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Role of Probe Molecule Structure in Sensing Solution Phase Interactions in Ternary Systems

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We report on the use of 1-pyrenebutyric acid (PBA) as a probe molecule to investigate aggregation phenomena in aqueous adipic acid solutions. Key issues in understanding solution phase aggregation phenomena are the length scale and the persistence time of the aggregates. We have chosen PBA to understand the characteristic length scale and role of probe molecule structure in the examination of solution phase aggregation phenomena. The steady-state emission response of PBA in adipic acid solutions yields little information because the carboxylic acid functionality of this probe molecule is not conjugated with the pyrene chromophore. Fluorescence lifetimes for PBA vary in a regular manner in the region of adipic acid saturation, suggesting that the chromophore is not in close spatial proximity to precrystalline aggregates that are known to form in these solutions. Rotational diffusion measurements of PBA reveal the presence of adipic acid aggregates in solution but, because of the length of the tether between the chromophore and the carboxylic acid functionality, the ability to resolve distinct intermolecular interactions is limited. This work points to the importance of close coupling between the chromophore and incorporating functionality for such measurements.

Introduction

Achieving an understanding of intermolecular interactions in the solution phase has been an active area of research for at least the past three decades.[1−22] The reason for this activity is that many chemical reactions and separation processes are carried out in solution and achieving predictability over intermolecular interactions would allow for less empiricism in these important areas. To date, the primary approach to the examination of solution phase intermolecular interactions has been to use the transient and/or steady-state optical response of chromophores present in low concentration in neat liquids. There have been many models devised to understand data on such systems and one conclusion of this body of work is that the nature of solvent−solute interactions can depend sensitively on the identities of both the solvent and solute molecules.

The probe molecule approach to understanding intermolecular interactions has proven to be useful not only for neat liquids but also for ternary systems where the third component can be either freely soluble in the solvent or present as a crystallizing moiety. Crystallization is an important industrial process for the separation and purification of many compounds, and achieving a molecular understanding of this process could put such efforts on a solid chemical and physical footing. For any ternary system, and for systems that can exhibit spontaneous phase separation in particular, a central issue is the local environment of the probe molecule. Most ternary liquid phase systems are heterogeneous on some length and time scale and the location of the probe molecule relative to these local inhomogeneities determines the information content of the experiment. It has been shown by the Berglund group that, for systems where the probe molecule is structurally distinct from the crystallizing moiety, the probe does not sense precrystalline aggregation effects efficiently.[23] Recent work by the Berglund and Blanchard groups has shown the utility of a "lock-and-key" approach to the study of crystallization, where the optically accessible probe molecule possesses a pendant functionality capable of incorporation into aggregates of the crystallizing moiety.[23−27]

The foci of the work we present here are to understand the role of probe molecule structure in "lock-and-key" investigations of precrystalline aggregate formation and to explore the relevant length scale over which the probe is sensitive to solution phase aggregation phenomena. Because of participation in local organization events, certain probe molecules exhibit changes in their optical responses that can be related to associative molecular interactions preceding crystallization. Recent work in our laboratories has demonstrated the utility of lock-and-key probes for interrogation of molecular interactions within different chemical systems.[27] Glycosyl resorufin[26] and 1-pyrenecarboxylic acid (PCA)[27] have been used to probe solution phase aggregation in aqueous glucose and adipic acid solutions, respectively. Studies of both systems demonstrate selective incorporation of the probe molecules into precrystalline aggregates and the ability of those probe molecules to provide structural information on the aggregates. Measurements of adipic acid solution phase aggregation using PCA as a probe have yielded considerable structural information, showing stepwise formation of solute oligomers with increasing adipic acid concentration. In that work, the probe molecule is in close spatial

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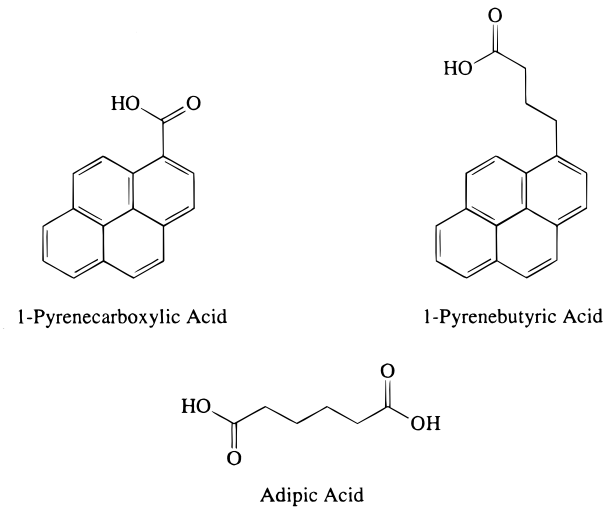

Figure 1. Structures of 1-pyrenecarboxylic acid (HPCA), 1-pyrenebutyric acid (HPBA), and adipic acid.

proximity to the adipic acid aggregates and thus the sensitivity of the probe optical response to solution phase local organization is high. Results from those experiments have raised a number of fundamental issues, such as the effect of probe molecule structure and the proximity of the chromophore to the aggregation event. To address these issues, we have measured steady-state and time-resolved optical properties of a similar probe molecule, 1-pyrenebutryic acid (PBA, Figure 1), in aqueous adipic acid solutions spanning concentrations from subsaturation to supersaturation. By changing the spacing between the functionalities in the probe molecule responsible for incorporation and optical response, we hope to elucidate the significance of chromophore proximity in reporting aggregation phenomena. For our experiments, PBA is present at the level of trace impurity (0.5 ppm, $\sim 10^{-7}$ M), a concentration low enough to likely avoid perturbations to the aqueous adipic acid system. The steady state emission spectra of PBA sense its local environment averaged over the fluorescence lifetime and we find the emission spectrum of this molecule to be largely independent of the protonation status of its carboxylic acid functionality and of changes in solution adipic acid concentration. The time domain response of PBA is sensitive to adipic acid concentration but we do not observe any discontinuous changes in lifetime with the onset of solute aggregation.[27] Measurement of the rotational diffusion dynamics of PBA in these systems provides insight into adipic acid self-association and, when compared to the response of 1-pyrenecarboxylic acid (PCA), sheds light on the length scale over which the probe chromophore is sensitive to local organization about its side group functionality. The key piece of information gained from this work is that the persistence length of solution-phase aggregation phenomena appears to be shorter than the C_4 tether between the incorporating functionality and the chromophore, despite the fact that adipic acid is a C_6 dicarboxylic acid. While the relative insensitivity of the probe molecule PBA to local organization would not be a surprising result for large systems such as biological membranes, it is not clear that this same intuitive understanding would apply to highly dynamic solution phase systems. Our data make this connection.

Experimental Section

Chemicals. Adipic acid (99%) was obtained from Aldrich and used as received. All solutions were prepared using Aldrich HPLC grade water. 1-Pyrenebutyric acid (PBA, 97%) was purchased from Aldrich and used without further purification. PBA was judged to be pure by the existence of a single band in thin layer chromatograms generated using several different solvent systems. The fluorescence lifetime of PBA in distilled water exhibited a single-exponential decay (vide infra).

Steady-State Fluorescence Measurements. Steady-state emission spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer using a 5 nm band-pass for both excitation and emission monochromators. The concentration of PBA in all solutions was 0.5 ppm ($\sim 1.0 \times 10^{-7}$ M). This concentration was sufficiently low to preclude aggregation or self-absorption effects.

Time-Correlated Single Photon Counting (TCSPC) Spectrometer. The time correlated single photon counting spectrometer used to measure fluorescence lifetimes and rotational diffusion time constants has been described in detail elsewhere,[28] and we provide only a brief outline of its salient features here. The light pulses used to excite the sample are generated with a cavity-dumped, synchronously pumped dye laser (Coherent 702-2) excited by the second harmonic output of a CW mode-locked Nd:YAG laser (Quantronix 416). Samples were excited at 323 nm (Kiton Red, Exciton, with Type I $LiIO_3$ SHG). The pulse repetition rate for these measurements was set to 1 MHz. PBA emission was monitored at 390 nm using a 10 nm band-pass. For lifetime and reorientation measurements, the sample cuvette was placed in a temperature-controlled brass block cell holder maintained at 293.0 $\pm$ 0.5 K (Neslab EX-221). For the fluorescence lifetime experiments, all solutions were subjected to at least three freeze−pump−thaw cycles to remove dissolved oxygen and emission was collected over all polarization angles to avoid contributions to the spectral dynamics due to reorientation of probe molecules. While this method of data collection can, in principle, lead to small deviations from data collected only at the magic angle, we observe exact agreement between the two methods for our experimental conditions.[29,30] Rotational diffusion measurements were made by collecting emission at polarizations parallel and perpendicular to the incident (vertical) electric field polarization. Fluorescence depolarization data were recorded using a 5 ns time window with 1024 resolution elements, corresponding to 4.88 ps/element. For each polarization collected, no less than 1000 counts were collected at maximum intensity. Anisotropy decays and fluorescence lifetimes were fit to a single-exponential beginning where the instrumental response function had decreased to at least 5% of its maximum value. Typically, the instrument response function for this system is $\sim$35 ps fwhm and the lifetimes measured range from 120 to 150 ns. Deconvolution of the response function from the experimental data was not required. For the reorientation measurements, deconvolution of the response function from the parallel and perpendicular polarization data prior to generation of the $R(t)$ function caused no change in the regressed τ_{OR} decay time constants.

Results and Discussion

A central purpose of the work we report here is developing a fundamental understanding of the role of probe molecule structure in relating the details of transient solution phase organization to chromophore optical response. This effort is part of a larger body of work aimed at detecting, characterizing, and understanding local organization and spontaneous self-assembly in the solution phase.[25−27] We have used PBA as the probe molecule in this work to understand both the characteristic length scale of solution phase adipic acid aggregation and also to determine the dependence of the pyrene chromophore response

on side group identity. We consider these questions in the context of steady state and time-domain fluorescence measurements and rotational diffusion data. We consider each of these bodies of information separately.

Steady-State Fluorescence. We have measured the steady-state emission response of PBA in solutions of adipic acid ranging in concentration between 20% and 110% of saturation (saturation concentration = 1.86% w/w, 0.127 M).[31] These solutions range in pH from 3.2 to 2.8 and we expect that the predominant species contributing to these spectra will be the protonated form of PBA (HPBA) in solutions containing adipic acid. In pure water we expect the dominant form to be deprotonated (PBA^-) on the premise that the pK_a of PBA is ~4.8. We base this estimate on the pK_a values for alkanoic acids, which fall in the range of 4.75−4.9.[32] We observe no differences between spectra recorded for PBA in pure water and solutions of adipic acid. On the basis of this result we conclude that the emission response of the PBA is not significantly sensitive to either the degree of protonation or the presence of adipic acid. We note that no change in the emission spectral profile of HPBA is seen in the region of adipic acid saturation. This is an expected result given the fact that the PBA carboxylic acid functionality is not conjugated to the pyrene chromophore ring system.

We contrast these results with those obtained using the structurally similar probe 1-pyrenecarboxylic acid (PCA), for which the protonated and deprotonated forms exhibit distinct emission spectra.[27] Differences in the pH-dependent steady-state emission spectra of PBA and PCA stem from the proximity of carboxylic acid groups to the pyrene chromophore (Figure 1). For PCA the carboxylic acid group is conjugated with the chromophore, while for PBA this conjugation is absent. The emission response of PBA is thus insensitive to protonation of the carboxylate moiety. An immediate conclusion of this comparison is that the steady-state spectral profile of PCA contains more information on the local environment than that of PBA.[27]

The steady state emission data for PBA are important because they underscore the central role of molecular structure in determining the sensitivity of the probe molecule to its local environment. Because of the absence of significant local environmental information in the PBA spectra, we have investigated the time-domain response of this molecule in adipic acid solutions in an attempt to elucidate the effect of chromophore distance from the putative complexation site. Fluorescence lifetime and rotational diffusion dynamics of PBA in adipic acid solution provide subtle but important information on the presence of solution-phase self-assembly in adipic acid solutions.

Lifetime Measurements. We show the fluorescence lifetime of PBA as a function of adipic acid concentration and in buffered solutions in Figure 2. The lifetime data are the average of at least six individual determinations and the error bars represent the uncertainty in the data at the 95% confidence level. The lifetime data exhibit an initial increase in going from pure water to 0.025 M adipic acid (20% of saturation) and we attribute this difference to a change in the predominant species from PBA^- in pure water to HPBA in solutions containing adipic acid. This change in lifetime is in agreement with the lifetime of PBA measured in solutions buffered at pH 12 and pH 2. Despite the absence of a pH dependence in the frequency domain, there is a clear difference between the protonated and deprotonated forms in the time domain. Over the range of adipic acid concentrations used here, PBA lifetimes exhibit a curvilinear relationship with solution composition. In comparison,

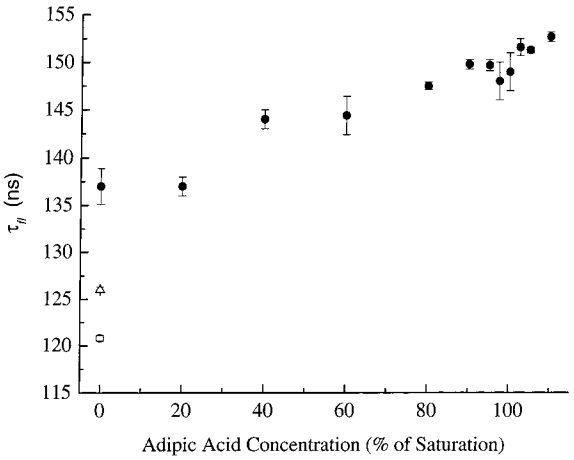

Figure 2. Dependence of PBA fluorescence lifetime on solution composition. Open symbols show τ_{fl} of PBA^- in pure water (○, no buffer; Δ, pH = 12). Solid circles represent τ_{fl} of HPBA in adipic acid solutions and water buffered to pH = 2.

PCA exhibits a discontinuous change in fluorescence lifetime near the saturation concentration and we have related that behavior to the existence of solute local organization. The form of the local organization is believed to be association with adipic acid as a probe/solute complex hydrogen bonded at their carboxylic acid groups.[27] There is no reason to expect significantly different adipic acid organization here and the absence of an anomalous change in PBA lifetime near saturation suggests that this probe molecule is relatively insensitive to solution phase self-assembly phenomena because of the distance between the associative complex and the chromophore moiety.

On the basis of our earlier work with PCA in adipic acid solutions, we expect significant association between protonated PBA and adipic acid. In contrast to PCA, the structure of PBA is such that the steady-state emission response is insensitive to the presence of adipic acid oligomers, as we discussed above. The fact that the chromophore and carboxylic acid functionalities are spaced further apart in PBA than in PCA accounts for the difference in the dependence of fluorescent lifetimes with adipic acid concentration for the two molecules. The observation that PBA exhibits no anomalous behavior in τ_{fl} near saturation is consistent with probe−solute association through the carboxylic acid functionality and not by van der Waals interactions between adipic acid and the pyrene ring system. If van der Waals interactions dominated the interactions between the probe molecule and adipic acid, both PCA and PBA would manifest similar lifetime behavior near saturation. We thus expect PBA to sense an environment that is better approximated by bulk solution properties than by local aggregation.

To this point the data we have reported on PBA in adipic acid have demonstrated that this probe molecule possesses limited sensitivity to the presence of adipic acid aggregation phenomena. This limitation arises from the structure of the probe and for two reasons. The active complexation site of PBA is not conjugated to the pyrene chromophore and that moiety is structurally isolated from the complexation site. Because of this latter structural condition and the relatively long fluorescence lifetime of this chromophore, significant environmental "averaging" mediates the experimental response and limits its information content. For these reasons we have also examined the rotational diffusion behavior of PBA in these same solutions.

Reorientation Dynamics. Rotational diffusion is a well-established technique for the examination of solution phase intermolecular interactions. The basis for the utility of this

measurement is the existence of a mature theoretical framework for the interpretation of experimental data.[11,33−39] In most treatments, the starting point is the Debye−Stokes−Einstein (DSE) model, in which the solute is treated as a hard sphere and the solvent as a continuum medium with no discrete molecular properties. Despite the obvious absence of a correspondence between the basic assumptions of this model and real systems, the DSE model has proven to be accurate to within at least a factor of 2 for most systems studied. Better agreement between experiment and theory can be achieved when the nonspherical shape of the molecule is accounted for[13] and the solvent−solute boundary condition is treated.[41,42] The resulting modified Debye−Stokes−Einstein (DSE) equation is used widely

$$\tau_{OR} = \frac{\eta V f}{k_B T S} \tag{1}$$

Equation 1 relates the orientational relaxation time constant of a molecule, τ_{OR}, to the solution bulk viscosity, η, the solute hydrodynamic volume, V, the Boltzmann constant, k_B, and the solution temperature, T. The interaction between the solvent and solute is parametrized by a frictional coefficient f [41,42] and a shape factor S [40] to account for the nonspherical shape of the volume swept out by the reorienting molecule. While there is limited chemical information contained in the measurement of an individual system owing to the assumptions involved in determining the quantities η and V and the model dependence of f and S, examining reorientation in systems where a single chemical property is varied in a regular manner can provide substantial insight into the nature and strength of intermolecular interactions.[21,43]

Experimentally, the rotational diffusion behavior of a chromophore is determined from TCSPC data by construction of the induced orientational anisotropy function, $R(t)$, from the time-resolved signals for emission polarized parallel and perpendicular to the vertically polarized excitation light source,

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

$R(t)$ can contain up to five exponential decays depending on the rotor shape describing solute motion and the orientation and angle between excitation and emission transition moments (δ) of the solute.[44] The information content of $R(t)$ can, in certain cases, be sufficient to elucidate the existence of complex solvation phenomena. Despite the number of factors that contribute to the experimental $R(t)$ signal, the most common functionality seen for the anisotropy decay is that of a single exponential.

$$R(t) = R(0) \exp(-t/\tau_{OR}) \tag{3}$$

This result can be obtained either because of the rotor shape and the orientation of the transition moments of the probe molecule or due to limitations in the S/N ratio of the data. The data we report here are, to the best of our ability to determine, characterized by a single-exponential decay in all cases. The functionality of the $R(t)$ decay offers insight into the dynamics of the molecule, and the zero-time anisotropy, $R(0)$, provides information on the spectroscopic properties of the solute. $R(0)$ is related to the transition moment angle δ according to[45]

$$R(0) = 0.4P_2(\cos \delta) \tag{4}$$

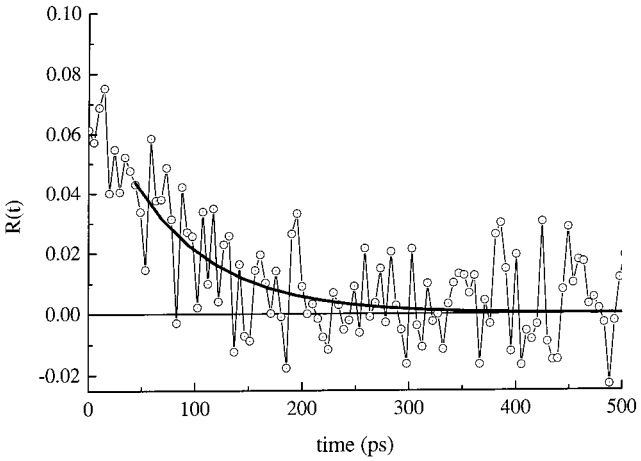

Figure 3. Representative experimental $R(t)$ decay function (points) shown with regressed fit (solid line). For these data, $\tau_{OR} = 76$ ps and $R(0) = 0.08$. The fitted region begins where the instrumental response function intensity is 5% of its maximum value.

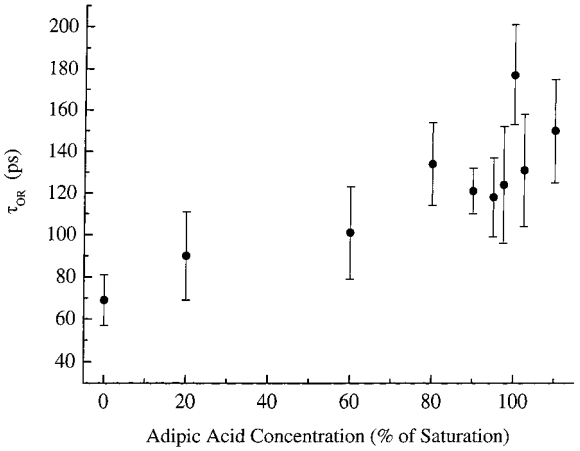

Figure 4. PBA reorientation times as a function of adipic acid concentration. The predominant species are PBA^- in water (0% of saturation) and HPBA in all solutions containing adipic acid.

where P_2 is the second-order Legendre polynomial,

$$P_2(\cos \delta) = \frac{1}{2}(3 \cos^2 \delta - 1) \tag{5}$$

Quantitating $R(0)$ is important in reorientation measurements because variations in δ for a solute as a function of solution conditions can produce subtle changes in the form and information content of the experimental $R(t)$ function.[46] For systems where $R(0)$ remains essentially constant over a range of experimental conditions, the quantities τ_{OR} can be compared to one another directly. We find $R(0)$ to be independent of solution composition for PBA, with the average angle $\delta \approx 45°$. A representative anisotropy decay curve is shown in Figure 3.

The adipic acid concentration dependence of the PBA reorientation time is presented in Figure 4. The τ_{OR} data shown in Figure 4 are the average of at least seven individual determinations with uncertainties reported as 95% confidence intervals. For all of the time constants measured, the experimental $R(t)$ data were fit best by a single-exponential decay. These data are consistent with PBA reorienting as a prolate rotor in aqueous adipic acid solution. We consider next the chemical information content of these data.

Equation 1 predicts that an increase in the reorientation time constant can be interpreted in the context of a change in any of several quantities. Assuming constant temperature, the variable

TABLE 1: Comparison of Molded τ_{OR} for PBA with Addition of Varying Numbers of Adipic Acid Molecules with Experimentally Observed Values

adipic acid concn (% saturation)	obsd τ_{OR} (ps)	species	τ_{OR} calculated (ps) "cis"	"trans"
0	69 ± 12	PBA^-	75	103
20−110	90 ± 21 to	HPBA + AA	113	156
	150 ± 25	HPBA + 2AA	151	210

parameters are the solution bulk viscosity, η, the solvent−solute friction coefficient, f, the solute hydrodynamic volume, V, and the solute shape factor, S. The solution viscosity can be determined experimentally. The viscosity of aqueous adipic acid solutions at 110% of saturation (1.0 cP) is greater than that of pure water (0.89 cP) by a small amount,[47] and changes in PBA reorientation due to viscosity changes over this range would not be resolvable given our experimental uncertainty. There are two important factors contributing to the uncertainty in these data. The first is the difference in time constants for reorientation and emission processes. The fluorescence lifetime of HPBA is ~120 ns, and its reorientation time in aqueous adipic acid solution is ~100 ps. This large discrepancy in time scales for the two processes produces a condition where 0.08% of the total emission intensity contains information on molecular orientational relaxation. The second factor is the angle δ being 45°, giving rise to an anisotropy function that is inherently small. Regardless of these factors, the adipic acid concentration dependence of PBA reorientation cannot be rationalized in terms of a variation in solution viscosity and our previous work on PCA in adipic acid solutions has established that HPCA participates in the formation of adipic acid oligomers. Accounting for changes in PBA reorientation times as a change in S is speculative considering the conformational freedom available to both solute and probe molecules. We interpret the PBA reorientation time variation with adipic acid concentration as a manifestation of oligomer formation near saturation. Oligomer formation in solution, where the probe molecule is one of the oligomer terminal units, can be modeled as a stepwise change in the hydrodynamic volume of the reorienting moiety.[27] The advantage of this approach is that it makes no assumptions about the conformation(s) of either the PBA probe molecule or the adipic acid oligomeric species.

Because we are measuring reorientation times in water, we assume that the data are interpretable in the framework of strong solvent−solute interactions, taken as the "stick" limit ($f = 1$). This solvent−solute boundary condition was shown to be appropriate for PCA reorientation in aqueous adipic acid solutions. We calculate the hydrodynamic volume of the reorienting species by adding the volume of individual adipic acid molecules (134 Å^3) to that of PBA (261 Å^3).[48] We tabulate the resulting volumes, V, and calculated reorientation times, τ_{OR}, in Table 1 and compare them to the experimental reorientation times. Despite the uncertainty in the conformation of the alkanoic acid side chain in PBA, we can identify two limiting cases, where the aliphatic chain is either trans ($S = 0.623$) or cis ($S = 0.864$).[40] Other, mixed conformations possess shape factors that fall between these limiting cases.

Comparing the experimental data to the oligomer model shows close agreement at both low and high adipic acid concentrations. This agreement is based on the association of PBA with one adipic acid molecule, on average, at low adipic acid concentrations and with two adipic acid molecules at concentrations near saturation (Table 1). Given the uncertainty in our data and the fact that we do not have explicit knowledge of the oligomer association persistence time, we cannot provide a more detailed correlation between experiment and model. The increase in τ_{OR} with adipic acid concentration reflects association of (protonated) PBA with adipic acid and we cannot resolve whether this concentration dependence is the result of changes in oligomer lifetime or average number, or some combination of both effects. We note that the τ_{OR} values calculated using the shape factor for the all-cis conformer are consistently in closer agreement with experimental values than those for the all-trans conformer. We believe this result to be fortuitous given the small energy difference between the conformers[49] and the inherent uncertainty in the parameters used in this model. We recognize that further information on oligomer formation might be obtained from measurements in the region between 0% and 20% of saturation where only a 1:1 solute/probe complex may be expected to form. However, our previous work suggests that the concentrations of free PBA and the 2:1 complex would be significant, and detecting a change in predominant species in this region would not be possible for reasons mentioned previously.

A major issue to be addressed in this work is the role of probe molecule structure in determining the information available from time domain experiments on solution phase organization. To that end, it is instructive to compare the results we report here on PBA to those we reported previously for PCA in the same solvent systems. On the basis of our data, several clear conclusions emerge: (1) It is advantageous to have the complexing moiety conjugated to the chromophore portion of the probe molecule. When this condition obtains, the steady state and transient emission responses of the probe are likely to be sensitive to complexation. (2) It is important in such experiments to obtain a reasonable match between fluorescence lifetime and reorientation time so that data acquisition can be efficient for molecular motion measurements. (3) It is important to have the chromophore portion of the probe molecule in close spatial proximity to the complexing functionality to minimize the degrees of structural freedom available to the probe and to ensure that the chromophore is sensitive to the local environment of interest.

Conclusions

We have measured the steady state and time-resolved emission responses of 1-pyrenebutyric acid in aqueous adipic acid systems. The purpose of this work has been to understand the utility of this probe molecule for reporting on solute self-assembly in precrystallizing systems. The data we report here show the emission spectrum of PBA to be insensitive to carboxylic acid protonation and the concentration of adipic acid. Fluorescence lifetime data are sensitive to both protonation of the probe carboxylic acid group and to adipic acid concentration, but the adipic acid concentration dependence in this response cannot be related clearly to the extent or nature of adipic acid organization in solution. Rotational diffusion data for PBA reveal transient association between HPBA and adipic acid, but due to the structural freedom of the probe molecule and the distance between the chromophore moiety and complexation site, the level of detail available for these measurements on local organization is limited. While this is perhaps intuitively obvious for probe molecules tethered to mesostructures characterized by moderately slow motional dynamics, to this point the correspondence of this intuition to highly dynamic molecular systems has not been made. With this information in hand, we have a better understanding of the requirements of a probe molecule for sensing solution phase self-assembly.

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