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Rotational Dynamics of Nondipolar Probes in Butanols: Correlation of Reorientation Times with Solute−Solvent Interaction Strengths

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Rotational relaxation 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 four isomeric butanols as a function of temperature in order to find out how the rotation of the solute molecules is influenced by the solute−solvent interaction strength. It has been observed that the hydrogen bonding interactions with the butanols do not influence the rotation of DMDPP. On the other hand, the rotation of DPP is affected by its interactions with the solvents, and as a result the reorientation times of DPP have been found to be over a factor of 2 longer than that of DMDPP. Two sets of reorientation times have been obtained, one corresponding to DMDPP and the other to DPP, when the reorientation times of both probes were normalized by the solvent viscosities. The observed pattern is a consequence of almost identical interaction strengths between the four isomeric butanols and the given probes. These results indicate that the relative differences in the hydrogen bond donating abilities of the butanols do not manifest in the measured reorientation times of the solute molecules.

1. Introduction

Understanding molecular rotation in the condensed phase has been and will continue to be an intractable problem especially when the intermolecular forces that are operative between the rotating entity and its surroundings are of an attractive nature. In view of this prevailing situation, incessant efforts are needed from different perspectives to tackle this problem. Hence, it is only inevitable that a large volume of work on this subject matter has appeared in the literature.[1−3] Despite numerous investigations on this topic a number of issues still remain unresolved, in particular the ones concerning electrostatic interactions between the solute and the solvent. It has been well established that these electrostatic interactions significantly hinder the rotation of the solute molecule. Among the electrostatic interactions, dielectric friction[4−19] and solute−solvent hydrogen bonding[19−29] are the two known mechanisms by which the rotation of the solute gets impeded. However, it is debatable as to whether these two mechanisms are a manifestation of the same physical scenario. Recent experimental studies,[19,27,28] including some from our group, have modeled hydrogen bonding interactions between the solute and the solvent as dielectric friction since both of them are electrostatic in nature. On the other hand, molecular dynamics studies by Kurnikova et al.[22] have treated these two interactions as separate entities.

In an attempt to find some kind of unified portrayal of these two different mechanisms, recently we have adopted a dynamic approach to the hydrogen bonding interactions involving nondipolar solutes in dipolar solvents, and we could correlate the observed reorientation times with the solute−solvent interaction strengths.[29] Nevertheless, such an approach is not entirely novel and has been hypothesized previously in the case of dipolar solutes.[1] To accomplish the above-mentioned task, one needs to select the solvents judiciously in such a way that they are capable of forming hydrogen bonds with the solutes; it should also be ensured that the solute−solvent interaction strengths would be different. Moreover, these solvents should be of similar size since it is a well-known fact that the reorientation time of the solute is also influenced by the size of the solvent.[30,31] In our earlier work,[29] we selected ethanol (EtOH) and 2,2,2-trifluoroethanol (TFE) as solvents based on the fact that TFE is a better hydrogen bond donor compared to EtOH, due to the electron-withdrawing capacity of the three fluorine atoms on the second carbon atom. As a consequence, we have observed significant differences in the viscosity normalized reorientation times of the probe containing only carbonyl groups, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) in EtOH and TFE. However, in case of the probe possessing both carbonyl and secondary amino groups, 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP), the normalized reorientation times in both EtOH and TFE have been found to be identical. This result has been rationalized on the basis of simultaneous strengthening and weakening of the hydrogen bonds at the sites having carbonyl and amino groups of the probe DPP with the two solvents.

As mentioned earlier, there are significant differences in the hydrogen bond donating abilities of the two ethanols, and accordingly the normalized reorientation times of the two solutes in these solvents have also been influenced. However, the situation is not so pronounced in other solvent systems such as

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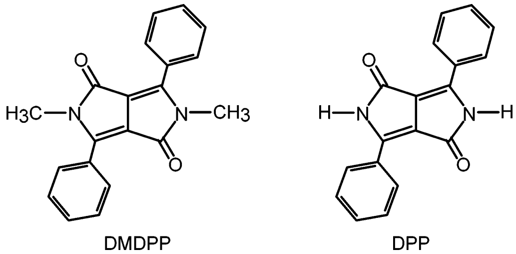

Figure 1. Molecular structures of the probes.

isomeric butanols, where the hydrogen bond donating capabilities of the butanols are determined by the relative positions of the alkyl groups on the carbon atom containing the hydroxyl group. It is not intuitively comprehensible whether such marginal differences in the hydrogen bond donating abilities of the butanols can have a profound influence on the rotation of the solute molecules dissolved in them. Nonetheless, a study carried out by Blanchard and Cihal[21] to understand the state dependent solvation effects on the rotational relaxation of oxazine 118 and resorufin in isomeric butanols at 300 K indicates that the differences in the viscosity normalized reorientation times of the cationic probe oxazine 118 with two amino groups in isomeric butanols are in the range of 30%−50%. However, such marked differences have not been observed in the case of anionic probe resorufin with two carbonyl groups. The results of the above-mentioned study point toward the fact that the relative position of the alkyl group on the carbon atom containing the hydroxyl group of a butanol does indeed have an influence on the rotation of the solute, which strongly interacts with the butanols. Whether this kind of effect is universal and will be observed in case of other hydrogen bonding solutes is not apparent. In other words, we are interested in finding out if the relative differences in the hydrogen bond donating abilities of these butanols can have an effect on the rotation of solute molecules with hydrogen bonding groups. In an attempt to address this issue, the present study has been undertaken and we hope to achieve our objective by following these steps. Temperature-dependent rotational relaxation of the two structurally similar solutes, DMDPP and DPP (see Figure 1 for their molecular structures), will be investigated in 1-butanol (1-BuOH), 2-butanol (2-BuOH), 2-methyl-1-propanol (2M1P), and 2-methyl-2-propanol (2M2P). The interaction strengths between the two solutes and the four solvents will be calculated using ab initio molecular orbital methods. The experimentally measured reorientation times of DMDPP and DPP in all four butanols will be normalized with respect to that of 1-BuOH, and the differences, if any, in the normalized reorientation times will be correlated with the solute−solvent interaction strengths. We believe that the outcome of this study will contribute to the understanding of molecular rotation in terms of the interaction strength between the solute and the solvent.

The outline of the paper is organized in the following sequence. Section 2 will briefly describe the experimental method involved in the measurement of rotational reorientation times. Ab initio molecular orbital methods employed in the calculation of the interaction strengths between the solutes and the solvents will be presented in section 3. The results will be presented and discussed in section 4, and the final section will summarize the conclusions of this study.

2. Experimental Section

The probes DMDPP and DPP are from Ciba Specialty Chemicals Inc. The solvents 1-BuOH and 2M2P are from Sisco Research Laboratories Pvt. Ltd., whereas 2-BuOH and 2M1P are from Aldrich and Sigma, respectively. 2M2P was dried with anhydrous potassium carbonate and was distilled. All other butanols are of the highest available purity and were used as such. The concentrations of the probes were maintained in the range of 10^{-5}−10^{-6} M.

Time-resolved fluorescence depolarization measurements were carried out using the time-correlated single-photon counting[32] facility at the Tata Institute of Fundamental Research, Mumbai, and details of the system have been described elsewhere.[24] In brief, the frequency-doubled output of a picosecond Ti:sapphire laser (Tsunami, Spectra Physics) was used as the excitation source and the probes DMDPP and DPP were excited at 460 nm with a vertically polarized pulse. The decay of the anisotropy, which was created by the preferential excitation, was monitored by measuring the fluorescence decays parallel $I_{\|}(t)$ and perpendicular $I_{\perp}(t)$ with respect to the polarization of the excitation source. Lifetimes were measured by collecting the fluorescence decays at the magic angle (54.7°) orientation of the emission polarizer. The emission in all three cases was monitored at 550 nm. For the parallel component of the decay, 10 000 peak counts were collected, and the perpendicular component of the decay was corrected for the G-factor of the spectrometer. The decays were collected in 512 channels with a time increment of 20 ps/channel. Each measurement was repeated at least two to three times, and the average values are reported. The measurements were performed in the range of 288−313 K, and only in the case of 2M2P the temperature range was 298−323 K. The desired sample temperature was achieved with the help of a temperature controller (Eurotherm).

The decays measured in this manner are convoluted with the instrument response function, which was measured by replacing the sample with a solution that scatters light. Lifetimes of the probes DMDPP and DPP in butanols were obtained from the fluorescence decays measured at magic angle polarization $I(t)$ and the instrument response function, by iterative reconvolution method using the Marquardt algorithm as described by Bevington.[33] Likewise, the anisotropy decay parameters were obtained by simultaneous fit[34,35] of parallel $I_{\|}(t)$ and perpendicular $I_{\perp}(t)$ components. The criteria for a good fit were judged by statistical parameters such as the reduced χ^2 being close to unity and the random distribution of the weighted residuals.

3. Computational Methods

Ab initio molecular orbital methods were used to determine the optimum structures of DMDPP and DPP solute molecules. The ground state global minimum geometries of both species were fully optimized at the Hartree−Fock level of theory with 6-31G* basis set. To study the effect of solvents, geometry optimizations were also performed for the DMDPP−1-BuOH, DMDPP−2-BuOH, DMDPP−2M1P, DMDPP−2M2P, DPP−1-BuOH, DPP−2-BuOH, DPP−2M1P, and DPP−2M2P solute−solvent complexes and for 1-BuOH, 2-BuOH, 2M1P, and 2M2P solvent molecules. With this basis set the total number of orbitals generated for each of the DMDPP−solvent and DPP−solvent complexes are 548 and 512, respectively. Using the ground state optimized geometries of the complexes, vertically excited singlet state calculations were performed using the configuration interaction (CI) method with single and double excitations (SDCI). However, with the present-day computer resources it is not possible to correlate all the valence electrons in the full valence CI space for the DMDPP or DPP complexes. In view of this, we have limited the CI calculations by taking 12 valence electrons and 12 orbitals for all the complexes, which resulted

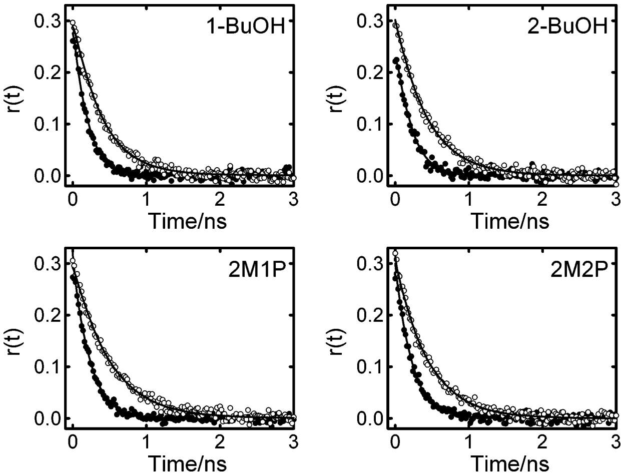

Figure 2. Anisotropy decays of DMDPP (●) and DPP (○) at 298 K in isomeric butanols. The smooth lines passing through them are the fitted ones to single-exponential functions.

TABLE 1: Rotational Reorientation Times (τ_r) of DMDPP and DPP in 1-Butanol as a Function of Temperature Together with the Solvent Viscosities[a]

		τ_r/ps	
temp/K	η^b/mPa s	DMDPP	DPP
288	3.38	218	483
293	2.98	205	427
298	2.61	165	372
303	2.29	154	346
313	1.79	128	264

[a] Uncertainties on the τ_r values are in the range of 5−8%. [b] Viscosity data from ref 41.

in 361 configurations for each complex. Solute−solvent interaction energy was calculated as the energy difference between the complex and the solute−solvent supermolecular species, where supermolecular species consists of solute and two solvent molecules placed 50 Å from the hydrogen bonding sites of the solute at their respective optimized geometries. All the calculations in this work were done using the GAMESS[36] electronic structure program.

TABLE 2: Rotational Reorientation Times (τ_r) of DMDPP and DPP in 2-Butanol as a Function of Temperature Together with the Solvent Viscosities[a]

		τ_r/ps	
temp/K	η^b/mPa s	DMDPP	DPP
288	4.21	263	604
293	3.68	211	479
298	3.04	182	405
303	2.53	158	355
313	1.80	121	250

[a] Uncertainties on the τ_r values are in the range of 5−8%. [b] Viscosity data from ref 41.

TABLE 3: Rotational Reorientation Times (τ_r) of DMDPP and DPP in 2-Methyl-1-propanol as a Function of Temperature Together with the Solvent Viscosities[a]

		τ_r/ps	
temp/K	η^b/mPa s	DMDPP	DPP
288	4.70	270	659
293	3.91	240	580
298	3.45	204	474
303	2.91	181	420
313	2.14	140	306

[a] Uncertainties on the τ_r values are in the range of 5−8%. [b] Viscosity data from ref 41.

TABLE 4: Rotational Reorientation Times (τ_r) of DMDPP and DPP in 2-Methyl-2-propanol as a Function of Temperature Together with the Solvent Viscosities[a]

		τ_r/ps	
temp/K	η^b/mPa s	DMDPP	DPP
298	4.42	297	661
303	3.35	237	513
308	2.63	194	422
313	2.08	167	351
323	1.40	112	232

[a] Uncertainties on the τ_r values are in the range of 5−8%. [b] Viscosity data from ref 41.

4. Results and Discussion

Fluorescence decays of both DMDPP and DPP in four butanols at all the temperatures could be adequately described by single-exponential functions with one lifetime τ_f. The τ_f values are around 6.8 and 5.8 ns for DMDPP and DPP, respectively, and are almost independent of the solvent used and the temperature at which they were measured. The decay of anisotropy also follows a single-exponential function for these two probes in butanols, and the decays at 298 K are displayed in Figure 2. The reorientation times obtained from the analysis of the anisotropy decays are given in Tables 1−4. The maximum uncertainty on the measured reorientation times is about 8%. A quick glance at the numbers in these tables reveals that the rotation of DPP is considerably slower than that of DMDPP, which is due to strong hydrogen bonding interactions between DPP and the butanols. This result is not startling considering the fact that it has been observed in a number of other solvent systems previously.[23−29] However, the central theme of this work is to investigate whether significant differences will be observed in the reorientation times of a given probe in different butanols and if they can be correlated with the solute−solvent interaction strengths. To accomplish this objective, the measured reorientation times will be compared with the well-established Stoke−Einstein−Debye (SED) hydrodynamic theory[1,2] and the magnitude of the deviations between the experimental and the theoretical numbers will be used to assess the influence of the specific interactions on the rotation of these solute molecules. According to the SED theory, the reorientation time τ_r of a solute molecule immersed in a continuum solvent of bulk viscosity η is given by

$$\tau_r = \frac{\eta V}{kT}(fC) \tag{1}$$

where V is the van der Waals volume of the solute molecule; f and C are the shape factor[37] and boundary condition parameter,[38] respectively. The shape factor is introduced to account for the nonspherical shape of the solute, and C is introduced to evaluate the extent of coupling between the solute and the solvent. For nonspherical solutes, $f > 1$ and the boundary condition parameter follows the inequality $0 < C \leq 1$. To model the systems investigated in the present study using the SED theory, the solute molecules were treated as asymmetric ellipsoids and their axial radii were measured with the aid of Corey−Pauling−Koltum scaled atomic models. Friction coefficients along the different symmetry axes were calculated from the axial ratios, and the diffusion coefficients were estimated from these friction coefficients using Einstein's relation.[39] From the diffusion coefficients, reorientation times were calculated using appropriate formulas. The details of the calculation have been presented in our earlier publication.[23]

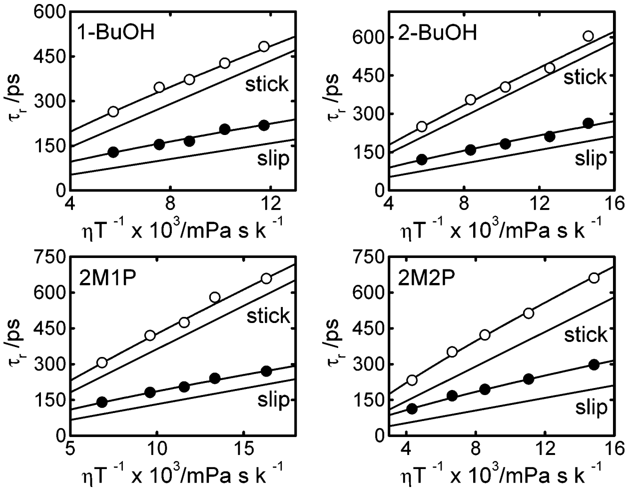

Figure 3. Plots of τ_r vs η/T for DMDPP (●) and DPP (○) in isomeric butanols. The solid lines through the experimental data points were obtained by fitting the data to nonlinear η/T relationships, and the functional forms are given in Table 5. Theoretically calculated lines with the SED model (“slip” for DMDPP and “stick” for DPP) are also shown in the figure.

TABLE 5: Relationship between τ_r and η/T Obtained from Logarithmic Fits of the Data in Four Butanols for DMDPP and DPP[a]

solvent	DMDPP	DPP
1-BuOH	$(33.1 \pm 5.8)(\eta/T)^{0.77\pm0.08}$	$(63.1 \pm 6.1)(\eta/T)^{0.82\pm0.04}$
2-BuOH	$(29.5 \pm 4.4)(\eta/T)^{0.80\pm0.06}$	$(51.3 \pm 7.6)(\eta/T)^{0.90\pm0.06}$
2M1P	$(31.6 \pm 3.1)(\eta/T)^{0.77\pm0.03}$	$(55.0 \pm 7.0)(\eta/T)^{0.89\pm0.05}$
2M2P	$(36.3 \pm 2.6)(\eta/T)^{0.78\pm0.03}$	$(69.2 \pm 4.9)(\eta/T)^{0.84\pm0.03}$

[a] In these expressions, the τ_r values are in ps and η/T in μPa s K^{-1}.

Figure 3 represents plots of τ_r vs η/T for DMDPP and DPP in the four isomeric butanols together with the theoretically calculated slip and stick lines. There is a linear relationship between τ_r and η/T for all the systems investigated. However, linear least-squares fit of the data resulted in positive intercepts in all the cases and such positive intercepts have been interpreted as free rotor times.[1,2] If these positive intercepts were due to the rotation of the solute in the inertial limit, then their magnitudes for a given solute molecule should have been identical in all the butanols. On the contrary, different values of the intercepts have been recovered for both DMDPP and DPP in the four butanols, thus ruling out the possibility that the positive intercepts are an indication of the free rotor times. In view of this prevailing situation, logarithmic fits of the data were performed and the resulting nonlinear τ_r vs η/T relationships have been presented in Table 5. However, it must be noted that these expressions must be considered as purely empirical as they are not based on any physical model.

It can be observed from the figure that the reorientation times of DMDPP and DPP in the four butanols are closer to the slip and stick limits, respectively. It is a well-known fact that, in the absence of specific interactions between the solute and the solvent, the reorientation times of medium-sized solute molecules such as the ones used in the present study are expected to be close to the slip limit. However, an exact match between theory and experiment is seldom found because of the inherent difficulties present in the calculation of the boundary condition parameter, which also depends on the size and free volume of the solvent.[30,31] On this basis, one can conclude that the specific interactions between the two carbonyl groups of DMDPP and the hydroxyl groups of butanols are not influencing its rotation, which can be further substantiated by the fact that the viscosity normalized reorientation times of DMDPP are almost identical in an alkane and alcohol of comparable size.[23] On the other hand, reorientation times of DPP are significantly longer than that of DMDPP, indicating that the specific interactions between the two secondary amino groups of the probe and the hydroxyl groups of the solvents are influencing its rotation.

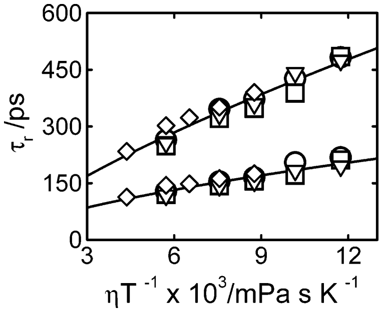

Figure 4. Comparison of the measured reorientation times of DMDPP and DPP in 1-BuOH (○), 2-BuOH (□), 2M1P (▽), and 2M2P (◇). The reorientation times in 2-BuOH, 2M1P, and 2M2P at each temperature were normalized to that of 1-BuOH by multiplying with the normalizing factors γ_1, γ_2, and γ_3, respectively, as described in the text. The lower set of data corresponds to DMDPP and the upper set to DPP. The reorientation times normalized in this manner can be scaled on a common curve for each probe. The two solid lines through the data points represent these curves, and their functional forms are given in the text.

Now the important issue that needs to be addressed is whether there is any difference in the rotation of DMDPP in the four butanols. Considering the fact that specific interactions do not play a role in its rotation, the viscosity normalized reorientation times of DMDPP in the four butanols are expected to be identical. To find out if it is indeed true, the reorientation times of DMDPP in 2-BuOH, 2M1P, and 2M2P measured at each temperature were normalized to that of 1-BuOH by multiplying them with the respective normalizing factors, $\gamma_1 = (\eta_{1-\mathrm{BuOH}}/\eta_{2-\mathrm{BuOH}})_T$, $\gamma_2 = (\eta_{1-\mathrm{BuOH}}/\eta_{2\mathrm{M1P}})_T$, and $\gamma_3 = (\eta_{1-\mathrm{BuOH}}/\eta_{2\mathrm{M2P}})_T$. The maximum difference observed in these normalized reorientation times at a particular temperature is about 20%, indicating that rotation of DMDPP is almost identical in all four butanols. The reorientation times normalized in this manner were plotted as a function of η/T in Figure 4. From the logarithmic fit of the normalized reorientation times vs η/T, it has been found that the rotation of the DMDPP in isomeric butanols can be described by the following empirical relation:

$$\tau_r = (42.7 \pm 5.2)\left(\frac{\eta}{T}\right)^{0.63\pm0.06} \qquad (N = 20, R = 0.936)$$

N and R are the number of data points and the regression coefficient, respectively. In view of the result obtained for DMDPP, it will be interesting to find out whether a similar relation can be attained for the rotation of DPP as well. By adopting the same procedure, we found that the normalized reorientation times of DPP at a given temperature in the four butanols do not vary by more than 20% as in the previous case. Figure 4 also displays the normalized reorientation times of DPP as a function of η/T for all the butanols. This exercise confirms that the rotation of DPP in all four butanols is identical despite being hindered by its interactions with them and the normalized reorientation times can be scaled on a common curve of the form given by

$$\tau_r = (74.1 \pm 7.2)\left(\frac{\eta}{T}\right)^{0.75\pm0.05} \qquad (N = 20, R = 0.968)$$

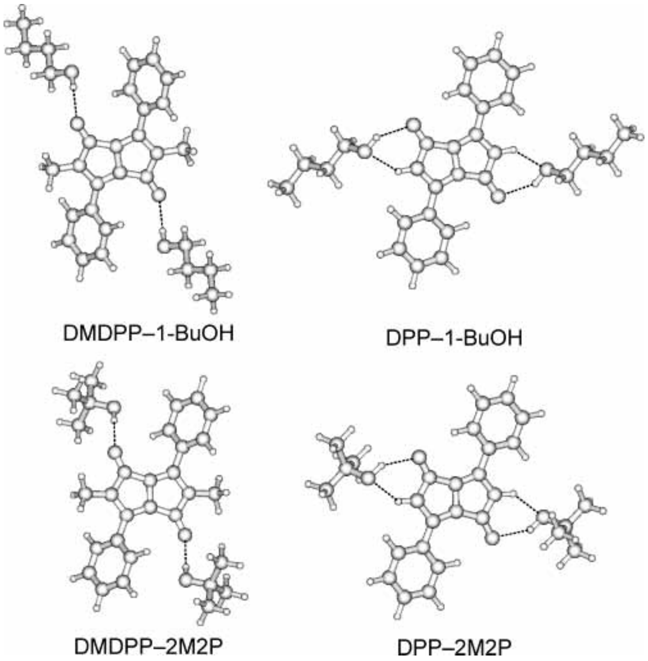

Figure 5. Optimized structures of the solute−solvent complexes obtained using the Hartree−Fock level of theory with 6-31G* basis set.

TABLE 6: Excited State Solute−Solvent Interaction Energies in kJ mol^{-1} Calculated Using ab Initio Molecular Orbital Theory

solvent	DMDPP	DPP
1-BuOH	64.1	88.3
2-BuOH	64.1	88.0
2M1P	64.7	88.4
2M2P	64.1	87.8
EtOH	64.3	85.1
TFE	76.6	81.2

The outcome of this analysis has resulted in two sets of normalized reorientation times: one corresponding to DMDPP and the other corresponding to DPP. For a given probe, however, the observed differences in the reorientation times in the four butanols are merely due to variation in their viscosities. This study establishes that, in the case of DMDPP, the interaction between the two carbonyl groups and the hydroxyl groups of the butanols are not strong enough to impede the rotation of the probe. On the other hand, the rotation of DPP is influenced by the interaction between the two NH groups and the hydroxyl groups of the solvents. The fact that a given probe is experiencing almost identical friction in the four isomeric butanols can be rationalized using the solute−solvent interaction strengths obtained with the help of ab initio molecular orbital methods. The optimized structures of DMDPP−1-BuOH, DMDPP−2M2P, DPP−1-BuOH, and DPP−2M2P solute−solvent complexes are presented in Figure 5. The interactions strengths for the eight solute−solvent complexes calculated as described in section 3 are given in Table 6. It is evident from the table that, as in the case of the reorientation times, two sets of interaction strengths have been obtained: one corresponding to DMDPP−butanols and the other corresponding to DPP−butanols. Since the lifetime of the solute−solvent hydrogen bonded complex is related to the interaction strength by an Arrhenius-type expression,[1] higher solute−solvent interaction strength results in longer reorientation times. However, it is not feasible to calculate the lifetimes of these solute−solvent complexes, as they are also a function of the frequency factor.

Despite this limitation, the experimentally measured reorientation times can be correlated with the theoretically calculated solute−solvent interaction strengths in a qualitative manner. It can be argued that calculation of solute−solvent interaction strength by considering only two solvent molecules per solute may be an oversimplification of a complex process like hydrogen bonding in solution. Nevertheless, the simplistic treatment of solute−solvent interactions adapted here taking into account only two solvent molecules per solute predicts the relative trends in the rotational behavior of DMDPP and DPP in isomeric butanols, at least qualitatively.

At this moment, it will be worthwhile to compare the results obtained in butanols to our earlier work in EtOH and TFE.[29] In the case of EtOH, the rotation of DMDPP and DPP is not influenced due to the specific interactions between carbonyl groups of the probes and hydroxyl group of the solvent, a result similar to the one observed in butanols. On the contrary, TFE, being a strong hydrogen bond donating solvent, could interact with the carbonyl groups of both DMDPP and DPP in such a manner that the rotation of both probes is affected. As a consequence, the viscosity normalized reorientation times of DMDPP in TFE have been found to be significantly longer than that in EtOH. However, in the case of DPP, the strong hydrogen bond donating ability of TFE rendered it to be a weak hydrogen bond acceptor, which resulted in the weakening of the hydrogen bonds at the two NH sites compared to EtOH. As a result, almost the same interaction strengths have been obtained for DPP−EtOH and DPP−TFE complexes, which is consistent with the experimental finding of indistinguishable normalized reorientation times of DPP in EtOH and TFE. The calculated interaction strengths between the two solutes and EtOH and TFE, which have been taken from our earlier work,[29] are also given in Table 6 for the sake of continuity. Butanols, however, could form strong hydrogen bonds only at the two NH groups of DPP, and therefore, its rotation is significantly affected compared to that of DMDPP. Moreover, the viscosity normalized reorientation times of DPP at a given temperature in all four butanols are almost identical. This observation is an indication that the relative positions of the alkyl groups on the carbon containing the hydroxyl group do not appear to be drastically influencing the hydrogen bond donating abilities of the butanols so that the rotational relaxation of the solute molecule is affected.

The findings of this work broach the question of whether there is any distinction in the hydrogen bond donating the abilities of the butanols at all. The answer is affirmative, which is evident from a somewhat similar but slightly different study by Cramer and Spears.[40] In their study, nonradiative intersystem crossing rates of an anionic probe rose bengal were obtained in a series of protic and aprotic solvents by measuring its fluorescence lifetimes. They could correlate the intersystem crossing rates with the strength of the interaction between rose bengal and the solvents. It has been conclusively demonstrated that 1-BuOH interacts more strongly with rose bengal than 2-BuOH and 2M2P as a consequence of its stronger hydrogen bond donating ability. However, such differences do not appear to be reflected in the measured reorientation times of the hydrogen bonding probe DPP in various butanols.

5. Conclusions

Our comprehension of molecular rotation in the condensed phase is based on the premise that the rotation of the solute molecule is influenced by specific interactions such as hydrogen bonding with its surroundings. Nonetheless, not much is understood as to how the energetics of these interactions govern the molecular rotation. With an intent to address this issue, rotational diffusion of two structurally similar nondipolar solutes, DMDPP and DPP, has been investigated in isomeric butanols. The important findings of this work are as follows. The interaction strength between the two carbonyl groups of DMDPP and the four butanols is not sufficient to impede the rotation of the probe. In contrast, the specific interactions between the two secondary amino groups of DPP and the hydroxyl groups of the solvents are strong enough to influence its rotation. It has been observed from the viscosity normalized reorientation times that all four isomeric butanols are interacting in an identical manner with a given probe, an outcome of which is reflected in the two sets of normalized reorientation times obtained, one corresponding to DMDPP and the other to DPP in the four butanols. Solute−solvent interaction strengths calculated using ab initio molecular orbital methods correlate with the experimentally observed trends in the reorientation times for all the systems investigated, albeit qualitatively.

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