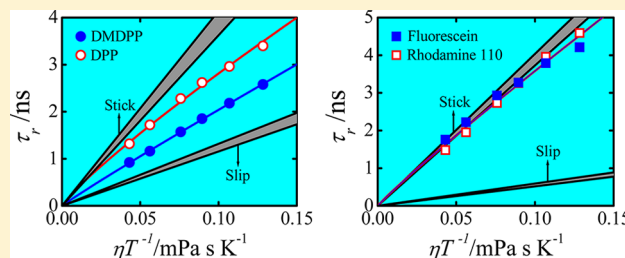


Role of Specific Interactions on the Rotational Diffusion of Organic Solutes in a Protic Ionic Liquid—Propylammonium Nitrate

Lalita Karve and G. B. Dutt*

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

ABSTRACT: Rotational diffusion of two pairs of structurally similar organic solutes has been examined in a protic ionic liquid, *n*-propylammonium nitrate (PAN), to understand the influence of specific interactions on solute rotation. It has been observed that the rotation of the nondipolar solute, 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) in PAN is 30–50% slower compared to its structurally similar counterpart 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP). Analysis of the data using Stokes–Einstein–Debye hydrodynamic theory indicates that the measured reorientation times of DMDPP and DPP are between the stick and slip limits. Furthermore, the rotation of the hydrogen bond accepting solute DMDPP was found to be 60% slower compared to the predictions of slip hydrodynamics, which has been rationalized on the basis of specific interactions between the solute and *n*-propylammonium cation of the ionic liquid. DPP, on the other hand, experiences specific interactions with both the anion and the cation of the ionic liquid due to the presence of hydrogen bond donating as well as accepting groups, resulting in slower rotation compared to DMDPP. The reorientation times of the ionic solutes fluorescein (FL) and rhodamine 110 (R110) are almost identical and closer to the predictions of stick hydrodynamics. The observed behavior is a consequence of the anionic solute FL and the cationic solute R110 experiencing hydrogen bonding interactions with *n*-propylammonium cation and nitrate anion, respectively. An attempt has also been made to rationalize these trends in terms of hydrogen bond acidity and basicity of PAN with the aid of existing scales, such as Kamlet–Taft and the Abraham model.



1. INTRODUCTION

The use of ionic liquids as alternate reaction media in synthesis, solvent extraction, catalysis, and electrochemical applications, owing to their varied physicochemical properties, has been well-documented.^{1–3} Widespread applications of ionic liquids in the field of the chemical industry have also been discussed in the literature.⁴ As the name implies, ionic liquids are essentially composed of ions and are liquids at ambient temperature. However, they differ from classical molten salts such as metal halide melts in two aspects. The ions comprising molten salts possess a higher degree of symmetry compared to the ones that constitute ionic liquids. Even though Coulombic interactions exist between the ions of the molten salts and ionic liquids, the latter also contain a cooperative network of hydrogen bonds between the cations and the anions, which induces structural directionality.² The propensity for hydrogen bonding between the cation and anion of an ionic liquid is essentially governed by the hydrogen bond donating and accepting abilities of the cation and anion, respectively. It may also be noted that specific interactions prevail between some of the dissolved solutes and the ions of the ionic liquid, which in turn control rates of chemical reactions. Thus, a good understanding of the nature of these interactions and the factors that influence them leads to a better appreciation of chemical reactivity in these media.

Among the many methodologies that are available, rotational diffusion of solutes dissolved in ionic liquids has been employed to understand the interactions between the solutes and the milieu.^{5–20} It has become evident from some of these studies

that specific interactions between the solutes and ions of ionic liquids do play an important role in governing the rotation of the solute molecules.^{11–20} The common feature, which can be noticed from the ensemble of results, is that hydrogen bond accepting solutes experience specific interactions with the cations of the ionic liquids, whereas specific interactions prevail between hydrogen bond donating solutes and the anions of the medium. This aspect can be further illustrated by the following examples. Fruchey and Fayer¹⁷ have observed a super stick behavior for a triply charged anionic solute, 8-methoxypyrene-1,3,6-sulfonate in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides due to specific interactions between the solute and the cation of the ionic liquid. On the other hand, Das and Sarkar²⁰ have noticed somewhat similar behavior for the solute 4-aminophthalimide (4-AP) in 1-ethyl-3-methylimidazolium alkylsulfate ionic liquids. The observed trend, however, is a consequence of hydrogen bonding interactions prevailing between the solute and the anion of the ionic liquid.

In a recent study, we have carried out rotational diffusion of a cationic solute rhodamine 110 (R110) in 1-butyl-3-methylimidazolium-based ionic liquids with various anions.¹⁶ Our results indicate that the rotation of the hydrogen bond donating solute R110 depends on the nature of the anion, and the

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variation observed in the solute–solvent coupling parameter correlates with the hydrogen bond basicities of the anions of the ionic liquids. However, it is not obvious from the study whether the observed trend is universal or specific to R110. In other words, it is not known if all the hydrogen bond donating solutes behave in a similar manner. Moreover, barring a few studies,^{14,18} a majority of the investigations have been carried out in aprotic ionic liquids. Among the measurements performed in protic ionic liquids, hydroxy-substituted imidazolium cations have been employed. From our work,¹⁴ it is evident that the hydrogen bond accepting solute 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) rotates 30% slower in 1-(2-hydroxyethyl)-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate compared to that observed in its ethyl counterpart as a consequence of specific interactions between the carbonyl groups of the solute and the hydroxyl group of the ionic liquid. Paul and Samanta¹⁸ have noticed slower rotation of 4-AP in 1-(hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide compared to aprotic solvents, which has been ascribed to the hydrogen bonding interactions between the carbonyl groups of the solute and the hydroxy group of the imidazolium cation. It may be noted that 4-AP can act as a hydrogen bond donor, as well, due to the presence of amino groups. Hence, the role of the hydroxy group on the imidazolium cation of the ionic liquid in the formation of specific interactions with the solute 4-AP is not clear. In essence, from the discussion presented here, it is apparent that a comprehensive understanding of solute rotation in protic ionic liquids is lacking due to insufficient data.

Therefore, to get a better grasp of solute rotation in protic ionic liquids, the present study has been undertaken, wherein rotational diffusion of two pairs of structurally similar organic solutes has been examined in *n*-propylammonium nitrate (PAN). The solutes chosen are the nondipolar DMDPP and its hydrogen bond donating analogue, 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP). The other set comprises negatively charged fluorescein (FL), which exists as a monoanion in PAN and the positively charged R110. Figure 1 gives molecular structures of the four solutes employed in this study. Since the two solute pairs, DMDPP and DPP and FL and R110, are similar in size and shape, their rotational diffusion can be directly compared. In other words, hydrodynamic friction experienced by the two nondipolar solutes and the two ionic solutes will be the same, and the differences

observed in their rotational diffusion can be used to assess the role of specific interactions with the medium. The ionic liquid, PAN, acts as a hydrogen bond donor as well as an acceptor due to the presence of propylammonium cation and nitrate anion, respectively. Moreover, its hydrogen bond acidity and basicity have been well-characterized.²¹ Thus, it would be interesting to find out how these parameters are going to affect the rotational diffusion of the four solutes chosen.

2. EXPERIMENTAL SECTION

The ionic liquid PAN was purchased from io-li-tec, Germany and was purified as described in the literature.²² The water content of the purified PAN is <100 ppm, which was estimated by Karl Fischer titration with the aid of a Metrohm 831 KF coulometer. The probes DMDPP and DPP were obtained from Ciba Specialty Chemicals, Inc., whereas FL and R110 are from Exciton. All these fluorophores are of the highest available purity and were used without further purification. Concentrations of the probes in PAN were chosen such that at the wavelength of excitation, which is 445 nm for all the probes, the absorbance is <0.2. The viscosities of PAN were measured as a function of temperature using a Physica MCR 101 rheometer, and the uncertainties on the measured numbers are ~5%.

Time-resolved fluorescence anisotropy measurements were carried out with a setup that works on the principle of time-correlated single-photon counting²³ (TCSPC) at the Tata Institute of Fundamental Research, Mumbai. Pulses (1 ps) of 890 nm radiation from a Ti-sapphire femto-/picosecond (Spectra Physics, Mountain View, CA) laser, pumped by a Nd:YAG laser (Millenia X, Spectra Physics), were frequency-doubled to 445 nm by using a frequency doubler (GWU, Spectra Physics). Fluorescence decay curves were obtained at the laser repetition rate of 4 MHz by the use of a microchannel plate photomultiplier (model R2809u; Hamamatsu Corp.) coupled to the setup. The decays were collected in 512 channels with a time increment of 39 ps/channel. The instrument response function (IRF) was obtained using a dilute colloidal suspension of nondairy coffee whitener. The full-width at half-maximum (FWHM) of the IRF was 40 ps. Anisotropy decay measurements were carried out by collecting parallel and perpendicular decay components with respect to the polarization of the excitation laser. For the parallel component of the decay, 20 000 peak counts were collected, and the perpendicular component of the decay was corrected for the polarization bias of the detection system or the G-factor of the spectrometer. The emission from the samples was monitored at 550 nm. Each measurement was repeated at least 2–3 times, and the average values are reported. Anisotropy decay measurements were carried out in the temperature range of 313–348 K, and the desired sample temperature was achieved with the help of a thermocouple-based temperature controller, which is regulated by a microprocessor (Eurotherm). The anisotropy decays were analyzed by an iterative reconvolution method, and the details of the analysis have been described in our earlier publication.²⁴

3. RESULTS AND DISCUSSION

Anisotropy decays of the four solutes in PAN could be adequately described by a single exponential function over the temperature range 313–348 K. The reorientation times (τ_r) of the solutes obtained from the analysis of the anisotropy decays have been listed in Table 1, together with the solvent viscosity.

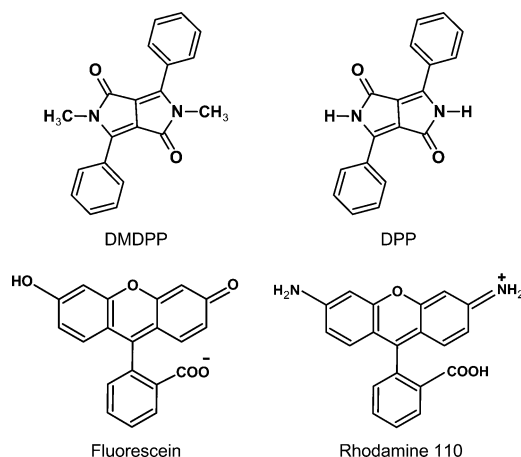
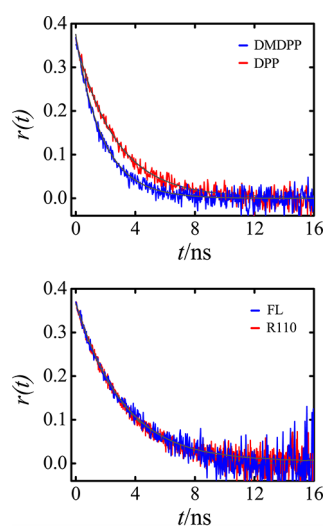


Figure 1. Molecular structures of the solutes.

Table 1. Reorientation Times of the Four Solutes in PAN as a Function of Temperature and Viscosity of the Ionic Liquid

T/K	$\eta/\text{mPa s}$	τ_r/ns			
		DMDPP	DPP	FL	R110
313	40.2	2.58	3.40	4.21	4.59
318	34.0	2.18	2.96	3.79	3.96
323	28.9	1.85	2.62	3.27	3.26
328	24.9	1.57	2.28	2.93	2.73
338	19.0	1.16	1.72	2.22	1.95
348	15.0	0.92	1.32	1.76	1.48

The uncertainties on the τ_r values are in the range of 5–10%. It can be noticed from the table that the reorientation times of DPP are 30–50% longer compared to DMDPP, whereas the rotation of the ionic solutes FL and R110 is almost identical. This fact has been illustrated in Figure 2, where anisotropy

**Figure 2.** Anisotropy decays of DMDPP and DPP (top) and FL and R110 (bottom) in PAN at 323 K. The fitted curves are also shown. It can be noticed that the anisotropy decay of DMDPP is faster compared to that of DPP, whereas the anisotropy decays of FL and R110 almost overlap.

decays of DMDPP and DPP as well as FL and R110 in PAN at 323 K are displayed. To assimilate these results, hydrodynamic friction experienced by the solute molecules has been estimated as a preliminary step. According to the Stokes–Einstein–Debye (SED) hydrodynamic theory,^{25,26} the reorientation time of a solute rotating in a solvent continuum is proportional to η/T , where η is the viscosity of the solvent and T is the temperature. The proportionality constant is given by VfC/k with V and f being the van der Waals volume and shape factor, respectively. These parameters, as their name suggests, depend on the size and shape of the solute molecule, and for nonspherical solutes, $f > 1$.²⁷ The parameter C describes the extent of coupling between the solute and the solvent and is known as the boundary condition parameter, which lies between the two limits, hydrodynamic stick and slip.²⁸ In other words, for a nonspherical solute molecule, the value of C follows the inequality, $0 < C \leq 1$, and the exact value of C is determined by the axial ratio of the solute. Thus, the reorientation time of a solute molecule is given by the following equation:

$$\tau_r = \frac{\eta VfC}{kT} \quad (1)$$

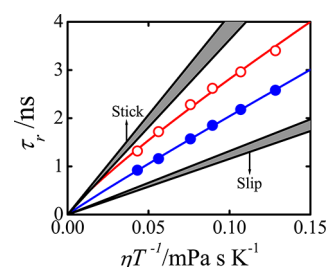
In the above equation, k is the Boltzmann constant. To calculate the reorientation times, the four solutes have been treated as asymmetric ellipsoids, and their axial radii were estimated using Corey–Pauling–Koltun scaled atomic models. van der Waals volumes were calculated using Edward’s increment method.²⁹ From the axial radii, friction coefficients with slip and stick boundary conditions were obtained by interpolating the numerical tabulations available in the literature.^{30,31} Einstein’s relation³² has been employed to calculate the diffusion coefficients from the friction coefficients, which in turn were used to obtain the reorientation times with the aid of standard formulas available in the literature.^{33,34} Details of this procedure have been described in our earlier publications.^{13,35} Table 2 lists the solute dimensions, van der

Table 2. Solute Dimensions and van der Waals Volumes Together with Shape Factors and Boundary Condition Parameters Calculated Using the SED Hydrodynamic Theory

solute	axial radii/Å ³	V/Å ³	f	C_{slip}
DMDPP	$8.2 \times 4.3 \times 1.9$	281	2.03	0.32
DPP	$8.2 \times 4.3 \times 1.9$	246	2.03	0.32
FL	$6.4 \times 5.5 \times 1.8$	267	1.93	0.14
R110	$6.7 \times 5.5 \times 1.8$	275	2.02	0.15

Waals volume, shape factor, and boundary condition parameter (C_{slip}) for the four solutes that were calculated using the SED hydrodynamic theory. It can be noticed from the table that the axial radii of DMDPP and DPP are identical, but the van der Waals volumes differ by 14%. In the case of FL and R110, there is a marginal difference in the long axial radius, which in turn causes subtle variation in the shape factors of the two solutes. Despite these minor disparities, SED hydrodynamic theory predicts more or less identical reorientation times for DMDPP and DPP and for FL and R110.

Figure 3 displays plots of τ_r versus η/T for DMDPP and DPP in PAN along with the SED slip and stick lines. It can be noticed from the figure that the reorientation times of the two solutes are between the stick and slip limits. From logarithmic fits of the data, the following relationships have been obtained between τ_r and η/T for DMDPP and DPP in PAN.

**Figure 3.** Plots of τ_r versus η/T for DMDPP (blue) and DPP (red) in *n*-propylammonium nitrate and the lines passing through data points were obtained by fitting the data to nonlinear η/T relationships, as described in the text. The SED slip and stick lines are also shown in the figure. The shaded areas in the figure represent the marginal differences in the calculated reorientation times of DMDPP and DPP as a result of a small variation in the van der Waals volumes of the two solutes.

$$\text{DMDPP} \quad \tau_r = (18.4 \pm 0.5)(\eta/T)^{0.96 \pm 0.01}$$

$$(N = 6, R = 0.999)$$

$$\text{DPP} \quad \tau_r = (20.7 \pm 1.9)(\eta/T)^{0.87 \pm 0.03}$$

$$(N = 6, R = 0.998)$$

In the above expressions, N and R are the number of data points and regression coefficient, respectively. It is evident from these expressions that there is a slight degree of nonlinearity in the relationships between τ_r and η/T for both solutes. However, no physical significance can be attached to the observed behavior. To further understand these results, the observed solute–solvent boundary parameter, C_{obs} has been calculated for both DMDPP and DPP from the measured reorientation times with the aid of eq 1. The C_{obs} values for DMDPP and DPP in PAN are 0.50 ± 0.01 and 0.80 ± 0.05 , respectively. In the case of DMDPP, C_{obs} in PAN is significantly higher than the average value (0.34 ± 0.04) obtained in 1-butyl-3-methylimidazolium-based ionic liquids with different anions, such as tris(pentafluoroethyl)trifluorophosphate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide, tetrafluoroborate, trifluoromethanesulfonate, and nitrate.¹⁶ Moreover, C_{obs} values of DMDPP in 1-butyl-3-methylimidazolium-based ionic liquids are closer to C_{slip} . It has been well-established that in the absence of specific solute–solvent interactions, the rotational diffusion of a medium-sized solute molecule follows slip hydrodynamics.^{33,36} Thus, these observations are an indication that DMDPP is experiencing strong hydrogen bonding interactions with the *n*-propylammonium cation via the two carbonyl groups. A similar behavior has been noticed for DMDPP when dissolved in strong hydrogen bond donating solvents, such as 1-(2-hydroxyethyl)-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate and 2,2,2-trifluoroethanol (TFE).^{14,37} In essence, it can be stated that DMDPP rotates about 60% slower compared to the predictions of slip hydrodynamics as a consequence of specific interactions between the solute and the cation of the ionic liquid.

As mentioned earlier, the rotation of DPP in PAN is 30–50% slower compared to DMDPP, and the C_{obs} value differs by 60%. Molecular orbital calculations indicate that DPP forms various types of aggregates in the solid state through intermolecular hydrogen bonding between the C=O and NH groups.³⁸ It must be noted that the hydrogen bonds between the aggregates need to be broken so that the monomer form of DPP dissolves in liquids. Thus, DPP is soluble only in those solvents with which it can form hydrogen bonds at the two NH sites. Though predominantly a hydrogen bond donor, DPP also acts as a hydrogen bond acceptor due to the presence of the two carbonyl groups. It has been established that the hydrogen bond donating ability and, to a lesser extent, hydrogen bond accepting ability of DPP significantly impedes its rotational diffusion in ionic liquids¹² and organic solvents.^{35–37} On the basis of these arguments, it can be inferred that DPP experiences specific interactions at the NH and C=O sites with the nitrate anion and the *n*-propylammonium cation, respectively, of the ionic liquid. Since hydrogen bonding interactions prevail at the secondary amino as well as the carbonyl groups, in the case of DPP, its rotation is considerably slower compared to that of DMDPP.

Figure 4 displays plots of τ_r versus η/T for FL and R110 in PAN along with the SED slip and stick lines. It can be noticed from the figure that the reorientation times of the two solutes

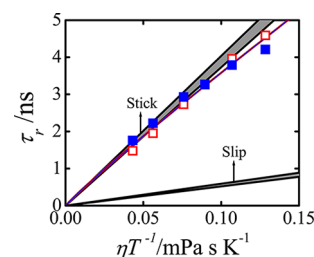


Figure 4. Plots of τ_r versus η/T for fluorescein (blue) and rhodamine 110 (red) in *n*-propylammonium nitrate. The line passing through the data points was obtained by fitting the data to the nonlinear η/T relationship as described in the text. The SED slip and stick lines are also shown. The shaded areas represent the marginal differences in the calculated reorientation times of FL and R110 as a result of small variation in the long axial radius of the two solutes.

are almost identical and also match with the predictions of stick hydrodynamics. From logarithmic fit of the data, a common τ_r versus η/T relationship has been obtained for FL and R110 in PAN, which is given below.

$$\text{FL-R110} \quad \tau_r = (30.8 \pm 3.8)(\eta/T)^{0.93 \pm 0.05}$$

$$(N = 12, R = 0.988)$$

The almost identical rotational behavior observed for FL and R110 in PAN is somewhat surprising. As mentioned earlier, both FL and R110 are structurally similar but have opposite charges, and hence, they are expected to experience strong specific interactions with the cation and anion of the ionic liquid, respectively. It may be noted that in the absence of polar functional groups, the rotational diffusion of both solutes would have been closer to the predictions of slip hydrodynamics. In fact, such a controlled experiment was performed in our earlier work,¹³ where fluorescence anisotropies of a structurally similar analogue 9-phenylanthracene (9-PA) have been measured in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim⁺][PF₆[−]]). It was observed that the rotational diffusion of 9-PA follows slip hydrodynamics in [bmim⁺][PF₆[−]]. On the basis of these facts, it can be concluded that the observed behavior of FL and R110 in PAN is due to the specific interactions between the solutes and the ions that constitute the ionic liquid.

A closer look at the molecular structure of FL (see Figure 1) reveals that it has C=O, COO[−] and OH groups. Two of the three functional groups present are hydrogen bond acceptors, and the hydroxyl group can act as a donor as well as an acceptor. However, in the case of FL, the OH group does not act as a donor, and this premise was based on the fact that FL is not soluble in numerous aprotic ionic liquids. If the OH group acted as a hydrogen bond donor, then FL would have been soluble in aprotic ionic liquids due to the prevalence of specific interactions between the anions of these ionic liquids and the hydroxyl group. The cationic solute R110, on the other hand, has NH₂, NH₂⁺, and COOH groups, and all of them are hydrogen bond donors. Thus, the three hydrogen bond acceptors present on FL and the three donors on R110 facilitate hydrogen bonding interactions with *n*-propylammonium cation and nitrate anion, respectively, which probably explains the identical rotational behavior observed for the two ionic solutes in PAN.

The discussion presented so far attempts to rationalize the observed trends in terms of the number of hydrogen bond accepting and donating groups present on the solute molecules

and how they can experience specific interactions with the cation and anion of the ionic liquid. However, it is the strength of the specific solute–solvent interaction rather than the number of solute–solvent hydrogen bonds that determines whether the solute rotation gets impeded. In other words, in the case of strong hydrogen bonds, there is no flexibility of the hydrogen bonds to angular motion, which causes the solvent to be dragged along, resulting in slower solute rotation.^{39,40} This premise has been experimentally verified by correlating the measured reorientation times of DMDPP and DPP in ethanol and TFE and also in isomeric butanols with the calculated solute–solvent interaction strengths.^{37,41} In principle, the strength of the specific solute–solvent interaction involving a particular solute molecule is determined by the hydrogen bond donating and accepting abilities of the solvent.

The properties of solvents such as dipolarity/polarizability, hydrogen bond acidity and hydrogen bond basicity are accounted for by two well-known multiparameter scales: Kamlet–Taft^{42,43} and the Abraham model.^{44,45} Both have been extended to describe the above-mentioned parameters for ionic liquids, as well.^{21,46–50} It may be noted that the Kamlet–Taft method employs solvatochromic comparisons of UV–vis spectral data of closely related dyes, whereas the Abraham model uses gas chromatography experiments to measure retention times of small solute molecules. Both predict qualitatively similar trends for the hydrogen bond basicities of the ionic liquids, and they mainly depend on the nature of the anion. In contrast, the trends predicted by the two scales for the hydrogen bond acidities are in conflict with each other. For example, 1-butyl-3-methylimidazolium-based ionic liquids are shown to be good hydrogen bond donors according to the Kamlet–Taft scale. However, results obtained with the aid of the Abraham model portray altogether a different scenario as it has been shown that the hydrogen bond donating ability of these ionic liquids is almost negligible.

In the same vein, the two scales have also predicted conflicting trends for the hydrogen bond acidities of the ionic liquid PAN,²¹ which is used in the present study. Welton and co-workers,^{47,48} rationalized this discrepancy by taking into consideration the presence and absence of charge on the solute molecules used in both methodologies. The Kamlet–Taft method uses Reichardt's dye, which has a phenoxide oxygen atom, whereas all the solute molecules used in the gas chromatography experiments are neutral. Thus, a strong coulombic component of the hydrogen bond is present in the solvatochromic experiment, but not in the gas chromatography experiment. On the basis of their work, it has been suggested that phenomena dominated by Coulombic interactions are better modeled using polarity scales based upon charged solutes, whereas those for which Coulombic interactions are not significant, polarity scales based upon neutral solutes need to be considered.⁴⁸ In view of these arguments, hydrogen bond acidity and basicity values of PAN that were obtained by employing the Abraham model have been used while rationalizing the rotational behavior of the nondipolar solutes DMDPP and DPP. In the case of ionic solutes FL and R110, hydrogen bond acidity and basicity values obtained using the Kamlet–Taft scale have been considered.

The hydrogen bond acidity (b) and basicity (a) values of PAN obtained using the Abraham model are 0.90 ± 0.07 and 3.5 ± 0.1 , respectively.²¹ These numbers indicate that the ionic liquid PAN is a stronger hydrogen bond acceptor than a donor. Experimental results indicate that both DMDPP and DPP are

experiencing specific interactions in PAN. As mentioned before, DMDPP due to the presence of the two carbonyl groups forms hydrogen bonds with the *n*-propylammonium cation, whereas DPP experiences specific interactions at the two NH sites as well with the nitrate anion. However, the specific interactions between the carbonyl groups and the *n*-propylammonium cation are weaker compared to $\text{NH} \cdots \text{NO}_3^-$ hydrogen bonding as a result of lower hydrogen bond acidity of PAN. In other words, the higher hydrogen bond basicity of PAN facilitates stronger specific interactions at the two NH sites of DPP, resulting in its slower rotation compared to DMDPP.

In contrast, the hydrogen bond acidity (α) and basicity (β) values of PAN, according to Kamlet–Taft scale, are 0.88 and 0.52, respectively,²¹ which indicates that PAN is a stronger hydrogen bond donor than acceptor. Since PAN possesses higher hydrogen bond acidity, FL should have experienced stronger specific interactions with the *n*-propylammonium cation and, consequently, slower rotation compared to R110. However, the observed results indicate that rotational diffusion of both FL and R110 is identical in PAN. In other words, the parameters α and β are unable to rationalize the trends observed in the rotational diffusion of the ionic solutes in PAN. The probable reason could be that hydrogen bond acidity and basicity parameters obtained using the Kamlet–Taft method are valid in the case of ionic solutes.^{47,48} It may be noted that although FL and R110 belong to this category, both of these solutes also contain hydrogen bonding entities that are neutral in nature. Under these circumstances, the applicability of the parameters α and β to the so-called ionic solutes is suspect, which is probably the reason why the observed behavior could not be assimilated using the Kamlet–Taft scale of acidity and basicity.

As an alternative method of analysis, the solventberg model has been considered in an attempt to explain the observed results. According to this model, when solute and solvent molecules experience specific interactions, the volume of the solute–solvent complex increases compared to the volume of the bare solute molecule, leading to an enhancement in the reorientation time. To implement this model for the systems employed in this study, two *n*-propylammonium cations (van der Waals volume = 68 \AA^3) have been attached at the two carbonyl sites of DMDPP, whereas for DPP, two nitrate anions (van der Waals volume = 38 \AA^3) have been joined at the two NH sites in addition to the two *n*-propylammonium cations at the carbonyl sites. For the ionic solute FL, three *n*-propylammonium cations have been attached at C=O, OH, and COO^- sites, and for R110, three nitrate anions to NH_2 , NH_2^+ , and COOH groups. The reorientation times of the solute–solvent complexes with slip and stick boundary conditions have been obtained by treating them as asymmetric ellipsoids. The dimensions of the solute–solvent complexes, van der Waals volumes, shape factors and C_{slip} values are listed in Table 3.

It can be noticed from the table that C_{slip} values for DMDPP–PAN and DPP–PAN complexes are significantly lower than the ones obtained for bare molecules. In contrast, for FL–PAN, C_{slip} is a factor of 2 higher compared to FL and for R110–PAN, it is 1.5 times higher than that obtained for R110. However, it must be noted that the calculated reorientation times depend on the magnitude of the hydrodynamic volume, V_h , which is a product of V , f , and C_{slip} . Although there is no noticeable change in the hydrodynamic volumes of DMDPP and DPP and their complexes with the

Table 3. Solute–Solvent Complex Dimensions and van der Waals Volumes Together with Shape Factors and Boundary Condition Parameters Calculated Using the SED Hydrodynamic Theory

solute–solvent complex	axial radii/Å ³	$V/\text{Å}^3$	f	C_{slip}
DMDPP–PAN	$8.2 \times 6.4 \times 1.9$	417	2.14	0.18
DPP–PAN	$8.2 \times 7.0 \times 1.9$	459	2.14	0.17
FL–PAN	$9.7 \times 5.5 \times 2.1$	472	2.54	0.28
R110–PAN	$8.5 \times 5.5 \times 2.0$	390	2.34	0.22

ionic liquid PAN, V_h values of FL–PAN and R110–PAN increase by a factor of 4.6 and 2.4, respectively, compared to FL and R110. From this result, it is evident that the calculations carried out in this manner fail to mimic the almost identical reorientation times obtained for the ionic solutes FL and R110 in PAN. Furthermore, these results may appear startling because the C_{slip} values of DMDPP–PAN and DPP–PAN are lower than those obtained for the bare solute molecules, despite a significant increase in the van der Waals volumes of the complexes. It may be noted that the attachment of solvent molecules at the carbonyl sites of DMDPP and carbonyl and NH sites of DPP increases the length of the short-in-plane axis, $2b$ for both DMDPP and DPP (see Tables 2 and 3), which leads to an enhancement in the value of b/a (a is the long axial radius) compared to the bare solute molecules. On the other hand, for FL and R110 complexes, attachment of solvent molecules takes place in such a manner that the length of the long axis increases, leading to a decrease in the value of b/a . It may be noted that when slip boundary condition is employed, the friction coefficients obtained are highly sensitive to the axial ratio of the ellipsoid, since only motions that displace solvent give rise to any friction. In view of the extremely sensitive nature of the ellipsoid-based hydrodynamic calculations, especially with slip boundary conditions, a better way to realize the prevalence of specific interactions between a solute and a solvent is to compare the reorientation time of a solute molecule with a structurally similar but chemically distinct analogue, which has been done in the present study.

CONCLUSIONS

Protic ionic liquids, due to their ability to donate and accept hydrogen bonds, experience a multitude of specific interactions with solutes dissolved in them. These specific interactions in turn influence dynamical processes such as solute rotation, solvation dynamics, and photoisomerization reactions. In an attempt to understand how specific interactions influence rotational diffusion of organic solutes in a typical protic ionic liquid, the present study has been undertaken, and the important conclusions are summarized in this section. Both the nondipolar solutes DMDPP and DPP experience specific interactions with the n -propylammonium cation of the ionic liquid PAN due to the presence of carbonyl groups. In addition, DPP also experiences hydrogen bonding interactions with the nitrate anion of the ionic liquid via the two NH sites, leading to its slower rotation compared to DMDPP. The hydrogen bond acidity and basicity of PAN that were obtained using the Abraham model have been found to be successful in explaining the observed trends in the rotational diffusion of DMDPP and DPP. The negatively charged FL and the positively charged R110 hydrogen bond with the cation and anion of PAN, respectively; however, their reorientation times are almost identical. Neither the Kamlet–Taft scale nor the Abraham

model of acidity and basicity could rationalize the identical rotational behavior that has been observed for FL and R110 in PAN, which is probably due to the partly ionic and partly neutral nature of the hydrogen bonding functional groups that these solutes possess.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gbdutt@barc.gov.in.

Notes

The authors declare no competing financial interest.

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