Does Addition of an Electrolyte Influence the Rotational Diffusion of Nondipolar Solutes in a Protic Ionic Liquid?

2 **AUTHORS**, INCLUDING:

Sugosh Prabhu

Bhabha Atomic Research Centre

10 PUBLICATIONS   **22** CITATIONS

SEE PROFILE

Does Addition of an Electrolyte Influence the Rotational Diffusion of Nondipolar Solutes in a Protic Ionic Liquid?

Sugosh R. Prabhu and G. B. Dutt*

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

Ⓢ Supporting Information

ABSTRACT: Rotational diffusion of two structurally similar nondipolar solutes, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DMDPP) and 1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP), has been examined in ethylammonium nitrate–lithium nitrate (EAN–LiNO$_3$) mixtures to understand the influence of added electrolyte on the local environment experienced by the solute molecules. The measured reorientation times of both DMDPP and DPP in EAN–LiNO$_3$ mixtures fall within the broad limits set by the hydrodynamic slip and stick boundary conditions. The hydrogen bond accepting DMDPP and the hydrogen bond donating DPP experience specific interactions with the cation and anion of the ionic liquid, respectively. Addition of LiNO$_3$ (0.1 and 0.2 mole fraction) to EAN induces only viscosity related effects on the rotational diffusion of the two nondipolar solutes. These observations suggest that the local environment experienced by DMDPP and DPP in EAN is not altered upon the addition of LiNO$_3$. Our results are consistent with the structural details available in the literature for EAN–LiNO$_3$ mixtures.

→ Li$^+$　● → C$_2$H$_5$-NH$_3^+$　◁ → NO$_3^-$
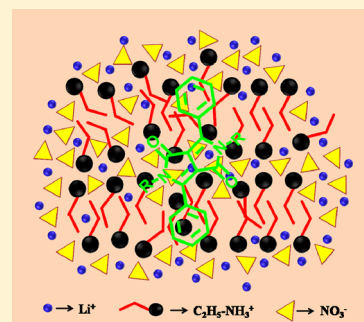
1. INTRODUCTION

Investigations dealing with the structure and physicochemical properties of protic ionic liquids have received considerable attention in recent times.[1−14] As the name suggests, protic ionic liquids possess both proton donating and accepting sites and their presence leads to the formation of a three-dimensional hydrogen bonded network in the bulk akin to that found in water.[3] Ethylammoniun nitrate (EAN), which was one of the first ionic liquids described by Walden[15] in 1914, belongs to this category whose melting point is around 286 K.[16] Although EAN has been known for more than 100 years, its structural details have only begun to emerge during the past decade. Small angle neutron scattering studies and computer simulations carried out with EAN and other protic ionic liquids indicate that these ionic liquids arrange into a sponge-like bicontinuous nanostructure consisting of polar and nonpolar domains.[1,6−8] Furthermore, an increase in the length of the alkyl chain results in a better segregation of polar and nonpolar domains. Since the length of the alkyl chain determines the size of these domains, they are merely of the order of 1 nm in EAN.[6]

Apart from the structural elucidation of neat protic ionic liquids, studies have also been performed to understand their structure in the presence of inorganic salts such as LiNO$_3$, Mg(NO$_3$)$_2$, Ca(NO$_3$)$_2$, Al(NO$_3$)$_3$, and ZnCl$_2$.[10−14] However, a majority of these efforts are focused on the EAN–LiNO$_3$ system. It has been deduced that, even at 0.2 mole fraction of LiNO$_3$ (x_{LiNO_3} = 0.2), the bulk structure of EAN is not appreciably affected. The presence of Li$^+$ and extra NO$_3^-$ ions in the polar domain disrupts packing in the nonpolar domain and produces a weak structure-breaking effect.[12] It has also been inferred that Li$^+$ ions in the polar domains progressively erode the hydrogen bonding network of the protic ionic liquid and decrease the extent of hydrogen bonding of the mixtures. As a consequence, orientational disorder is induced in the polar domains and this effect is more pronounced in the case of protic ionic liquids with longer alkyl chains where a lower degree of hydrogen bonding prevails.[15]

Even though the structural details of the EAN–LiNO$_3$ system are well-documented, the dynamics of solute molecules dissolved in them has not been explored so far. Addition of Li$^+$ ions to EAN is likely to increase the viscosity of the solution, which can have a significant impact on the rotational diffusion of solute molecules. However, it is not obvious whether the bulk viscosity (η) of the solution or the local viscosity governs the solute rotation in this system. Moreover, it is not known if the rotational diffusion of the solute molecules will be affected due to specific interactions with Li$^+$ ions. Thus, to address these issues, the present study has been undertaken wherein fluorescence anisotropies of two structurally similar nondipolar solutes, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]-pyrrole (DMDPP) and 1,4-dioxo-3,6-diphenyl-pyrrolo[3,4-c]-pyrrole (DPP), have been measured in EAN–LiNO$_3$ mixtures. Figure 1 gives the molecular structures of the two solutes, and it can be noticed from the figure that DMDPP has two carbonyl groups, whereas DPP has two secondary amino groups in addition to the two carbonyl groups. Due to this reason, DMDPP and DPP are hydrogen bond accepting and hydrogen bond donating solutes, respectively. The rotational diffusion of these solutes has been examined in organic solvents[17−22] and
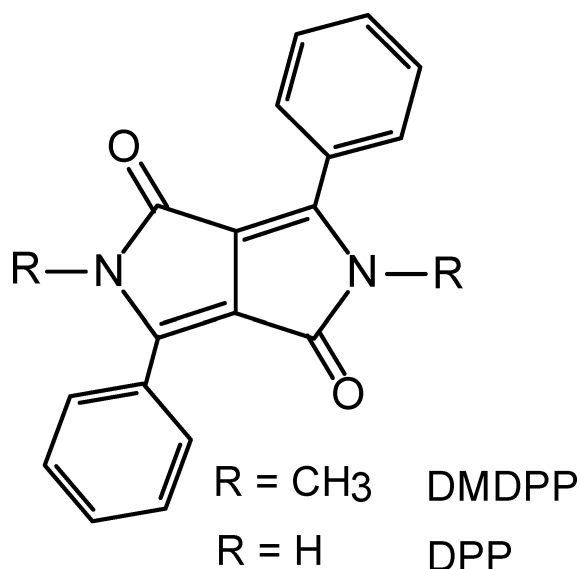
Figure 1. Molecular structures of DMDPP and DPP.

ionic liquids.[23−25] It has been noticed that the rotation of DPP is significantly slower compared to DMDPP, as the former experiences specific interactions with hydrogen bond accepting solvents via the two NH groups.

It may be noted that rotational diffusion of organic solutes has been extensively investigated in ionic liquids[23,24,26−48] and ionic liquid−organic solvent mixtures[25,49−53] to understand the solute−ionic liquid interactions, the role of organized structure on solute rotation, and also the local environment experienced by the solute molecules. However, only one study is available in the literature that deals with the rotational diffusion of an organic solute in ionic liquid−electrolyte mixtures. Lawler and Fayer[54] have measured fluorescence anisotropies of the planar organic solute perylene in 1-butyl-3-methylimidazolium bis-(trifluoromethyl)sulfonylimide with varying amounts of lithium bis(trifluoromethyl)sulfonylimide. They have observed a decrease in the friction coefficients of perylene with the in-plane coefficient decreasing to a greater extent than the out-of-plane coefficient upon increasing the concentration of Li$^+$ ions. These observations have been rationalized on the basis of electrolyte induced changes in the organized structure of the ionic liquid. The above-mentioned study has been carried out in aprotic ionic liquid−electrolyte mixtures, whereas the present study is an endeavor to find out the influence of added electrolyte on the rotational diffusion of nondipolar solutes in a protic ionic liquid.

2. EXPERIMENTAL SECTION

The ionic liquid EAN and LiNO$_3$ were purchased from io-li-tec, Germany, and Aldrich, USA, respectively. The solutes DMDPP and DPP were obtained from Ciba Specialty Chemicals, Inc., Switzerland. The stated purity of EAN is >97%, which was purified and dried as described in the literature.[6] LiNO$_3$ (>99% purity) was powdered and dried in a vacuum oven at 400 K for a few days to remove the water. Samples with 0.1 and 0.2 mole fraction of LiNO$_3$ in EAN were prepared by weighing and mixing appropriate amounts of the salt and ionic liquid in glass bottles. Both LiNO$_3$ and EAN are miscible upon gentle heating and sonication. The water content of the samples was estimated by Karl Fischer titration with the aid of a Metrohm 831 KF Coulometer and found to be <100 ppm.

Absorption and fluorescence spectra of the samples were recorded using a Jasco V-650 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. The absorbance of the samples was maintained in the range 0.1−0.15 at the wavelength of excitation. Fluorescence anisotropy decays were measured using a time-correlated single-photon counting spectrometer that was purchased from Horiba Jobin Yvon, U.K. The instrumental details and the description concerning the measurement of anisotropy decays have been discussed in our earlier publication.[38] The samples containing the probes DMDPP and DPP were excited with a 445 nm diode laser, and the emission was monitored around 550 nm. The anisotropy decay measurements of DMDPP and DPP were carried out over the temperature range 298−348 K. Each measurement was repeated 2−3 times, and the average values are reported. Reorientation times were obtained from the analysis of anisotropy decays with the aid of the software supplied by Horiba Scientific. Viscosities of EAN and EAN−LiNO$_3$ mixtures were measured as a function of temperature using a Physica MCR 101 rheometer, and the uncertainties on the measured numbers are about 5%.

3. RESULTS AND DISCUSSION

The viscosity of neat EAN is 34.2 mPa s at 298 K, and it agrees well with the value reported by Poole.[16] Figure 2 gives the
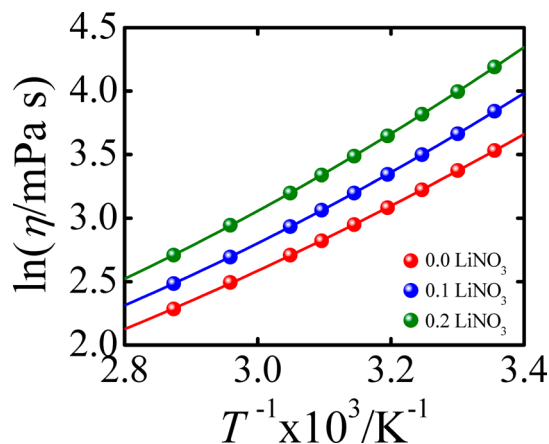
Figure 2. Plots of $\ln(\eta)$ versus T^{-1} for EAN−LiNO$_3$ mixtures. The curves passing through data points are drawn as a visual aid.

variation of viscosity with temperature for neat EAN, x_{LiNO_3} = 0.1 and 0.2. It can be noticed from the figure that addition of LiNO$_3$ significantly increases the viscosity of the solution. The significant increase in the viscosity arises as a consequence of Li$^+$ ions that are embedded in the polar domains of EAN coordinate with about 4 NO$_3^-$ ions, which leads to a decrease in the mobility of the ions.[11,12] Thus, it would be interesting to find out how such a large increase in solution viscosity influences the rotational diffusion of the solute molecules.

Anisotropy decays, $r(t)$, of DMDPP and DPP in neat EAN and EAN−LiNO$_3$ mixtures are adequately described by a single exponential function, which is given by

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

where r_0 and τ_r are the limiting anisotropy and the reorientation time, respectively. Typical anisotropy decays of DMDPP and DPP in EAN−LiNO$_3$ mixtures and the respective residual distributions are shown in the Supporting Information. The

measured reorientation times of DMDPP and DPP in EAN, x_{LiNO_3} = 0.1 and 0.2, along with the solution viscosities are also given in the Supporting Information. The uncertainties on the reorientation times are about 5−10%. To comprehend the rotational diffusion of these solutes in EAN−LiNO$_3$ mixtures, Stokes−Einstein−Debye hydrodynamic (SED) theory is employed.[55,56] According to this theory, the reorientation time of a solute molecule is given by eq 2.

$$\tau_r = \frac{\eta V f C}{kT} \tag{2}$$

In the above equation, V and f are the volume and shape factor of the solute molecule, respectively, while C is the boundary condition parameter that determines the extent of coupling between the solute and the solvent. The two limiting cases for C are the hydrodynamic slip (C_{slip}), which satisfies the inequality $0 < C_{slip} \leq 1$, and the hydrodynamic stick with C_{stick} = 1. k and T are the Boltzmann constant and absolute temperature, respectively. The van der Waals volume of DMDPP is 281 Å^3, and that of DPP is 246 Å^3. The two solute molecules are treated as asymmetric ellipsoids, and their shape factors and the boundary condition parameters have been calculated and the details are described in our earlier publication.[17] The parameters f and C_{slip} are found to be identical (f = 2.03 and C_{slip} = 0.32) for DMDPP and DPP due to their similarity in shape and size. Since viscosity and temperature are the two parameters that govern solute rotation according to SED theory, the reorientation time of a solute molecule at a given η/T should be independent of the solvent employed. To find out how well this premise holds for the systems under investigation, anisotropy decays of DMDPP and DPP in EAN, x_{LiNO_3} = 0.1 and 0.2, are plotted in Figure 3. Because the viscosities of EAN and EAN−LiNO$_3$ mixtures are different, temperatures have been chosen such that η/T for the three systems are identical, which is 0.045 mPa s K^{-1}. It can be noticed from the figure that anisotropy decays of DMDPP in EAN and EAN−LiNO$_3$ mixtures are indistinguishable from one another and a similar pattern has been obtained for DPP as well.

To get a better appreciation of the entire data, τ_r versus η/T plots are presented for DMDPP and DPP in Figures 4 and 5, respectively. Least-squares fits of the data resulted in $\tau_r = A(\eta/T)^n$ type relationships, and the values of A and n are listed in Table 1. It may be noted that these kinds of power-law fits are purely empirical and do not have any physical significance. However, a substantial deviation of n from unity implies the breakdown of the SED theory. Inspection of Table 1 reveals that the values of n fluctuate around 1 and there is no systematic variation in the values of either A or n with an increase in the concentration of LiNO$_3$ for both DMDPP and DPP. In view of this observation, a least-squares fit was performed by considering the entire data for DMDPP in EAN−LiNO$_3$ mixtures and a similar fit was carried out with data involving DPP. The following τ_r versus η/T relationships have been obtained.

DMDPP/EAN−LiNO$_3$ $\tau_r = (21.0 \pm 0.6)(\eta/T)^{1.03\pm0.01}$

(N = 27, R = 0.9987)

DPP/EAN−LiNO$_3$ $\tau_r = (27.6 \pm 0.6)(\eta/T)^{1.04\pm0.01}$

(N = 27, R = 0.9992)
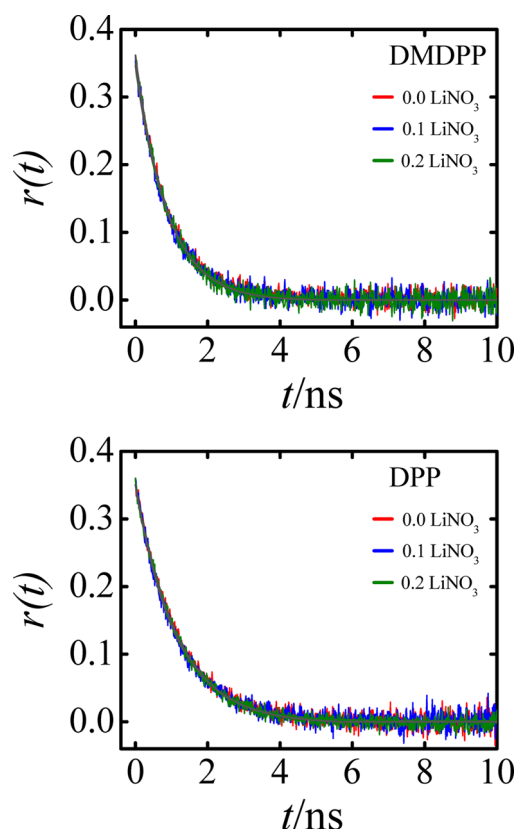
Figure 3. Anisotropy decays of DMDPP and DPP in EAN−LiNO$_3$ mixtures along with the fitted curves. The temperatures have been chosen such that η/T values for the three systems are identical, which is 0.045 mPa s K^{-1}.
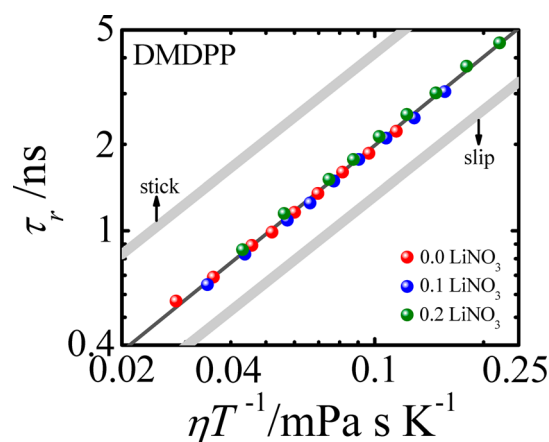
Figure 4. Plots of τ_r versus η/T for DMDPP in EAN−LiNO$_3$ mixtures. The line passing through the data points is obtained by a linear least-squares fit. The SED slip and stick lines are also shown in the figure.

In the above expressions, τ_r values are in ns and η/T in mPa s K^{-1} with N and R being the number of data points and the regression coefficient, respectively. The analysis carried out so far suggests that the rotational diffusion of DPP is slower by 20−30% compared to DMDPP in EAN−LiNO$_3$ mixtures. Furthermore, addition of LiNO$_3$ to EAN merely slows down the rotation of both of the solutes due to an enhancement in the viscosity of the solution; however, no deviations from the SED theory have been noticed. These aspects will be elaborated in the remainder of this article.
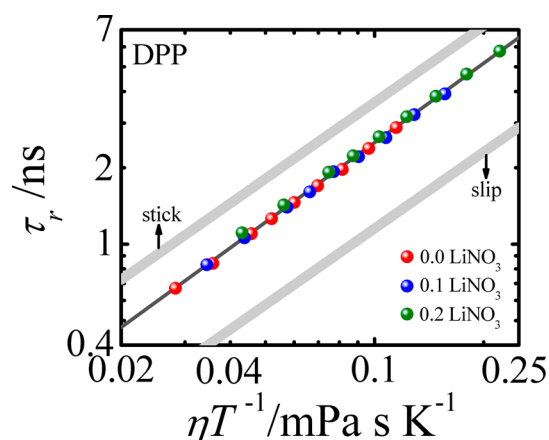
Figure 5. Plots of τ_r versus η/T for DPP in EAN−LiNO$_3$ mixtures. The line passing through the data points is obtained by a linear least-squares fit. The SED slip and stick lines are also shown in the figure.
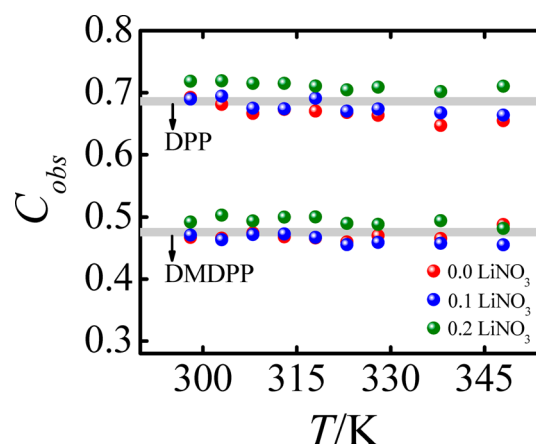

Figure 6. Plots of C_{obs} versus T for DMDPP and DPP in EAN−LiNO$_3$ mixtures. The C_{obs} values for the two solutes are independent of the [LiNO$_3$] and temperature. The gray-colored lines passing through the points represent the average values.

The differences in the rotational diffusion of DMDPP and DPP can be better appreciated by comparing the observed boundary condition parameter (C_{obs}), which has been calculated from the measured reorientation times using the formula $C_{obs} = \tau_r/\tau_r^{stick}$, where τ_r^{stick} is the reorientation time calculated with the stick boundary condition. The C_{obs} obtained in this manner should be independent of viscosity and temperature. Figure 6 displays plots of C_{obs} versus T for DMDPP and DPP in EAN−LiNO$_3$ mixtures, and as expected, there is no systematic variation of C_{obs} with temperature. Another feature that is evident from the figure is that the C_{obs} values are independent of LiNO$_3$ concentration for both DMDPP and DPP. However, the important information that can be gleaned from the figure is that the C_{obs} values of DMDPP are significantly lower compared to DPP. As mentioned in the Introduction, EAN is a protic ionic liquid and it can donate and accept hydrogen bonds. DMDPP, due to the presence of the two carbonyl groups, experiences specific interactions with ethylammonium cations of the ionic liquid. It may be noted that the rotational diffusion of DMDPP has been examined in numerous 1-alkyl-3-methylimidazolium-based ionic liquids[32] and the C_{obs} values are close to C_{slip}, which is 0.32. It is a well-established fact that rotational diffusion of medium-sized solutes follows slip hydrodynamics in the absence of specific interactions.[22,55,56] However, in protic ionic liquids such as 1-(2-hydroxyethyl)-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate and n-propylammonium nitrate, DMDPP experiences specific interactions and the C_{obs} values are higher by 30−50% compared to C_{slip}.[30,33] The solute DPP, on the other hand, can donate and accept hydrogen bonds in principle. However, once it forms hydrogen bonds with NO$_3^-$ ions at the two NH sites, steric hindrance prevents the accessibility of the two carbonyl groups to the large ethylammonium cations, which renders DPP predom-

inantly as a hydrogen bond donating solute. The rotational diffusion of DPP is slower, as it experiences stronger specific interactions in EAN compared to DMDPP.

As mentioned earlier, addition of LiNO$_3$ has no influence on the rotational diffusion of DMDPP and DPP in EAN. It may be noted that LiNO$_3$ does not alter the organized structure of EAN significantly.[11−14] Furthermore, the presence of Li$^+$ and NO$_3^-$ ions in the polar domains of EAN neither facilitates nor impedes the specific interactions between these nondipolar solutes and constituent ions of the ionic liquid, which is evident from the lack of variation in the C_{obs} values with an increase in LiNO$_3$ concentration. This result is in contrast to what has been observed for the rotational diffusion of a nonpolar solute perylene in 1-butyl-3-methylimidazolium bis(trifluoromethyl)-sulfonylimide in the presence of lithium bis(trifluoromethyl)-sulfonylimide by Lawler and Fayer.[54] They have observed a decrease in the in-plane and out-of-plane friction coefficients of perylene by more than a factor of 6 and 3, respectively, with an increase in the mole fraction of lithium bis(trifluoromethyl)-sulfonylimide from 0 to 0.4. The significant decrease in the friction coefficients of perylene has been attributed to a change in the configuration of the 1-butyl-3-methylimidazolium cations with an increase in the electrolyte concentration, which in turn alters the organization of the butyl chains that solvate perylene in alkyl regions. However, in the present work, lack of variation in the C_{obs} values with an increase in LiNO$_3$ concentration could be due to the smaller size of the organized domains present in EAN and also specific interactions between the solutes and the ionic liquid. Further insight can be gained by extending these studies in protic ionic liquids with longer alkyl chains.

Table 1. Values of A and n Obtained for DMDPP and DPP in EAN−LiNO$_3$ Mixtures from Linear Least-Squares Fits of log−log Plots of τ_r versus η/T

	DMDPP		DPP	
x_{LiNO_3}	A/ns K (mPa s)$^{-1}$	n	A/ns K (mPa s)$^{-1}$	n
0.0	18.6 ± 0.7	0.98 ± 0.01	27.1 ± 0.5	1.04 ± 0.01
0.1	20.4 ± 0.4	1.02 ± 0.01	26.3 ± 0.5	1.03 ± 0.01
0.2	21.2 ± 0.1	1.02 ± 0.01	26.5 ± 0.2	1.01 ± 0.01

CONCLUSIONS

Fluorescence anisotropy decays of two structurally similar nondipolar solutes, DMDPP and DPP, have been measured in the protic ionic liquid EAN and EAN–LiNO$_3$ mixtures to understand the influence of added electrolyte on solute dynamics. The important conclusion of this study is that addition of LiNO$_3$ has no influence on the reorientation times of both of the solute molecules apart from viscosity related effects. The solutes DMDPP and DPP experience specific interactions with the cation and anion of the ionic liquid, respectively. However, the added LiNO$_3$ does not alter the hydrogen bonding interactions between the solutes and the constituent ions of the ionic liquid, which is noticeable from the C_{obs} values that are invariant with electrolyte concentration. The results of this work in conjunction with the ones available in the literature suggest that addition of LiNO$_3$ to EAN affects neither the organized structure of the ionic liquid nor the dynamics of solute molecules dissolved in them.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Reorientation times of DMDPP and DPP in EAN–LiNO$_3$ mixtures and their viscosities as a function of temperature. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b02853.

AUTHOR INFORMATION

Corresponding Author

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

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Atkin, R.; Warr, G. G. The Smallest Amphiphiles: Nanostructure in Protic Room-Temperature Ionic Liquids with Short Alkyl Groups. *J. Phys. Chem. B* 2008, *112*, 4164–4166.

(2) Kennedy, D. F.; Drummond, C. J. Large Aggregated Ions Found in Some Protic Ionic Liquids. *J. Phys. Chem. B* 2009, *113*, 5690–5693.

(3) Fumino, K.; Wulf, A.; Ludwig, R. Hydrogen Bonding in Protic Ionic Liquids: Reminiscent of Water. *Angew. Chem., Int. Ed.* 2009, *48*, 3184–3186.

(4) Ludwig, R. A Simple Geometrical Explanation for the Occurrence of Specific Large Aggregated Ions in Some Protic Ionic Liquids. *J. Phys. Chem. B* 2009, *113*, 15419–15422.

(5) Greaves, T. L.; Kennedy, D. F.; Mudie, S. T.; Drummond, C. J. Diversity Observed in the Nanostructure of Protic Ionic Liquids. *J. Phys. Chem. B* 2010, *114*, 10022–10031.

(6) Hayes, R.; Imberti, S.; Warr, G. G.; Atkin, R. Amphiphilicity Determines Nanostructure in Protic Ionic Liquids. *Phys. Chem. Chem. Phys.* 2011, *13*, 3237–3247.

(7) Hayes, R.; Imberti, S.; Warr, G. G.; Atkin, R. Pronounced Sponge-Like Nanostructure in Propylammonium Nitrate. *Phys. Chem. Chem. Phys.* 2011, *13*, 13544–13551.

(8) Hayes, R.; Imberti, S.; Warr, G. G.; Atkin, R. Effect of Cation Alkyl Chain Length and Anion Type on Protic Ionic Liquid Nanostructure. *J. Phys. Chem. C* 2014, *118*, 13998–14008.

(9) Song, X.; Hamano, H.; Minofar, B.; Kanzaki, R.; Fujii, K.; Kameda, Y.; Kohara, S.; Watanabe, M.; Ishiguro, S.; Umebayashi, Y. Structural Heterogeneity and Unique Distorted Hydrogen Bonding in Primary Ammonium Nitrate Ionic Liquids Studied by High-Energy X-ray Diffraction Experiments and MD Simulations. *J. Phys. Chem. B* 2012, *116*, 2801–2813.

(10) D'Angelo, P.; Zitolo, A.; Ceccacci, F.; Caminiti, R.; Aquilanti, G. Structural Characterization of Zinc(II) Chloride in Aqueous Solution and in the Protic Ionic Liquid Ethyl Ammonium Nitrate by X-ray Absorption Spectroscopy. *J. Chem. Phys.* 2011, *135*, 154509/1–154509/7.

(11) Méndez-Morales, T.; Carrete, J.; Cabeza, O.; Russina, O.; Triolo, A.; Gallego, L. J.; Varela, L. M. Solvation of Lithium Salts in Protic Ionic Liquids: A Molecular Dynamics Study. *J. Phys. Chem. B* 2014, *118*, 761770.

(12) Hayes, R.; Bernard, S. A.; Imberti, S.; Warr, G. G.; Atkin, R. Solvation of Inorganic Nitrate Salts in Protic Ionic Liquids. *J. Phys. Chem. C* 2014, *118*, 21215–21225.

(13) Russina, O.; Caminiti, R.; Méndez-Morales, T.; Carrete, J.; Cabeza, O.; Gallego, L. J.; Varela, L. M.; Triolo, A. How Does Lithium Nitrate Dissolve in a Protic Ionic Liquid? *J. Mol. Liq.* 2014, DOI: 10.1016/j.molliq.2014.08.007.

(14) Méndez-Morales, T.; Carrete, J.; Rodŕguez, J. R.; Cabeza, O.; Russina, O.; Varela, L. M. Nanostructure of Mixtures of Protic Ionic Liquids and Lithium Salts: Effect of Alkyl Chain Length. *Phys. Chem. Chem. Phys.* 2015, *17*, 5298–5307.

(15) Walden, P. Molecular Weights and Electrical Conductivity of Several Fused Salts. *Bull. Russ. Acad. Sci.: Phys.* 1914, *1800*, 405–422.

(16) Poole, C. F. Chromatographic and Spectroscopic Methods for the Determination of Solvent Properties of Room Temperature Ionic Liquids. *J. Chromatogr. A* 2004, *1037*, 49–82.

(17) Dutt, G. B.; Srivatsavoy, V. J. P.; Sapre, A. V. Rotational Dynamics of Pyrrolopyrrole Derivatives in Alcohols: Does Solute–Solvent Hydrogen Bonding Really Hinder Molecular Rotation? *J. Chem. Phys.* 1999, *110*, 9623–9629.

(18) Dutt, G. B.; Krishna, G. R. Temperature-Dependent Rotational Relaxation of Nonpolar Probes in Mono and Diols: Size Effects versus Hydrogen Bonding. *J. Chem. Phys.* 2000, *112*, 4676–4682.

(19) Dutt, G. B. Rotational Dynamics of Nondipolar Probes in Alkane–Alkanol mixtures: Microscopic Friction on Hydrogen Bonding and Nonhydrogen Bonding Solute Molecules. *J. Chem. Phys.* 2000, *113*, 11154–11158.

(20) Dutt, G. B.; Ghanty, T. K. Rotational Dynamics of Nondipolar Probes in Electrolyte Solutions: Can Specific Interactions be Modeled as Dielectric Friction? *J. Chem. Phys.* 2002, *116*, 6687–6693.

(21) Dutt, G. B.; Ghanty, T. K. Rotational Dynamics of Nondipolar Probes in Ethanols: How Does the Strength of the Solute–Solvent Hydrogen Bond Impede Molecular Rotation? *J. Chem. Phys.* 2003, *119*, 4768–4774.

(22) Dutt, G. B. Molecular Rotation as a Tool for Exploring Specific Solute–Solvent Interactions. *ChemPhysChem* 2005, *6*, 413–418.

(23) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Do Organic Solutes Experience Specific Interactions with Ionic Liquids? *J. Chem. Phys.* 2005, *123*, 174504/1–174504/7.

(24) Gangamallaiah, V.; Dutt, G. B. Influence of the Organized Structure of 1-Alkyl-3- methylimidazolium Tetrafluoroborates on the Rotational Diffusion of Structurally Similar Nondipolar Solutes. *J. Phys. Chem. B* 2014, *118*, 13711–13717.

(25) Prabhu, S. R.; Dutt, G. B. Effect of Low Viscous Nondipolar Solvent on the Rotational Diffusion of Structurally Similar Nondipolar Solutes in an Ionic Liquid. *J. Phys. Chem. B* 2015, *119*, 2019–2025.

(26) Ingram, J. A.; Moog, R. S.; Ito, N.; Biswas, R.; Maroncelli, M. Solute Rotation and Solvation Dynamics in a Room-Temperature Ionic Liquid. *J. Phys. Chem. B* 2003, *107*, 5926–5932.

(27) Ito, N.; Arzhantsev, S.; Heitz, M.; Maroncelli, M. Solvation Dynamics and Rotation of Coumarin 153 in Alkylphosphonium Ionic Liquids. *J. Phys. Chem. B* 2004, *108*, 5771–5777.

(28) Jin, H.; Baker, G. A.; Arzhantsev, S.; Dong, J.; Maroncelli, M. Solvation and Rotational Dynamics of Coumarin 153 in Ionic Liquids: Comparisons to Conventional Solvents. *J. Phys. Chem. B* 2007, *111*, 7291–7302.

(29) Fruchey, K.; Fayer, M. D. Dynamics in Organic Ionic Liquids in Distinct Regions Using Charged and Uncharged Orientational Relaxation Probes. *J. Phys. Chem. B* **2010**, *114*, 2840−2845.

(30) Dutt, G. B. Influence of Specific Interactions on the Rotational Dynamics of Charged and Neutral Solutes in Ionic Liquids Containing Tris(pentafluoroethyl)trifluorophosphate (FAP) Anion. *J. Phys. Chem. B* **2010**, *114*, 8971−8977.

(31) Karve, L.; Dutt, G. B. Rotational Diffusion of Neutral and Charged Solutes in Ionic Liquids: Is Solute Reorientation Influenced by Nature of Cation? *J. Phys. Chem. B* **2011**, *115*, 725−729.

(32) Karve, L.; Dutt, G. B. Rotational Diffusion of Neutral and Charged Solutes in 1-Butyl-3- Methylimidazolium Based Ionic Liquids: Influence of Nature of Anion on Solute Rotation. *J. Phys. Chem. B* **2012**, *116*, 1824−1830.

(33) Karve, L.; Dutt, G. B. Role of Specific Interactions on the Rotational Diffusion of Organic Solutes in a Protic Ionic Liquid−Propylammonium Nitrate. *J. Phys. Chem. B* **2012**, *116*, 9107−9113.

(34) Gangamallaiah, V.; Dutt, G. B. Rotational Diffusion of Nonpolar and Ionic Solutes in 1-Alkyl-3-Methylimidazolium bis-(trifluoromethylsulfonyl)imides: Is Solute Rotation Always Influenced by the Length of the Alkyl Chain on the Imidazolium Cation? *J. Phys. Chem. B* **2012**, *116*, 12819−12825.

(35) Gangamallaiah, V.; Dutt, G. B. Fluorescence Anisotropy of a Nonpolar Solute in 1-Alkyl-3- Methylimidazolium-Based Ionic Liquids: Does the Organized Structure of the Ionic Liquid Influence Solute Rotation? *J. Phys. Chem. B* **2013**, *117*, 5050−5057.

(36) Gangamallaiah, V.; Dutt, G. B. Influence of the Organized Structure of 1-Alkyl-3- Methylimidazolium-Based Ionic Liquids on the Rotational Diffusion of an Ionic Solute. *J. Phys. Chem. B* **2013**, *117*, 9973−9979.

(37) Gangamallaiah, V.; Dutt, G. B. Effect of Alkyl Chain Length on the Rotational Diffusion of Nonpolar and Ionic Solutes in 1-Alkyl-3-Methylimidazolium bis(trifluoromethylsulfonyl)- imides. *J. Phys. Chem. B* **2013**, *117*, 12261−12267.

(38) Prabhu, S. R.; Dutt, G. B. Rotational Diffusion of Nondipolar and Charged Solutes in Alkyl Substituted Imidazolium Triflimides: Effect of C2Methylation on Solute Rotation. *J. Phys. Chem. B* **2014**, *118*, 9420−9426.

(39) Khara, D. C.; Samanta, A. Rotational Dynamics of Positively and Negatively Charged Solutes in Ionic Liquid and Viscous Molecular Solvent Studied by Time-Resolved Fluorescence Anisotropy Measurements. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7671−7677.

(40) Khara, D. C.; Samanta, A. Fluorescence Response of Coumarin-153 in N-Alkyl-N- methylmorpholinium Ionic Liquids: Are These Media More Structured than the Imidazolium Ionic Liquids? *J. Phys. Chem. B* **2012**, *116*, 13430−13438.

(41) Khara, D. C.; Kumar, J. P.; Mondal, N.; Samanta, A. Effect of the Alkyl Chain Length on the Rotational Dynamics of Nonpolar and Dipolar Solutes in a Series of N-Alkyl-N- Methylmorpholinium Ionic Liquids. *J. Phys. Chem. B* **2013**, *117*, 5156−5164.

(42) Das, S. K.; Sarkar, M. Solvation and Rotational Relaxation of Coumarin 153 and 4-Aminophthalimide in a New Hydrophobic Ionic Liquid: Role of N−H. . .F Interaction on Solvation Dynamics. *Chem. Phys. Lett.* **2011**, *515*, 23−28.

(43) Das, S. K.; Sarkar, M. Solvation and Rotational Relaxation of Coumarin 153 in a New Hydrophobic Ionic Liquid: An Excitation Wavelength Dependence Study. *J. Lumin.* **2012**, *132*, 368−374.

(44) Das, S. K.; Sarkar, M. Rotational Dynamics of Coumarin-153 and 4-Aminophthalimide in 1-Ethyl-3-methylimidazolium Alkylsulfate Ionic Liquids: Effect of Alkyl Chain Length on the Rotational Dynamics. *J. Phys. Chem. B* **2012**, *116*, 194−202.

(45) Das, S. K.; Sahu, P. K.; Sarkar, M. Diffusion−Viscosity Decoupling in Solute Rotation and Solvent Relaxation of Coumarin153 in Ionic Liquids Containing Fluoroalkylphosphate (FAP) Anion: A Thermophysical and Photophysical Study. *J. Phys. Chem. B* **2013**, *117*, 636−647.

(46) Sahu, P. K.; Das, S. K.; Sarkar, M. Toward Understanding Solute−Solvent Interaction in Room-Temperature Mono- and Dicationic Ionic Liquids: A Combined Fluorescence Spectroscopy

and Mass Spectrometry Analysis. *J. Phys. Chem. B* **2014**, *118*, 1907−1915.

(47) Guo, J.; Han, K. S.; Mahurin, S. M.; Baker, G. A.; Hillesheim, P. C.; Dai, S.; Hagaman, E. W.; Shaw, R. W. Rotational and Translational Dynamics of Rhodamine 6G in a Pyrrolidinium Ionic Liquid: A Combined Time-Resolved Fluorescence Anisotropy Decay and NMR Study. *J. Phys. Chem. B* **2012**, *116*, 7883−7890.

(48) Guo, J.; Mahurin, S. M.; Baker, G. A.; Hillesheim, P. C.; Dai, S.; Shaw, R. W. Influence of Solute Charge and Pyrrolidinium Ionic Liquid Alkyl Chain Length on Probe Rotational Reorientation Dynamics. *J. Phys. Chem. B* **2014**, *118*, 1088−1096.

(49) Paul, A.; Samanta, A. Effect of Nonpolar Solvents on the Solute Rotation and Solvation Dynamics in an Imidazolium Ionic Liquid. *J. Phys. Chem. B* **2008**, *112*, 947−953.

(50) Liang, M.; Zhang, X.-X.; Kaintz, A.; Ernsting, N. P.; Maroncelli, M. Solvation Dynamics in a Prototypical Ionic Liquid + Dipolar Aprotic Liquid Mixture: 1-Butyl-3- methylimidazolium Tetrafluoroborate + Acetonitrile. *J. Phys. Chem. B* **2014**, *118*, 1340−1352.

(51) Prabhu, S. R.; Dutt, G. B. Rotational Diffusion of Nonpolar and Charged Solutes in Propylammonium Nitrate−Propylene Glycol Mixtures: Does the Organized Structure of the Ionic Liquid Influence Solute Rotation? *J. Phys. Chem. B* **2014**, *118*, 2738−2745.

(52) Prabhu, S. R.; Dutt, G. B. Rotational Diffusion of Organic Solutes in 1-Methyl-3- octylimidazolium Tetrafluoroborate−Diethylene Glycol Mixtures: Influence of Organic Solvent on the Organized Structure of the Ionic Liquid. *J. Phys. Chem. B* **2014**, *118*, 5562−5569.

(53) Barra, K. M.; Sabatini, R. P.; Zachery, P.; McAtee, Z. P.; Heitz, M. P. Solvation and Rotation Dynamics in the Trihexyl(tetradecyl)-phosphonium Chloride Ionic Liquid/Methanol Cosolvent System. *J. Phys. Chem. B* **2014**, *118*, 12979−12992.

(54) Lawler, C.; Fayer, M. D. The Influence of Lithium Cations on Dynamics and Structure of Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2014**, *117*, 9768−9774.

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

(56) 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.