Dynamics of 4-Benzylamino-7-nitrobenzofurazan in the 1-Propanol/Water Binary Solvent System. Evidence for Composition-Dependent Solvent Organization

Sarah A. Stevenson and G. J. Blanchard*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322

Received: December 3, 2005; In Final Form: January 19, 2006

We report on the fluorescence lifetime and rotational diffusion dynamics of 4-benzylamino-7-nitrobenzofurazan (BBD) in a series of 1-propanol/water binary solvent systems. The fluorescence lifetime of BBD increases monotonically with increasing 1-propanol concentration. The rotational diffusion dynamics of BBD also vary with solution 1-propanol content, but this variation is not monotonic. Comparison of the BBD rotational diffusion time constant to solution viscosity and 1-propanol composition reveals the presence of a solution composition dependence of solvent−solute interactions, with a relative decrease in solvent−solute interaction strength for solvent system compositions where the 1-propanol/water azeotrope is known to exist. These data point collectively to the existence of microscopic heterogeneity in these binary solvent systems.

Introduction

The interactions between dissimilar molecules in the solution phase have been the subject of a great deal of study because of the importance of such interactions in processes that include chemical separations, synthesis, and both heterogeneous and homogeneous catalysis. In all of this work, the common underlying issue that has been most difficult to address is the existence, persistence length, and characteristic time-scale of local heterogeneity. We have been investigating micellar systems[1−5] and have found that the composition of the solutions from which the micelles are formed can have an influence on the resulting micelles. In an effort to understand these effects and in a larger sense to determine whether solution-phase heterogeneity plays a role in the solutions that we use, we have studied the lifetime and motional dynamics of a chromophore dissolved in a series of 1-propanol/water binary solvent systems.

A variety of spectroscopic methods have been utilized to probe solution-phase systems, including vibrational relaxation,[6−16] fluorescence lifetime, and molecular reorientation measurements.[5,17−33] In this study, we have chosen to use time-resolved fluorescence lifetime and anisotropy measurements of 4-benzylamino-7-nitrobenzofurazan (BBD) because of the properties of this chromophore and the wide use of its structural derivatives in the study of micellar and lipid bilayer structures.[34−37] We study rotational diffusion due to the relatively high information content of the experimental data and the established theoretical framework that is available for interpretation of the data.[38−42] While the interpretation of fluorescence lifetime data is less straightforward and more system-dependent, for the chromophore that we use here, there is an established dependence of its fluorescence lifetime on the "polarity" of the local environment.[34−37] The chromophore that we have chosen for this work (BBD, Figure 1) is a member of a family of chromophores with the 7-nitrobenz-2-oxa-1,3-diazol-4-yl (NBD) group. These chromophores are known to exhibit absorption and emission band positions that are sensitive to solvent polarity, causing them to be used widely as fluorescent probes in biological and model membrane systems.[43−46] Shorter fluorescence lifetimes are observed with more polar solvents, making these probes well-suited for studies of binary solvent systems. We have investigated the 1-propanol/water solvent system to understand whether there is discernible local heterogeneity in this system. Our data show that there is indeed local heterogeneity in this binary solvent system and that the characteristic persistence time of this transient organization lies in the time window between the chromophore reorientation time (ca. 100 ps) and its fluorescence lifetime (several nanoseconds). Our reorientation data do not follow the simple viscosity dependence predicted by the Debye−Stokes−Einstein (DSE) model (vide infra), and the composition of the solvent system modulates the strength of solvent−solute interactions measurably. We find that for the 1-propanol/water binary system, there is a range of propanol concentrations for which the solvent−solvent interactions are strong enough to alter the chromophore interactions with the solvent system. The range of 1-propanol concentrations for which this occurs coincides with the concentration range for which 1-propanol and water are known to form an azeotrope. These findings shed new light on the heterogeneity of the local environment in binary solvent systems.

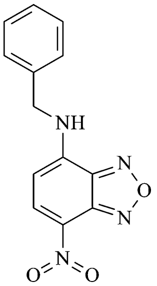

Figure 1. The structure of 4-benzylamino-7-nitrobenzylfurazan (BBD).

Experimental Section

Materials. 4-Bezylamino-7-nitrobenzofurazan (BBD) was obtained from Sigma-Aldrich, Inc. and used as received. 1-Propanol was acquired from CCI, Inc., and used as received. Water was distilled in house. The BBD concentration for all

---

* To whom correspondence should be addressed. E-mail: blanchard@chemistry.msu.edu.

10.1021/jp057039g CCC: $33.50

solutions was 10 μM. Solution temperatures were maintained at 298 ± 0.5 K (Neslab EX100-DD) for all time-resolved fluorescence lifetime and anisotropy measurements.

Time-Correlated Single-Photon-Counting Measurements. Fluorescence lifetime and anisotropy measurements of BBD in a series of 1-propanol/water solutions were made using a time-correlated single-photon-counting (TCSPC) instrument that has been described in detail previously,[47] and we recap only its salient features here. The source laser is a mode-locked CW Nd:YAG laser (Coherent Antares 76s), that produces 100 ps, 1064 nm pulses at a 76 MHz repetition rate. A Coherent 702-2 cavity-dumped dye laser is synchronously pumped using the third harmonic (355 nm) of the Nd:YAG laser. The dye laser produces 460 nm, 5 ps pulses at a 4 MHz repetition rate using Stilbene 420 laser dye (Exciton). Excitation power at the sample was ≤1 mW average power for all measurements. Fluorescence signals were detected using a Hamamatsu R3809U microchannel plate photomultiplier tube with a Tennelec 454 quad constant fraction discriminator and Tennelec 864 time-to-amplitude converter and biased amplifier for signal processing. The reference channel was delayed optically and detected using an in-house-built fiber optic delay line. Fluorescence was collected at 0°, 54.7°, and 90° with respect to the vertically polarized excitation pulse. Data were acquired, and the collection wavelength and polarization selector were computer-controlled using a program written with LabVIEW v. 7.1. Lifetimes range from ~800 to ~6000 ps, while an instrument response function of typically 35 ps fwhm is observed for this system. We did not deconvolute the instrument response function from the fluorescence transients.

Steady-State Spectroscopy. Absorption spectra were recorded with 1 nm spectral resolution using a Cary model 300 double-beam UV−visible absorption spectrometer. Spontaneous emission spectra were acquired with a Spex Fluorolog 3 spectrometer with both excitation and emission monochromators set to 3 nm resolution.

Semiempirical Calculations. The permanent dipole moment of BBD was calculated for the ground state (S_0) and first excited electronic state (S_1) using Hyperchem, v. 6.0, with PM-3 parametrization.[48]

Results and Discussion

We have been involved in the study of micellar systems using optical spectroscopic methods. Such studies require the incorporation of fluorescent molecules into micelles, a task that is not always straightforward. Owing to the typically limited solubility of fluorescent probe molecules in aqueous solutions, concentrated chromophore solutions made with an alcohol cosolvent are sometimes used. Even for a small amount of an alcohol in the micellar solution, there is a question of how the micelles are altered by its presence, and this is an issue that we have addressed experimentally.[4] In this work, we are concerned with the intrinsic solution-phase heterogeneity that attends binary 1-propanol/water solvent systems. If there is, in fact, detectable solution-phase heterogeneity in alcohol/water binary systems, such transient solution-phase organization could give rise to unexpected partitioning phenomena in multicomponent solutions in which micelles are formed. Our fluorescence lifetime and anisotropy measurements point to local heterogeneity with a characteristic persistence time on the subnanosecond time scale in 1-propanol/water solutions. We find that the 1-propanol/water system interacts with the chromophore BBD in a manner that depends sensitively on the composition of the solvent system with the nominally weakest BBD−solvent interactions occurring for solvent ratios close to those for which 1-propanol and water form an azeotrope.

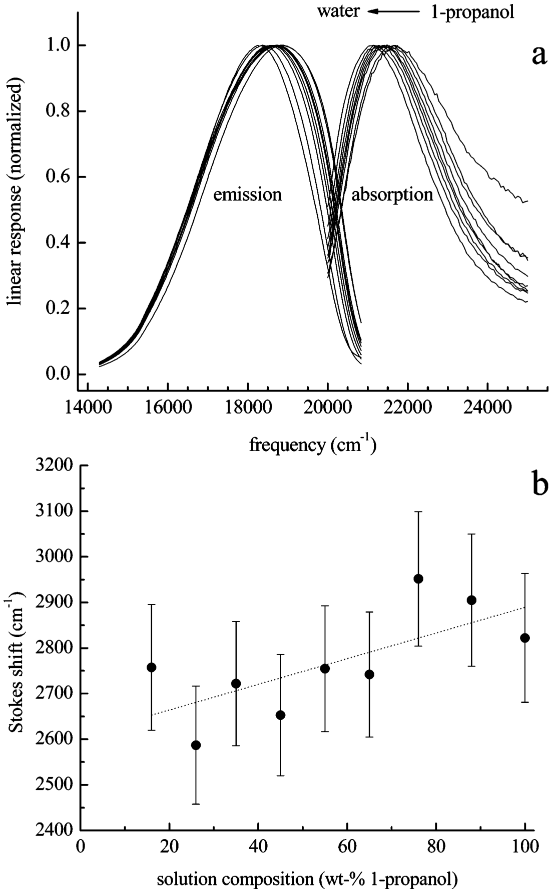

Figure 2. (a) Absorption and emission spectra of BBD as a function of 1-propanol/water solvent system composition. The absorption and emission spectra shift to shorter wavelength with increasing 1-propanol concentration. (b) The Stokes shift of BBD as a function of 1-propanol/water solvent system composition (5% error). The dashed line is a best-fit regression of the data, yielding a slope of 0.28 cm^{-1}/wt %.

Steady-State Spectroscopy. As a first step in the characterization of BBD in 1-propanol/water solvent systems, we consider the solvent dependence of the chromophore steady-state absorption and emission spectra (Figure 2). The absorption maximum of BBD is shifted to shorter wavelengths with increasing 1-propanol concentration. This is an expected result since it is known that as the polarity of the solution increases, the absorption maximum shifts to the red.[34−37] While the physical origin of the spectral band position dependence on solvent polarity remains to be elucidated for this chromophore, these steady-state data demonstrate that, on average, as the 1-propanol content of the solvent system is increased, the chromophore senses this change in a proportional manner. This is not a surprising result, owing to the expected transient nature of local organization in the solution phase, and these data are consistent with the fluorescence lifetime data (vide infra). Since the ground- and excited-state dipole moments are not being perturbed, the steady-state data can be thought of in the context of simple energy-level shifts.

Fluorescence Lifetime Measurements. Fluorescence lifetime data are useful for a variety of reasons. For some chromophores, such as BBD, the fluorescence lifetime is related to the polarity of the medium, analogous to the relationship seen for the BBD steady-state spectra and solvent polarity. To the best of our knowledge, there is not an adequate mechanistic explanation for the relationship between solvent properties and the spec-

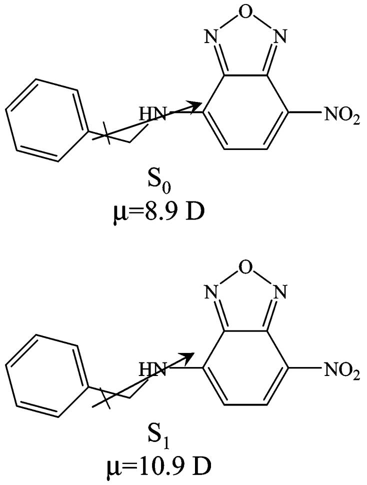

Figure 3. Permanent dipole moment magnitude and orientation for S_0 (top) and S_1 (bottom) BBD. These calculations were performed at the semiempirical level using a PM-3 parametrization. Note that the orientation of the permanent dipole moment changes little on excitation.

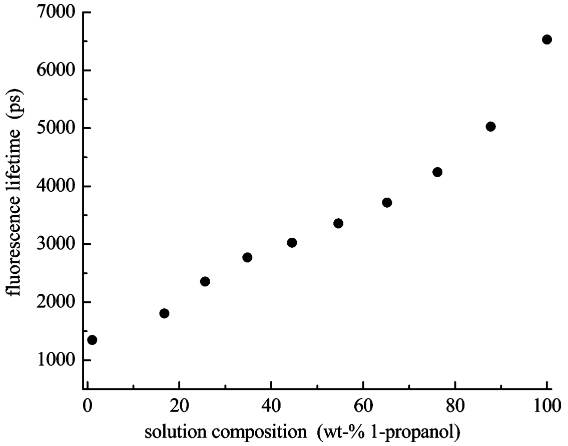

Figure 4. Fluorescence lifetime of BBD as a function of 1-propanol concentration.

troscopic response of BBD, but there are still several interesting points that can be discerned from these data.

For many solvatochromic chromophores, the Stokes shift and emission band positions are related to the ability of the solvent medium to preferentially stabilize the chromophore ground or excited electronic state. We observe for BBD that both the absorption and emission bands blue shift as the polarity of the solvent system is reduced, while the Stokes shift remains constant or at most increases negligibly with the change in solvent polarity (Figure 2b). These data suggest that both the S_0 and S_1 electronic states of this chromophore are relatively polar, the S_1 state being more polar than the S_0. Specifically, there appears not to be any site-specific solvent−solute interaction that gives rise to the preferential stabilization of either the S_1 or S_0 electronic states. This interpretation is supported by semiempirical calculations of BBD (Figure 3) indicating the S_0 dipole moment to be 8.9 D and the S_1 dipole moment to be 10.9 D. The finding of negligible change in the Stokes shift with variations in solvent system is important in the sense that we will not have to consider solvent-dependent changes in the reorientation dynamics of BBD associated with large-scale variations in the electron density distribution of the S_1.[30,31] The S_1 lifetime increases as the bulk polarity of the solvent decreases and, in all cases, decays as a single-exponential (Figure 4). Clearly the data we present here do not provide sufficient information to elucidate the basis for the dependence of the fluorescence lifetime on the solvent system polarity, but we do note that, even if there is discernible heterogeneity in the solvent system, this structural heterogeneity is effectively averaged over the lifetime of the S_1 state of BBD, thereby placing an upper bound on the persistence time of any solvent system transient organization (vide infra). With this information in hand, we turn to a discussion of the fluorescence anisotropy data.

Molecular Reorientation. For the systems under study here, fluorescence anisotropy transients are accounted for in the context of molecular rotational motion. We obtain fluorescence depolarization data experimentally by exciting BBD with a vertically polarized light pulse and collecting the emission decay transients polarized parallel and perpendicular to the excitation polarization. These data are combined to produce the induced orientational anisotropy function, $R(t)$,

$$R(t) = \frac{I_{\|}(t) - I_{\perp}(t)}{I_{\|}(t) + 2I_{\perp}(t)} \qquad (1)$$

where $I_{\|}$(t) and $I_{\perp}$(t) are the polarized emission intensities. The chemical information contained in these data resides in the decay time constant(s) of $R(t)$ and its zero-time value, $R(0)$. There is a well-established body of theory for the interpretation of $R(t)$.[38−42] In principle, $R(t)$ can decay with up to five exponential terms, but for most chromophores, Chuang and Eisenthal's theory[38] reduces to either one or two exponential decay components, depending on the shape of the ellipsoid swept out by the rotating moiety and the orientation of the chromophore transition dipole moments relative to the rotational motion axes. Experimentally, the most common result is the recovery of a single exponential decay component in $R(t)$, and that is the functional form of the data we have acquired for BBD in 1-propanol/water. The functional form of $R(t)$ allows the interpretation of our data within the framework of the modified Debye−Stokes−Einstein model.

The modified Debye−Stokes−Einstein (DSE) equation is given by eq 2[39,40]

$$\tau_{\mathrm{or}} = \frac{\eta V f}{k_{\mathrm{B}} T S} \qquad (2)$$

where η is the solvent bulk viscosity, V is the solute hydrodynamic volume,[49] T is the temperature, k_B is the Boltzmann constant, f is the frictional interaction term,[41] and S is the solute molecular shape factor.[40] The DSE model is limited in the sense that it does not account for the molecular nature of the solvent, yet for many systems, it provides remarkably close agreement with experimental data. The success of this model lies in the fact that the recovered time constant averages over the many fast molecular interactions that are collectively responsible for solvation. It is only when the characteristic time constant for the molecular solvent−solute interactions becomes on the order of the reorientation time constant that one observes a substantial contribution from discrete intermolecular interactions. When experimental values diverge from the modified DSE model predictions, the discrepancy between experiment and model is typically attributed to deviations in the solvent viscosity, solute hydrodynamic volume, frictional boundary condition, or solute shape factor. Given the experimental information available in most cases, it is not possible to clearly distinguish which of these quantities accounts for observed behavior. Solvent−solute interactions dominated by frictional interactions or a discrepancy between the microscopic and bulk solvent viscosity usually are taken to account for deviations in the trends predicted by DSE, whereas nonmonotonic variations in τ_{or} with solvent system

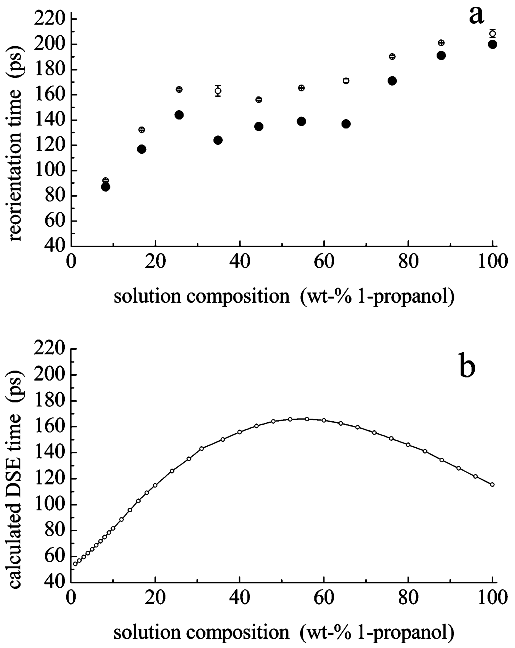

Figure 5. (a) Fluorescence anisotropy decay times (○) as a function of solution 1-propanol concentration and the calculated model times (●) from Table 1 for comparison to the experimental data. Error bars are indicated on individual data points and are the result of at least six individual determinations of each point. (b) Calculated DSE reorientation time for BBD in 1-propanol/water as a function of solvent composition. The curvilinear dependence on 1-propanol concentration reflects variations in the solution bulk viscosity as a function of 1-propanol concentration.[55−57]

properties such as composition or bulk viscosity typically imply an important role for molecular-scale processes. The shape of the volume swept out by the probe molecule during reorientation is, in general, ellipsoidal and is described by Perrin's equations.[40] In many cases, especially where single-exponential anisotropy decays are recovered experimentally, the actual volume swept out by the reorienting moiety is not simply that of the probe molecule. The hydrodynamic volume of the reorienting moiety can deviate from model predictions due to preferential, relatively long-lived solvent−solute interactions (e.g., H-bonding), and there have been several accounts of such behavior in binary solvent systems.[50−54]

We recover single-exponential anisotropy decays for BBD in all 1-propanol/water solvent systems. Our data are consistent with BBD reorienting as a prolate rotor, assuming the $S_1 \leftarrow S_0$ transition moment lies in the chromophore π-system plane along the long axis. We recognize that the orientation of the transition dipole moment may deviate slightly from this geometric axis due to the asymmetric substitution of the chromophore six-membered ring, but such an effect does not bear on the substance of our findings. We calculate the hydrodynamic volume of BBD to be 215 Å^3,[49] $T = 300$ K, and $f = 1$ (stick limit). We have not reported a value for S because of the uncertainty in the volume swept out by the reorienting chromophore because of the bulky amino-methylphenyl substituent. On the basis of these quantities and using eq 2, we calculate $\tau_{or}/\eta = 51.9$ ps/cP in the stick limit. We show in Figure 5a (open circles) the dependence of the experimental reorientation time on the solvent system composition. These data do not follow a trend that is monotonic with respect to the solvent system bulk composition, and it is this point that requires a more detailed treatment.

As noted above, trends in reorientation data that scale linearly with solution viscosity can indicate molecular motion being mediated by processes that are averaged over a large number of molecular-scale events. To address whether the reorientation data that we report here do, in fact, vary monotonically with solvent viscosity, we must understand how the viscosity of the 1-propanol/water system depends on composition. These data have been tabulated in the literature,[55−57] and there is a nonlinear dependence of solution viscosity on solution composition. Using the DSE model parameters given above and the literature data on 1-propanol/water viscosity, we show the calculated τ_{or} times in Figure 5b. Clearly the calculated results do not agree well with the experimental data. At high 1-propanol concentrations, the experimental τ_{or} values are much larger than the calculated values, and for 1-propanol concentrations in the region of 30%, there is an anomalous spike in the experimental reorientation data which is not reflected in the calculations. The experimental reorientation data cannot be understood wholly in the context of solvent properties, and the physicochemical phenomena that give rise to these data operate on a time scale commensurate with the measured anisotropy decay time(s).

TABLE 1: Solvent Association Calculations for $V = V_{probe} + nV_{solvent}$[a]

wt % propanol	V (calcd from exptl data)	n	V ($V_{BBD} + nV_{PrOH}$)	τ_{or} calcd (ps)	τ_{or} exptl (ps)
100	388	3	425	200	209 ± 3
88	321	2	355	191	201 ± 1
76	271	1	285	171	190 ± 1
65	227	0	215	137	171 ± 2
55	214	0	215	139	166 ± 1
45	208	0	215	135	156 ± 1
35	236	0	215	124	163 ± 4
26	272	1	285	144	164 ± 1
17	270	1	285	117	132 ± 1
8	261	1	285	87	92 ± 1

[a] Values of V calculated from experimental τ_{or} times are shown in the second column, and from these data we can estimate the number of 1-propanol molecules that reorient with the BBD chromophore. From this estimate of n and experimental viscosity data (from refs 55−57), we calculate a model τ_{or}.

As noted above, the hydrodynamic volume of BBD is calculated to be 215 Å^3 using Edward's model.[49] This model is well established and yields results that are consistent with the reorientation dynamics of many chromophores in neat solvents. The experimental, nonmonotonic deviations from the DSE model predictions are not associated with the calculated volume of BBD, but the total volume of the reorienting moiety can vary with solution composition. It is possible that one or more solvent molecules (presumably propanol) are associated with the probe molecule, yielding a reorienting species that has a larger hydrodynamic volume than that of the chromophore alone. In this case, we describe $V = V_{BBD} + nV_{solvent}$, where V is the total hydrodynamic volume of the reorienting entity, $V_{BBD} = 215$ Å^3, $V_{solvent}$ is the hydrodynamic volume of a solvent (1-propanol) molecule, and n is the number of solvent molecules that are closely associated with BBD. Using Edward's method, we calculate $V_{solvent} = 70$ Å^3 for 1-propanol, and within the context of this explanation, the added solvent volume required for consistency of the model with the data is $n = 1$ for low 1-propanol concentrations, reducing to no added solvent volume for solution compositions where 1-propanol and water are known to form an azeotrope, and then increasing to a high value of $n = 3$ at the highest 1-propanol concentrations (see Table 1). We note that the agreement between this model and the experimental data is not exact, but there is excellent qualitative agreement (Figure 5a, solid circles). We believe that the discrepancies between model and data lie in the fact that we have assumed simplistically that a solvent is either interacting strongly enough to reorient with the BBD chromophore or not. This assumption can be re-expressed in terms of the average lifetime of the solvent−solute interactions, where we assume that the 1-propanol−BBD interaction persists for a time interval that is longer, on average, than the anisotropy decay time of the reorienting moiety. If this is not the case, then we would expect in this model to recover solvent-related "additional volume" that would be a fraction of whole solvent molecule(s), and indeed, if we were to invoke this parameter, we could achieve better correspondence between experiment and model. We do not have any experimental information, however, on the lifetime of the 1-propanol−BBD interaction, so we do not feel justified in pushing the model this far. It is also possible that our model is simply offset in its predictions due to a slight, systematic underestimation of V (e.g., failure to account for any water that is bound tightly to the chromophore over all 1-propanol concentrations). The fact that we observe such agreement with the functional form of the data over the entire range of solvent composition suggests that this model is fundamentally correct.

It is not surprising, in our view, to find that there exist strong solvent−solute interactions between BBD and 1-propanol. What is interesting is that our data are consistent with the extent of solvent−solute interactions varying in a nonmonotonic manner with solvent system composition. This finding implies that over a significant composition range for the 1-propanol/water system, the interactions between water and 1-propanol are sufficiently strong to preclude 1-propanol interacting strongly with the BBD chromophore. We note that the formation of an azeotrope for a binary solvent system implies significant interactions between the two solvents, and for 1-propanol and water, the azeotrope-forming composition range lies between 28 and 70 wt % 1-propanol. In this solvent system composition range, it is possible that the most stable solvent configuration(s) are those for which 1-propanol and water are interacting more strongly with themselves than with BBD. In concentration regions away from where an azeotrope forms, the individual solvent molecules could, in principle, interact more strongly with BBD.

The above explanation is phenomenologically consistent with our experimental data, but it cannot provide more detail, based in part on the dearth of molecular-scale information extant on the nature of azeotrope(s) between 1-propanol and water. While there is some excellent recent work on the calculation of solvent−"solute" interactions that combine molecular mechanics and quantum mechanical approaches,[58−60] these calculations do not appear to provide insight into the 1-propanol/water system we have focused on in this work. It appears that the strength of interactions between BBD and the 1-propanol/water system are closely matched with 1-propanol/water interactions, and that in all cases these interactions must persist over a time scale that is consistent with hydrogen bond formation and breakage. Regardless of the inability to provide a detailed picture of the solvation dynamics of BBD in the 1-propanol/water system, it is clear that, depending on the amount of alcohol present in solution, there can be significant intermolecular interactions between chromophores and solvents, and these interactions can, in principle, have some influence on the formation of micelles.

Conclusions

We have examined the fluorescence lifetime and rotational diffusion dynamics of BBD in the 1-propanol/water solvent system. The increase of the fluorescence lifetime of BBD with increasing 1-propanol concentration is fully consistent with the known behavior of chromophores containing an NBD group and indicates that the persistence time of any local organization is less than nanoseconds. Modeling the reorientation behavior of BBD in the context of the modified DSE model indicates that, for higher concentrations of 1-propanol, the experimental anisotropy decay times are significantly longer than expected. Because of the nonmonotonic nature of the reorientation data, we understand this anomalous behavior in the context of strong, associative solvent−solute interactions, the persistence time of the interactions being on the order of the measured reorientation time. While strong solvent−solute association has been seen before,[5,24−26] this is a particularly pronounced example of solvent-composition-dependent interactions, and we note that the solvent−solute interactions are weakest in the 1-propanol concentration regime where azeotropes are formed with water. It is clear that in the 1-propanol/water solvent system, there is discernible microscopic solvent heterogeneity, the details of this transient solution-phase structure depending sensitively on the composition of the solvent system.

Acknowledgment. We are grateful to the National Science Foundation for support of this work through Grant 0445492.

References and Notes

(1) DelaCruz, J. L.; Blanchard, G. J. *J. Phys. Chem. B* **2003**, *107*, 7102.

(2) Kelepouris, L.; Blanchard, G. J. *J. Phys. Chem. B* **2002**, *106*, 6600.

(3) Kelepouris, L.; Blanchard, G. J. *J. Phys. Chem. B* **2003**, *107*, 1079.

(4) Stevenson, S. A.; Blanchard, G. J., manuscript in preparation.

(5) Dela Cruz, J. L.; Blanchard, G. J. *J. Phys. Chem. A* **2001**, *105*, 9328.

(6) Goldie, S. N.; Blanchard, G. J. *J. Phys. Chem. A* **2001**, *105*, 6785.

(7) Goldie, S. N.; Blanchard, G. J. *J. Phys. Chem. A* **1999**, *103*, 999.

(8) Jiang, Y.; Blanchard, G. J. *J. Phys. Chem.* **1994**, *98*, 9411.

(9) Jiang, Y.; Blanchard, G. J. *J. Phys. Chem.* **1995**, *99*, 7904.

(10) Heilweil, E. J.; Casassa, M. P.; Cavanagh, R. R.; Stephenson, J. C. *Annu. Rev. Phys. Chem.* **1989**, *40*, 143.

(11) Heilweil, E. J.; Cavanagh, R. R.; Stephenson, J. C. *Chem. Phys. Lett.* **1987**, *134*, 181.

(12) Casassa, M. P.; Heilweil, E. J.; Stephenson, J. C.; Cavanagh, R. R. *J. Chem. Phys.* **1986**, *84*, 2361.

(13) Cavanagh, R. R.; Heilweil, E. J.; Stephenson, J. C. *J. Electron Spectrosc. Relat. Phenom.* **1987**, *45*, 31.

(14) McCarthy, P. K.; Blanchard, G. J. *J. Phys. Chem.* **1995**, *99*, 17748.

(15) McCarthy, P. K.; Blanchard, G. J. *J. Phys. Chem.* **1996**, *100*, 5182.

(16) McCarthy, P. K.; Blanchard, G. J. *J. Phys. Chem.* **1996**, *100*, 14592.

(17) Millar, D. P.; Shah, R.; Zewail, A. H. *Chem. Phys. Lett.* **1979**, *66*, 435.

(18) Fleming, G. R.; Morris, J. M.; Robinson, G. W. *Chem. Phys.* **1976**, *17*, 91.

(19) Pauls, S. W.; Hedstrom, J. F.; Johnson, C. K. *Chem. Phys.* **1998**, *237*, 205.

(20) Truong, T. V.; Shen, Y. R. *J. Chem. Phys.* **2005**, *122*, 091104/1.

(21) Balabai, N.; Sukharevsky, A.; Read, I.; Strazisar, B.; Kurnikova, M.; Hartman, R. S.; Coalson, R. D.; Waldeck, D. H. *J. Mol. Liq.* **1998**, *77*, 37.

(22) Hartman, R. S.; Konitsky, W. M.; Waldeck, D. H. *J. Am. Chem. Soc.* **1993**, *115*, 9692.

(23) Sanders, M. J.; Wirth, M. J. *Chem. Phys. Lett.* **1983**, *101*, 361.

(24) Mukherjee, A.; Bagchi, B. *PhysChemComm* **2003**, 28.

(25) Von Jena, A.; Lessing, H. E. *Chem. Phys. Lett.* **1981**, *78*, 187.

(26) Dela Cruz, J. L.; Blanchard, G. J. *J. Phys. Chem. A* **2002**, *106*, 10718.

(27) Srinivas, G.; Bhattacharyya, S.; Bagchi, B. *J. Chem. Phys.* **1999**, *110*, 4477.

(28) Labhart, H.; Pantke, E. R. *Chem. Phys. Lett.* **1973**, *23*, 482.

(29) Blanchard, G. J. *J. Chem. Phys.* **1987**, *87*, 6802.

(30) Blanchard, G. J. *J. Phys. Chem.* **1988**, *92*, 6303.

(31) Blanchard, G. J. *Anal. Chem.* **1989**, *61*, 2394.

(32) Blanchard, G. J.; Wirth, M. J. *J. Phys. Chem.* **1986**, *90*, 2521.

(33) Templeton, E. F. G.; Quitevis, E. L.; Kenney-Wallace, G. A. *J. Phys. Chem.* **1985**, *89*, 3238.

(34) Chattopadhyay, A.; Mukherjee, S. *J. Phys. Chem. B* **1999**, *103*, 8180.

(35) Keller, S. L.; Radhakrishnan, A.; McConnell, H. M. *J. Phys. Chem. B* **2000**, *104*, 7522.

(36) Mukherjee, S.; Chattopadhyay, A. *Biochemistry* **1996**, *35*, 1311.

(37) Rukmini, R.; Rawat, S. S.; Biswas, S. C.; Chattopadhyay, A. *Biophys. J.* **2001**, *81*, 2122.

(38) Chuang, T. J.; Eisenthal, K. B. *J. Chem. Phys.* **1972**, *57*, 5094.

(39) Debye, P. *Polar Molecules*; Chemical Catalog Co.: New York, 1929.

(40) Perrin, F. *J. Phys. Radium* **1936**, *7*, 1.

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

(42) Zwanzig, R.; Harrison, A. K. *J. Chem. Phys.* **1985**, *83*, 5861.

(43) Fery-Forgues, S.; Fayet, J.-P.; Lopez, A. *J. Photochem. Photobiol., A: Chem.* **1993**, *70*, 229.

(44) Lin, S.; Struve, W. S. *Photochem. Photobiol.* **1991**, *54*, 361.

(45) Mukherjee, S.; Chattopadhyay, A. *J. Fluoresc.* **1995**, *5*, 237.

(46) Mukherjee, S.; Chattopadhyay, A.; Samanta, A.; Soujanya, T. *J. Phys. Chem.* **1994**, *98*, 2809.

(47) DeWitt, L.; Blanchard, G. J.; LeGoff, E.; Benz, M. E.; Liao, J. H.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 12158.

(48) Froimowitz, M. *BioTechniques* **1993**, *14*, 1010.

(49) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261.

(50) Bhattacharyya, S.; Bagchi, B. *J. Chem. Phys.* **2001**, *115*, 9065.

(51) Dutt, G. B.; Doraiswamy; Periasamy, N. *J. Chem. Phys.* **1991**, *94*, 5360.

(52) Alavi, D. S.; Waldeck, D. H. *J. Phys. Chem.* **1991**, *95*, 4848.

(53) Mukherjee, A.; Bagchi, B. *J. Phys. Chem. B* **2001**, *105*, 9581.

(54) Beddard, G. S.; Doust, T.; Hudales, J. *Nature (London)* **1981**, *294*, 145.

(55) *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1980−1981.

(56) Mikhail, S. Z.; Kimel, W. R. *J. Chem. Eng. Data* **1963**, *8*, 323.

(57) Wensink, E. J. W.; Hoffmann, A. C.; van Maaren, P. J.; van der Spoel, D. *J. Chem. Phys.* **2003**, *119*, 7308.

(58) Cubero, E.; Luque, F. J.; Orozco, M.; Gao, J. *J. Phys. Chem. B* **2003**, *107*, 1664.

(59) Cummins, P. L.; Gready, J. E. *J. Comput. Chem.* **1997**, *18*, 1496.

(60) Zheng, Y.; Roberts, J. A. *J. Phys.: Condens. Matter* **1996**, *8*, 8089.