η/T. The n values obtained in this manner have been used in conjunction with eq 2 to calculate temperature-independent C_{obs} values. A similar procedure has been adopted by Miyake et al.[27] to account for the nonlinear dependence of τ_r on η/T. It has been noticed that the C_{obs} values thus calculated using eq 2 are almost independent of temperature. Plots of τ_r versus η/T for the two solutes in six ionic liquids along with linear and nonlinear fits are given in the Supporting Information. The C_{obs} values calculated using eqs 1 and 2 for DMDPP and R110 at six temperatures in all the ionic liquids used in this study are also given in the Supporting Information. The corresponding average values of C_{obs} are listed in Table 1. However, it may be noted that both of these methods yielded

Table 1. Boundary Condition Parameters of DMDPP and R110 in 1-Butyl-3-methylimidazolium-Based Ionic Liquids with Various Anions Obtained from the Measured Reorientation Times

ionic liquid	DMDPP		R110	
	$C_{obs}{}^a$	$C_{obs}{}^b$	$C_{obs}{}^a$	$C_{obs}{}^b$
$[bmim^+]$ $[FAP^-]$	0.37 ± 0.03	0.36 ± 0.01	0.68 ± 0.05	0.61 ± 0.01
$[bmim^+]$ $[PF_6^-]$	0.27 ± 0.01	0.27 ± 0.01	0.64 ± 0.06	0.83 ± 0.04
$[bmim^+]$ $[Tf_2N^-]$	0.36 ± 0.02	0.36 ± 0.01	0.93 ± 0.05	0.85 ± 0.01
$[bmim^+]$ $[BF_4^-]$	0.33 ± 0.01	0.33 ± 0.01	0.88 ± 0.02	0.94 ± 0.01
$[bmim^+]$ $[TfO^-]$	0.31 ± 0.01	0.31 ± 0.01	0.91 ± 0.04	1.00 ± 0.01
$[bmim^+]$ $[NO_3^-]$	0.37 ± 0.03	0.43 ± 0.01	1.00 ± 0.04	1.14 ± 0.01

^{a}Average value of C_{obs} obtained at six temperatures using eq 1. ^{b}Average value of C_{obs} obtained at six temperatures using eq 2.

qualitatively similar trends for the C_{obs} values, the sole exception being R110 in $[bmim^+][PF_6^-]$. Only in cases where the parameter n is very much different from unity, significant differences have been noticed between the C_{obs} values obtained using eqs 1 and 2. In view of this scenario, further analysis of the data has been carried out using both sets of data.

Inspection of Table 1 reveals that there is almost no change in the C_{obs} values of DMDPP upon varying the anion of the ionic liquid and they are close to C_{slip}, which is 0.32. Only in the case of $[bmim^+][PF_6^-]$, C_{obs} is 20% lower than C_{slip}. This data essentially implies that SED hydrodynamic theory alone is adequate to describe the rotational diffusion of DMDPP in these ionic liquids and there is almost no influence of the nature of the anion on solute rotation. In contrast, the influence of various anions on C_{obs} values of R110 can be clearly noticed from Table 1, which follows the trend as indicated below when eq 1 was employed.

$$C_{obs}^{[PF_6^-]} \simeq C_{obs}^{[FAP^-]} < C_{obs}^{[Tf_2N^-]} \simeq C_{obs}^{[BF_4^-]} \simeq C_{obs}^{[TfO^-]}$$
$$< C_{obs}^{[NO_3^-]}$$

A marginal alteration has been noticed in the trend when eq 2 was used to calculate C_{obs} values, which is given below.

$$C_{obs}^{[FAP^-]} < C_{obs}^{[PF_6^-]} \simeq C_{obs}^{[Tf_2N^-]} < C_{obs}^{[BF_4^-]} < C_{obs}^{[TfO^-]}$$
$$< C_{obs}^{[NO_3^-]}$$

It may be noted that these two trends are not significantly different from one another considering the fact that the uncertainties on the average C_{obs} values when eq 1 was employed are rather high. The observed result for R110 in various ionic liquids employed in this study can be understood in the following manner.

Recent studies[20,21] from our group established that R110 experiences specific interactions with the anions of the ionic liquids, which leads to its slower rotation. It has been suggested that, under such circumstances, the reorientation time of a solute molecule depends on the strength of the solute–solvent hydrogen bond.[31] This hypothesis has, in fact, been verified in the case of the rotational diffusion of DMDPP and its hydrogen

bonding counterpart, 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]-pyrrole (DPP) in ethanol and 2,2,2-trifluoroethanol and also in isomeric butanols by correlating the measured reorientation times with the calculated solute−solvent interaction strengths.[34,35] However, in the case of ionic liquids, due to the prevalence of a multitude of interactions between the cations and anions, it is nontrivial to obtain the solute−solvent interaction strengths with the aid of *ab initio* molecular orbital calculations.

As mentioned in the preceding paragraph, the reorientation time and in turn C_{obs} of R110 depend on how strongly it can interact with a given anion of the ionic liquid. Since R110 is a hydrogen bond donating solute due to the presence of two $-NH_2$ groups, its ability to experience specific interactions with an anion, in principle, should depend on the hydrogen bond accepting capability of the anion, which is quantified by the parameter, hydrogen bond basicity. At present, two multiparameter scales are available in the literature that describe properties such as dipolarity/polarizability, hydrogen bond acidity, and hydrogen bond basicity of the ionic liquids. These are the Kamlet−Taft scale and the Abraham model.[1,37] According to the data available in the literature, the trends predicted by both of these scales for hydrogen bond basicities are qualitatively similar, but the absolute values are higher in the case of the Abraham model compared to the Kamlet−Taft scale. For assimilating the results presented in this work, we have employed the values of hydrogen bond basicities obtained using the Abraham model, which is usually designated by *a*, and the reasons for doing so are as follows. In the Abraham model, the hydrogen bond basicity depends only on the nature of the anion. Moreover, for the recently synthesized anions such as [FAP⁻], the hydrogen bond basicities have only been obtained using the Abraham model.[39] It must be mentioned that the hydrogen bond basicity of a given anion decreases linearly upon increasing temperature and the temperature-dependent values for the hydrogen bond basicities obtained with the aid of the Abraham model are readily available in the literature[38,39] for five of the six ionic liquids employed in this study. The hydrogen bond basicities for the various anions employed in this study obey the following trend.

$$a^{[FAP^-]} < a^{[PF_6^-]} \simeq a^{[Tf_2N^-]} \simeq a^{[BF_4^-]} < a^{[TfO^-]} < a^{[NO_3^-]}$$

To find out how the observed boundary condition parameter of R110 correlates with the hydrogen bond basicities of various anions, C_{obs} values at 348 K obtained using eqs 1 and 2 were plotted as a function of *a* in Figure 5A and B, respectively. The *a* values also correspond to the same temperature; the sole exception is the [NO₃⁻] anion for which the hydrogen bond basicity is available only at 354 K in literature.[40] Another point that needs to be mentioned is that the hydrogen bond basicity of [FAP⁻] corresponds to that of [hmim⁺][FAP⁻] but not that of [bmim⁺][FAP⁻]. This approximation is reasonable considering the fact that the hydrogen bond basicity solely depends on the nature of the anion according to the Abraham model.[37] It can be noticed from the figure that, barring the data for [PF₆⁻], C_{obs} increases with an increase in the hydrogen bond basicity of the anion of the ionic liquid when eq 1 was employed (see Figure 5A). Nonetheless, when C_{obs} was calculated using eq 2, even [PF₆⁻] data complies with the trend (see Figure 5B). However, it must be noted that the increase in C_{obs} is not uniform and attains saturation at higher
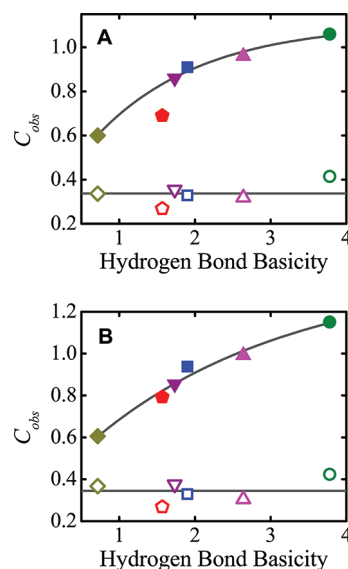

Figure 5. Plots of C_{obs} versus hydrogen bond basicity for R110 at 348 K in 1-butyl-3-methylimidazolium-based ionic liquids with the anions [FAP⁻] (◆), [PF₆⁻] (⬟), [Tf₂N⁻] (▼), [BF₄⁻] (■), [TfO⁻] (▲), and [NO₃⁻] (●). The corresponding points for DMDPP are represented as open symbols. The lines passing through the data points are drawn as a visual aid. It can be noticed from the figure that for the cationic solute R110 C_{obs} increases with an increase in the hydrogen bond basicity of the anion, whereas for DMDPP it is almost independent of the nature of the anion. Plots A and B represent the different methods of analyses employed to obtain C_{obs} values (see text for details).

values of *a* when eq 1 was employed to obtain C_{obs}. From [FAP⁻] to [Tf₂N⁻], C_{obs} increases by more than 40%, but, from [Tf₂N⁻] to [NO₃⁻], the increase is merely 20% even though the hydrogen bond basicity varies by almost an identical margin. In contrast, the increase in C_{obs} with the hydrogen bond basicity appears to be somewhat uniform when eq 2 was used to calculate C_{obs}. The variation of C_{obs} with *a* at all six temperatures follows more or less the same trend, and this has been pictorially depicted in the Supporting Information. Thus, from the analysis of the data using either eq 1 or eq 2, it can be realized that the rotational diffusion of a hydrogen bond donating probe in an ionic liquid is governed by the hydrogen bond accepting ability of the constituent anion in addition to the viscosity of the medium. This can be further corroborated by the fact that C_{obs} values of the neutral solute DMDPP are more or less insensitive to the hydrogen bond basicity (see Figure 5).

Another important issue that needs to be addressed is the marginally lower C_{obs} values obtained for DMDPP as well as R110 in [bmim⁺][PF₆⁻] when eq 1 was used. On the basis of this analysis, it is possible to conclude that both solutes are experiencing microviscosity, which is lower than the bulk viscosity of the ionic liquid. Somewhat similar behavior has been reported by Funston et al.[16] for the solute coumarin 153 in ammonium- and pyrrolidinium-based ionic liquids with [Tf₂N⁻] anion. However, as mentioned earlier, when eq 2 was employed, the C_{obs} value for R110 in [bmim⁺][PF₆⁻] has been found to be significantly higher than that obtained from eq 1. To find out if this behavior is specific to ionic liquids having [PF₆⁻] anions, rotational diffusion of DMDPP and R110 was also examined in the ionic liquids [emim⁺][PF₆⁻] and [hmim⁺][PF₆⁻] and the C_{obs} values have been calculated

from the measured reorientation times using eq 1 as well as eq 2. The measured reorientation times and the calculated C_{obs} values at each temperature for the two solutes in the three ionic liquids are presented in the Supporting Information, and the average C_{obs} values are listed in Table 2. It can be noticed from

Table 2. Boundary Condition Parameters of DMDPP and R110 in 1-Alkyl-3-methylimidazolium Hexafluorophosphate Ionic Liquids Obtained from the Measured Reorientation Times

	DMDPP		R110	
ionic liquid	$C_{obs}{}^a$	$C_{obs}{}^b$	$C_{obs}{}^a$	$C_{obs}{}^b$
$[emim^+]$ $[PF_6{}^-]$	0.27 ± 0.01	0.26 ± 0.01	0.61 ± 0.02	0.58 ± 0.01
$[bmim^+]$ $[PF_6{}^-]$	0.27 ± 0.01	0.27 ± 0.01	0.64 ± 0.06	0.83 ± 0.04
$[hmim^+]$ $[PF_6{}^-]$	0.26 ± 0.02	0.30 ± 0.01	0.68 ± 0.09	1.19 ± 0.06

[a]Average value of C_{obs} obtained at six temperatures using eq 1.
[b]Average value of C_{obs} obtained at six temperatures using eq 2.

the table that, in $[emim^+][PF_6{}^-]$ and $[hmim^+][PF_6{}^-]$, the C_{obs} values for DMDPP are found to be comparable to the ones obtained in $[bmim^+][PF_6{}^-]$ irrespective of the equation used. However, when C_{obs} values were calculated for R110 with the aid of eq 2, significantly higher values were obtained in $[bmim^+][PF_6{}^-]$ and $[hmim^+][PF_6{}^-]$ compared to the ones obtained with the aid of eq 1, which is due to the parameter n being significantly less than unity. Thus, it is not possible to conclude whether the observed result is a consequence of the solutes experiencing the effects of microviscosity in ionic liquids having $[PF_6{}^-]$ anion or due to the differences in the treatment of the data.

CONCLUSIONS

Rotational diffusion of an organic solute dissolved in an ionic liquid can be influenced by either the anion or the cation or both. To get a better appreciation of the role of the anion on solute rotation, the present investigation has been undertaken, wherein reorientation times of neutral and charged solutes have been examined in 1-butyl-3-methylimidazolium-based ionic liquids with anions such as $[FAP^-]$, $[PF_6{}^-]$, $[Tf_2N^-]$, $[BF_4{}^-]$, $[TfO^-]$, and $[NO_3{}^-]$. It has been noticed that the nature of the anion has no influence on the rotational diffusion of DMDPP, which is essentially governed by the viscosity of the ionic liquid. This has been manifested in the C_{obs} values that are close to the slip boundary condition. In contrast, rotational diffusion of R110 was found to be closer to the predictions of stick boundary condition as a result of specific interactions between the solute and the anion of the ionic liquid. Moreover, a significant variation has been noticed in the C_{obs} values from $[bmim^+][FAP^-]$ to $[bmim^+][NO_3{}^-]$. To explain this behavior, hydrogen bond basicities of the anions ionic liquids have been considered and C_{obs} values of R110 correlate with this parameter.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables listing reorientation times and boundary condition parameters of DMDPP and R110 in the eight ionic liquids and the viscosities of these ionic liquids as a function of temperature. Plots of τ_r versus η/T for DMDPP and R110 in

1-butyl-3-methylimidazolium-based ionic liquids with various anions together with linear and nonlinear fits and also plots of C_{obs} versus hydrogen bond basicity for R110 at six different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Hallett, J. P.; Welton, T. *Chem. Rev.* **2011**, *111*, 3508 and references therein.
(2) Dupont, J. *Acc. Chem. Res.* **2011**, *44*, 1223.
(3) Behar, D.; Gonzalez, C.; Neta, P. *J. Phys. Chem. A* **2001**, *105*, 7607.
(4) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *104*, 5468.
(5) Tiwari, S.; Kumar, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4824.
(6) Tiwari, S.; Khupse, N.; Kumar, A. *J. Org. Chem.* **2008**, *73*, 9075.
(7) Bhattacharya, B.; Samanta, A. *J. Phys. Chem. B* **2008**, *112*, 10101.
(8) Santhosh, K.; Samanta, A. *J. Phys. Chem. B* **2010**, *114*, 9195.
(9) Mali, K. S.; Dutt, G. B.; Mukherjee, T. *J. Chem. Phys.* **2008**, *128*, 124515.
(10) Samanta, A. *J. Phys. Chem. B* **2006**, *110*, 13704.
(11) Samanta, A. *J. Phys. Chem. Lett.* **2010**, *1*, 1557.
(12) Paul, A.; Samanta, A. *J. Phys. Chem. B* **2007**, *111*, 4724.
(13) Ingram, J. A.; Moog, R. S.; Ito, N.; Biswas, R.; Maroncelli, M. *J. Phys. Chem. B* **2003**, *107*, 5926.
(14) Ito, N.; Arzhantsev, S.; Heitz, M.; Maroncelli, M. *J. Phys. Chem. B* **2004**, *108*, 5771.
(15) Jin, H.; Baker, G. A.; Arzhantsev, S.; Dong, J.; Maroncelli, M. *J. Phys. Chem. B* **2007**, *111*, 7291.
(16) Funston, A. M.; Fadeeva, T. A.; Wishart, J. F.; Castner, E. W. *J. Phys. Chem. B* **2007**, *111*, 4963.
(17) Mali, K. S.; Dutt, G. B.; Mukherjee, T. *J. Chem. Phys.* **2005**, *123*, 174504.
(18) Mali, K. S.; Dutt, G. B.; Mukherjee, T. *J. Chem. Phys.* **2008**, *128*, 054504.
(19) Dutt, G. B. *Ind. J. Chem. A* **2010**, *49*, 705.
(20) Dutt, G. B. *J. Phys. Chem. B* **2010**, *114*, 8971.
(21) Karve, L.; Dutt, G. B. *J. Phys. Chem. B* **2011**, *115*, 725.
(22) Fruchey, K.; Fayer, M. D. *J. Phys. Chem. B* **2010**, *114*, 2840.
(23) Khara, D. C.; Samanta, A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7671.
(24) Stoesser, R.; Herrmann, W.; Zehl, A.; Strehmel, V.; Laschewsky, A. *ChemPhysChem* **2006**, *7*, 1106.
(25) Strehmel, V.; Rexhausen, H.; Strauch, P. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1933.
(26) Miyake, Y.; Hidemori, T.; Akai, N.; Kawai, A.; Shibuya, K.; Koguchi, S.; Kitazume, T. *Chem. Lett.* **2009**, *38*, 124.
(27) Miyake, Y.; Akai, N.; Kawai, A.; Shibuya, K. *J. Phys. Chem. A* **2011**, *115*, 6347.
(28) Seddon, K. R.; Stark, A.; Torres, M. J. Viscosity and Density of 1-Alkyl-3-methylimidazolium Ionic Liquids. In *Clean Solvents*; Abraham, M., Moens, L., Eds.; American Chemical Society: Washington, DC, 2002; Vol. *819*, p 34.
(29) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103.
(30) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: London, 1984.

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

(32) 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.

(33) Perrin, F. *J. Phys. Radium* **1934**, *5*, 497.

(34) Hu, C. M.; Zwanzig, R. *J. Chem. Phys.* **1974**, *60*, 4354.

(35) Dutt, G. B.; Ghanty, T. K. *J. Chem. Phys.* **2003**, *119*, 4768.

(36) Dutt, G. B.; Ghanty, T. K. *J. Phys. Chem. A* **2004**, *108*, 6090.

(37) Abraham, M. H. *Chem. Soc. Rev.* **1993**, *22*, 73.

(38) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247.

(39) Zhao, Q.; Eichhorn, J.; Pitner, W. R.; Anderson, J. L. *Anal. Bioanal. Chem.* **2009**, *395*, 225.

(40) Sobota, M.; Dohnal, V.; Vrbka, P. *J. Phys. Chem. B* **2009**, *113*, 4323.