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# Rotational Diffusion of Neutral and Charged Solutes in Ionic Liquids: Is Solute Reorientation Influenced by the Nature of the Cation?

## Lalita Karve and G. B. Dutt*

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

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To assess the influence of the nature of cation on solute reorientation, 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 four ionic liquids containing tris(pentafluoroethyl)trifluorophosphate (FAP) anion over the temperature range 308−348 K. The ionic liquids used in the study are 1-butyl-1-methylpyrrolidinium FAP (BMPL FAP), 1-(2-methoxyethyl)-1-methylpyrrolidinium FAP (MOEMPL FAP), 1-(2-methoxyethyl)-1-methylpiperidinium FAP (MOEMPIP FAP), and *N*-(2-methoxyethyl)-*N*-methylmorpholinium FAP (MOEMMO FAP). Analysis of the data carried out with the aid of Stokes−Einstein−Debye hydrodynamic theory reveals that the rotation of the neutral solute DMDPP in all the four ionic liquids is essentially governed by the viscosity of the medium and the reorientation times follow slip boundary condition. In contrast, the results obtained for the cationic solute, which experiences specific interactions with the FAP anion, are somewhat different. The reorientation times of R110 are in between stick and slip limits and found to be independent of the nature of the cation of the ionic liquid except in case of highly viscous MOEMMO FAP, wherein it has been observed that the rotation of R110 is faster by a factor of 1.5. The observed behavior has been rationalized on the basis of highly associative nature of the MOEMMO cation, which precludes R110 from experiencing strong specific interactions with the FAP anion.

## 1. Introduction

Room temperature ionic liquids, as their name suggests, are composed of ions and exist as liquids at room temperature. Of late considerable efforts have been directed toward research dealing with ionic liquids due to their "interesting" physicochemical properties, nonvolatile nature, and diverse applications in numerous areas of chemistry. The spectrum of utility ranges from their use as alternative reaction media for chemical transformations, electrochemical applications, extractions, and drug delivery vehicles.[1−5] However, to exploit the tremendous potential it is necessary to have a thorough grasp on their physicochemical properties, which in turn are governed by the intermolecular interactions that prevail between the cations and anions of the ionic liquids. The hybrid organic−ionic nature of ionic liquids and the ensuing interplay between different intermolecular forces give rise to a complex phenomenology whose decoding requires a close integration of experimental, theoretical, and computational techniques. Dielectric relaxation,[6,7] solvation dynamics,[8−13] and rotational diffusion[10−21] are some of the processes, which have been examined to understand the nature of the interactions between the cations and anions of the ionic liquids and also the interactions with the added solute molecules. Rotational diffusion studies in particular are useful to explore the specific interactions between solute and the ions that constitute the ionic liquids.[15−20]

In recent times, we have explored the role of specific interactions on the rotational diffusion of medium sized organic solute molecules dissolved in ionic liquids.[15−17] These investigations have emphasized the importance of specific interactions between non-dipolar[15] and charged[16,17] solute molecules, and the anions of the ionic liquids on solute rotation. A rotational

diffusion study[17] involving a cationic solute, rhodamine 110 (R110), and a neutral solute, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) in a series of 1-alkyl-3-methylimidazolium ionic liquids (alkyl = ethyl, butyl, hexyl, and 2-hydroxyethyl) containing tris(pentafluoroethyl)trifluorophosphate (FAP) anion reveals that the viscosity normalized reorientation times of R110 increase by 30% with an increase in the alkyl chain length of the cation even though the solute molecule experiences specific interactions with the FAP anion. The observed behavior is due to the association of R110 with a larger solvent molecule, which increases the effective hydrodynamic volume of the rotating entity and thus leading to slower rotation. Somewhat similar result has been observed by Fruchey and Fayer[18] for the anionic solute sodium 8-methoxypyrene-1,3,6-sulfonate in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides. In contrast to R110, the rotational diffusion of DMDPP has been found to be independent of the alkyl chain length on the imidazolium cation as its reorientation is exclusively governed by the viscosity of the medium. However, it has been noticed that the viscosity normalized reorientation times of DMDPP are 30% longer in 2-hydroxyethyl-3-methylimidazolium FAP compared to its ethyl counterpart, which is assimilated by invoking specific interactions between the carbonyl groups of DMDPP and the hydroxyl group of the ionic liquid.

It may be recalled that, barring a few,[11−13] a majority of the investigations have been carried out in imidazolium-based ionic liquids. Even these limited studies have employed a neutral dipolar solute coumarin 153, which does not experience specific interactions with the constituents of the ionic liquids. Thus, it is not clear whether the rotation of a charged solute is influenced by the nature of the cation of the ionic liquid. To address this issue, the present study has been undertaken wherein rotational

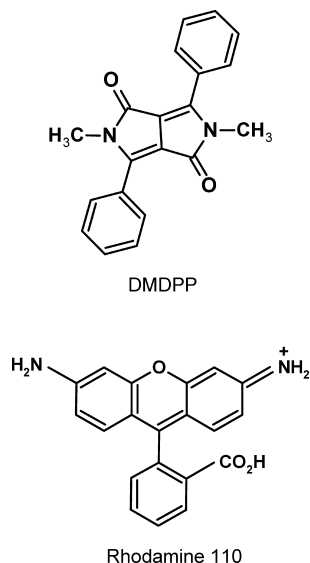* To whom correspondence should be addressed. E-mail: gbdutt@barc.gov.in.

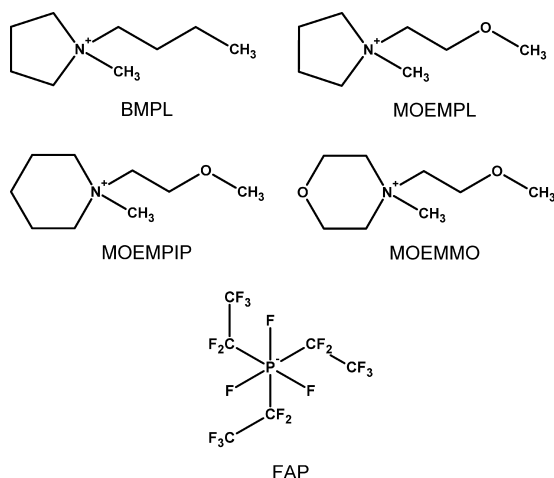**Figure 1.** Molecular structures of the solutes used in the study.



**Figure 2.** Molecular structures of the four cations along with FAP anion of the ionic liquids.

diffusion of a neutral solute DMDPP and a cationic solute R110 (see Figure 1 for their molecular structures) has been examined in ionic liquids containing FAP anion over the temperature ($T$) range 308−348 K. The four ionic liquids used in the study are 1-butyl-1-methylpyrrolidinium FAP (BMPL FAP), 1-(2-methoxyethyl)-1-methylpyrrolidinium FAP (MOEMPL FAP), 1-(2-methoxyethyl)-1-methylpiperidinium FAP (MOEMPIP FAP), and N-(2-methoxyethyl)-N-methylmorpholinium FAP (MOEMMO FAP). Figure 2 gives structures of the four cations and the FAP anion of the ionic liquids. It may be noted that FAP-based ionic liquids were developed as replacements for ionic liquids containing hexafluorophosphate anion by Ignat'ev and co-workers[22] in 2005 and possess properties such as excellent hydrolytic, thermal, and electrochemical stability.[23] Moreover, it was also shown that these are the most hydrophobic of all the ionic liquids, which have been synthesized so far.[23] Inspection of Figure 2 reveals that the ionic liquids BMPL FAP and MOEMPL FAP are structurally similar and almost identical in size. Likewise, MOEMPIP FAP and MOEMMO FAP are indistinguishable except for the ring oxygen atom, which is present in case of MOEMMO FAP. Thus, it would be interesting to find out how these two sets of ionic liquids that have structural semblance influence the rotational diffusion of neutral and charged solutes.

## 2. Experimental Section

The ionic liquids BMPL FAP, MOEMPL FAP, MOEMPIP FAP, and MOEMMO FAP were purchased from Merck, Germany. The purity of the liquids is >99% with <100 ppm water content and <100 ppm halide ion concentration. The solvents, 1-octanol and ethylene glycol, whose purity is 99%, were procured from Fluka, Germany. The probes DMDPP and R110 were obtained from Exciton and Ciba Specialty Chemicals, Inc., respectively. All these chemicals are of the highest available purity and were used without further purification. 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.

Time-resolved fluorescence measurements were carried out with a setup that works on the principle of time-correlated single-photon counting.[24] 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.[17] 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 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. The anisotropy measurements dealing with ionic liquids were carried out over the temperature range 308−348 K, whereas anisotropy decays of R110 in 1-octanol and ethylene glycol were measured from 298 to 348 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 impulse reconvolution method as well as tail fit of the anisotropy data (without reconvolution). Both the methods of analysis yielded identical numbers for the anisotropy decay constants since the smallest time constant measured in the present study is 400 ps, which is 4 times longer than the FWHM of the IRF. The viscosities ($\eta$) of the four ionic liquids were measured as a function of temperature using a Physica MCR 101 rheometer.

## 3. Results and Discussion

The anisotropy decays of DMDPP and R110 in the four ionic liquids have been measured over the temperature range 308−348 K. Measurements below 308 K could not be performed because the reorientation times ($\tau_r$) of DMDPP and R110 are more than 3 times longer compared to their fluorescence lifetimes ($\tau_f$) as a consequence of high viscosities of the ionic liquids, especially in the case of MOEMMO FAP. The anisotropy decays of both the solutes could be adequately fitted with a single exponential
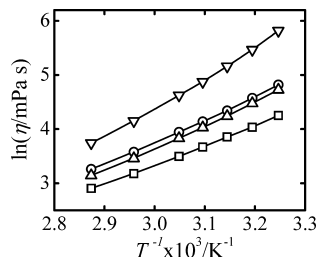
**Figure 3.** Plots of ln ($\eta$) versus $1/T$ for BMPL FAP (O), MOEMPL FAP (□), MOEMPIP FAP (△), and MOEMMO FAP (▽). The lines passing through the data points are drawn as visual aid.
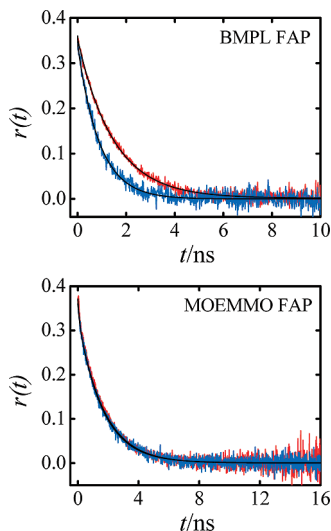


**Figure 4.** Anisotropy decays of DMDPP (blue) and R110 (red) in BMPL FAP and MOEMMO FAP at 348 K. The smooth lines passing through the experimental curves are the fitted ones. It can be noticed from the figures that anisotropy decays of R110 are slower compared to DMDPP in BMPL FAP, whereas they are identical in MOEMMO FAP.

function over the temperature range studied and the functional form is given by

$$r(t) = r_0 \exp(-t/\tau_r) \qquad (1)$$

where $r_0$ is the limiting anisotropy, whose magnitude is determined by the angle between absorption and emission transition dipoles of the solute molecule. The reorientation times of DMDPP and R110 in the four FAP-based ionic liquids and the viscosities of these ionic liquids over the temperature range 308−348 K are reported in the Supporting Information. The uncertainties on the reorientation times are in the range of 5−10%, while the measured viscosities have about 5% error. Plots of ln ($\eta$) vs $1/T$ for the four ionic liquids are given in Figure 3. It is evident from the figure that the viscosities of MOEMMO FAP are significantly higher compared to the other three ionic liquids. Typical anisotropy decays of DMDPP and R110 in BMPL FAP and MOEMMO FAP at 348 K are displayed in Figure 4. It can be noticed from the figure that the anisotropy decay of R110 is significantly slower compared to that of DMDPP in BMPL FAP, whereas the decays of both the solutes overlap in MOEMMO FAP. The reorientation times of R110 are, in fact, longer by about a factor of 1.5 compared to DMDPP in BMPL FAP, MOEMPL FAP, and MOEMPIP FAP. In contrast, they are almost identical in MOEMMO FAP except at 308 and 313 K, where the reorientation times of DMDPP
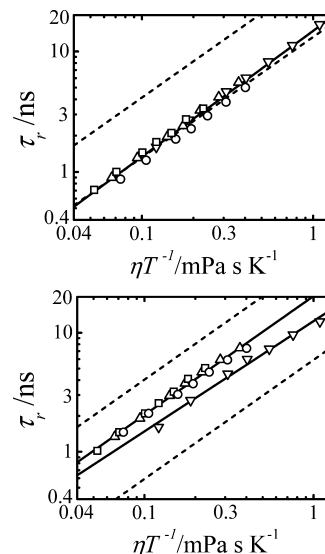


**Figure 5.** Plots of $\tau_r$ vs $\eta/T$ for DMDPP (top) and R110 (bottom) in BMPL FAP (O), MOEMPL FAP (□), MOEMPIP FAP (△), and MOEMMO FAP (▽). The lines passing through the points were obtained by performing least-squares fit of all the data points. Theoretically calculated reorientation times using SED theory with slip and stick boundary conditions are also shown (dashed lines) in the figures.

are longer by a factor of 1.3−1.2. To understand the observed results, Stoke−Einstein−Debye (SED) hydrodynamic theory[25,26] has been employed. According to this theory, the rotation of a solute molecule immersed in a solvent continuum occurs by small-step diffusion and its reorientation time is proportional to $\eta/T$. The proportionality constant is a ratio of hydrodynamic volume $V_h$ of the solute to the Boltzmann constant $k$. Thus, the reorientation time $\tau_r$ is given by

$$\tau_r = \frac{V_h}{k}\left(\frac{\eta}{T}\right) \qquad (2)$$

The hydrodynamic volume, in turn is a product of van der Waals volume $V$ of the solute, shape factor $f$, and boundary condition parameter $C$, which leads to $V_h = VfC$. The shape of the solute molecule is usually incorporated into the model by treating it as either a symmetric or an asymmetric ellipsoid.[27] The boundary condition parameter describes the extent of coupling between the solute and the solvent, and the magnitude of $C$ depends on the axial ratio of the solute molecule. The two limiting cases are the hydrodynamic stick and slip.[28] When the sizes of solute and solvent molecules are comparable, and also when the solute molecule does not experience specific interactions with the solvent, its rotation is usually described by slip boundary condition.[29]

The solutes DMDPP and R110 have been treated as asymmetric ellipsoids, and the reorientation times were calculated with slip and stick boundary conditions. Details of the calculation have been described in our earlier publications.[16,17,30] The calculated van der Waals volume, shape factor, and boundary condition parameter for DMDPP are 281 Å$^3$, 2.03, and 0.32 respectively, and the corresponding values for R110 are 275 Å$^3$, 2.02, and 0.15. Plots of $\tau_r$ vs $\eta/T$ for the two solutes in the four ionic liquids are given in Figure 5. The slip and stick lines, which have been calculated with the aid of SED hydrodynamic theory are also shown in the figure. It can be noticed from the figure that the reorientation times of the neutral solute DMDPP
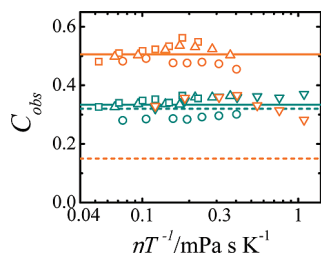
**Figure 6.** Plots of $C_{obs}$ vs $\eta/T$ for DMDPP (dark cyan) and R110 (orange) in BMPL FAP ($\bigcirc$), MOEMPL FAP ($\square$), MOEMPIP FAP ($\triangle$), and MOEMMO FAP ($\nabla$). The lines passing through the points represent the average of all the $C_{obs}$ values for each solute. In case of R110, the values corresponding to MOEMMO FAP are not included while considering the average. The broken lines represent the slip boundary condition.

vary almost linearly with $\eta/T$ and there is no distinction in the solute rotation in the four ionic liquids. Moreover, the rotational diffusion of DMDPP matches with the predictions of slip hydrodynamics. In contrast to DMDPP, the reorientation times of the charged solute, R110 are in between stick and slip limits and are similar in BMPL FAP, MOEMPL FAP, and MOEMPIP FAP. However, in the highly viscous MOEMMO FAP the rotational diffusion of R110 is significantly faster compared to the other three ionic liquids. The following relationships have been obtained between $\tau_r$ and $\eta/T$ for DMDPP and R110 from the least-squares analysis of the log−log plots with $N$ and $R$ being the number of data points and regression coefficient, respectively.

DMDPP/BMPL FAP, MOEMPL FAP, MOEMPIP FAP, and MOEMMO FAP

$$\tau_r = (14.8 \pm 0.8)(\eta/T)^{1.04\pm0.02} \quad (N = 28, R = 0.994)$$

R110/BMPL FAP, MOEMPL FAP, and MOEMPIP FAP

$$\tau_r = (20.3 \pm 0.9)(\eta/T)^{1.00\pm0.02} \quad (N = 21, R = 0.995)$$

R110/MOEMMO

$$\tau_r = (12.5 \pm 0.6)(\eta/T)^{0.93\pm0.04} \quad (N = 7, R = 0.995)$$

Since the true extent of solute−solvent coupling is represented by the observed boundary condition parameter $C_{obs}$, this parameter has been calculated from the measured reorientation time using the following equation, which was obtained by rearranging the SED equation

$$C_{obs} = \frac{\tau_r kT}{\eta V f} \quad (3)$$

The values of $C_{obs}$ obtained in this manner are plotted as a function of $\eta/T$ in Figure 6 for DMDPP and R110 in the four ionic liquids and the average values are reported in the Supporting Information. The $C_{obs}$ value thus reported for each solute−ionic liquid combination is an average of the boundary condition parameters obtained at 7 different temperatures. It can be noticed from the figure that the $C_{obs}$ values of DMDPP in the four ionic liquids are almost identical and fluctuate around the $C_{slip}$ value of 0.32. On the other hand, $C_{obs}$ values of R110

are similar only in three of the four ionic liquids and the average value is $0.51 \pm 0.03$. In case of MOEMMO, the $C_{obs}$ values of R110 are lower by a factor of 1.5 compared to the average value and overlap with those of DMDPP. It can also be noticed from the figure that for both DMDPP and R110 there appears to be no systematic variation of $C_{obs}$ with temperature.

Extensive studies carried out by us indicate that the rotational diffusion of neutral solute DMDPP is essentially governed by the viscosity and size of the solvent in ionic liquids[15,16] as well as in conventional solvents.[29,31−38] However, it has also been noticed that the two carbonyl groups of DMDPP (see Figure 1) experience specific interactions such that its rotation is hindered only in case of strong hydrogen bond donating solvents such as 2,2,2-trifluoroethanol[37] and 1-(2-hydroxyethyl)-3-methylimidazolium FAP.[17] Thus, it implies that in solvents having identical size and moderate hydrogen bond donating ability the rotational diffusion of DMDPP is essentially governed by the viscosity of the medium. To illustrate this point, the $C_{obs}$ values of DMDPP in ionic liquids 1-ethyl-3-methylimidazolium FAP (EMIM FAP), 1-butyl-3-methylimidazolium FAP (BMIM FAP), and 1-hexyl-3-methylimidazolium FAP (HMIM FAP) and also in conventional solvents such as 1-octanol, ethylene glycol, and glycerol have been considered, which are reported in the Supporting Information. The average value of $C_{obs}$ obtained for DMDPP in 10 different solvent systems is $0.36 \pm 0.04$. This exercise confirms that the rotational diffusion of DMDPP is akin to a typical medium-sized solute molecule, which experiences only viscous friction and its reorientation follows slip hydrodynamics.

As mentioned before, the reorientation times of R110 are longer compared to DMDPP by a factor of 1.5. However, such a comparison is not pragmatic as the two solutes are not structurally similar even though they are almost identical in size. The fact that R110 experiences specific interactions with the anions of the ionic liquids was substantiated by comparing its rotational diffusion with a structurally similar nonpolar solute 9-phenylanthracene (9-PA). A rotational diffusion study carried out in the ionic liquid 1-butyl-3-methylimidazolium hexafluo- rophosphate has indicated that the reorientation times of 9-PA are close to the predictions of slip hydrodynamics, whereas the rotation of a structurally similar analogue R110 follows stick hydrodynamics.[16] The observed result has been rationalized on the basis of specific interactions between the positively charged R110 and the negatively charged hexafluorophosphate anion of the ionic liquid. In other words, it has been established that the solute R110 experiences specific interactions with the anions of the ionic liquids. A similar behavior has been noticed in case of 1-alkyl-3-methylimidazolium ionic liquids (alkyl = ethyl, butyl, hexyl, and 2-hydroxyethyl) containing FAP anions.[17] Since the solute R110 experiences specific interactions with the anions of the ionic liquid it will be of interest to find out whether the nature of the cation has any bearing on its rotational diffusion. As the title of the article suggests, this issue is the central theme of the present study. Results obtained here indicate that the rotational diffusion of R110 is influenced by the specific interactions with FAP anion of the ionic liquids. It has been noticed that the rotational diffusion of R110 is identical in BMPL FAP, MOEMPL FAP, and MOEMPIP FAP, which implies that the nature of cation on solute rotation is not important in three of the four ionic liquids studied. Nonetheless, only in the case of MOEMMO FAP, the rotation of R110 is faster by a factor of 1.5 compared to the other three ionic liquids.

What is the reason for the observed faster rotation of R110 in MOEMMO FAP? Even though R110 experiences specific

interactions with FAP anion of the ionic liquid, the manner in which the anion associates with the solute molecule appears to be dependent on the nature of the cation. Inspection of Figure 2 reveals that MOEOMPIP FAP and MOEMMO FAP are identical except for the ring oxygen atom, which is present in case of morpholinium-based ionic liquid. The presence of oxygen atom in the ring renders the nitrogen atom more electropositive due to the inductive effect, which in turn enhances its association with the FAP anion. The strong association between MOEMMO cation and FAP anion is evident from its viscosity, which is higher by a factor of 2−3 compared to MOEMPIP FAP. Thus, the highly associative nature of the MOEMMO cation inhibits R110 from forming stronger hydrogen bonds with FAP anion. It must be noted that the reorientation time of a solute molecule depends on the solute−solvent interaction strength; stronger solute−solvent hydrogen bonds lead to slower rotation of the solute.[29,37,38] From the fluorescence anisotropy measurements carried out with R110 in 1-alkyl-3-methylimidazolium (alkyl = ethyl, butyl, and hexyl) FAP and in conventional solvents, $C_{obs}$ values have been obtained and they are reported in the Supporting Information. It can be noticed from the data that $C_{obs}$ decreases significantly with an increase in solvent association. In 1-octanol, the $C_{obs}$ value is 3.2 and it decreases to 1.0 in ethylene glycol, which further reduces to 0.63 in glycerol. In essence, these results substantiate that the ability of R110 to experience strong specific interactions with surroundings diminishes as the degree of association between the solvent molecules increases.

## Conclusions

Rotational diffusion of DMDPP and R110 has been examined in ionic liquids BMPL FAP, MOEMPL FAP, MOEMPIP FAP, and MOEMMO FAP to find out whether the reorientation of neutral and charged solutes is influenced by the nature of the cation of the ionic liquid. The important findings of this study are summarized in this section. It has been observed that the reorientation times of the neutral solute DMDPP scale linearly with the viscosity of the ionic liquid and are described by the slip hydrodynamics. The rotational diffusion of DMDPP is not affected by the dissimilar characteristics of the cations of the ionic liquids. In contrast, the rotational diffusion of cationic solute R110 has been found to be similar in three of the four ionic liquids studied and the reorientation times lie between the stick and slip limits. Only in case of highly viscous MOEMMO FAP, the viscosity normalized reorientation times of the solute are found to be shorter by a factor of 1.5 compared to the other three ionic liquids. The faster rotation of R110 in MOEMMO FAP is due to the highly associative nature of the morpholinium cation, which thwarts the cationic solute from experiencing strong specific interactions with the FAP anion. In essence, this study establishes that even though specific interactions transpire between the cationic solute and the anion of an ionic liquid, the cation of the ionic liquid does play a role in determining how strongly the solute associates with the anion and thus influences its rotation.

**Supporting Information Available:** Tables listing reorientation times of DMDPP and R110 in the four FAP-based ionic liquids and the viscosities of these ionic liquids as a function of temperature and also boundary condition parameters of the two solutes in different ionic liquids and in conventional solvents. This information is available free of charge via the Internet at http://pubs.acs.org.

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