THE JOURNAL OF PHYSICAL CHEMISTRY B

ARTICLE

pubs.acs.org/JPCB

Solvation and Rotational Dynamics of Coumarin-153 in Ethylammonium Nitrate Containing γ-Cyclodextrin

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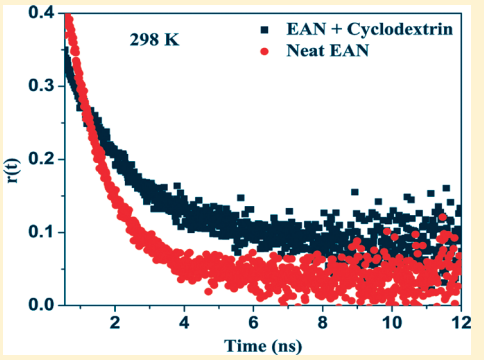
ABSTRACT: Carbohydrates are known to serve as an abundant, diverse, and reusable source of carbon, but their derivatization for industrial applications is still a challenging task because of their low solubility in solvents other than water; they are only sparingly soluble in common organic solvents as well as in weakly coordinating ionic liquids, such as 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$). In this manuscript, we have shown that the solubility of cyclodextrins (CDs) in ethylammonium nitrate (EAN), at 298 K is comparable to that in water. This combination of EAN and γ-CD can be useful in many ways: (i) combination of both γ-CD and EAN can provide selectivity and resolution for separations that otherwise are not possible (vide infra); (ii) the combination of these two can find interesting applications in protein−detergent systems (vide infra), and (iii) they can improve chiral resolutions in simultaneous enantioseparation by capillary electrophoresis method (vide infra). In this study, we have characterized this system using the following techniques: By the use of the competitive fluorescence method we have shown that there is no inclusion complex formation between EAN and γ-CD. Using the Benesi Hildebrand equation, we have shown the variation of binding constant of the C-153/γ-CD complex with temperature. The negative entropy and enthalpy changes indicated that the formation of the above C-153/γ-CD complex is entropically unfavorable and enthalpy-driven. We have also investigated the effect of temperature on the fluorescence anisotropy decays and the solvation dynamics of coumarin-153 (C-153) using picosecond time-resolved spectroscopy. Finally, we have shown that the aggregation behavior of γ-CD in EAN is entirely different from that in water, and the increase in average solvation time on going from neat EAN to EAN containing γ-CD is very small compared to the increase in solvation time on going from pure water to water containing γ-CD.



1. INTRODUCTION

Dynamics of solvent molecules and its effect on chemical reactions such as electron transfer and charge transfer processes will always remain an interesting field of importance in physical chemistry.[1−14] A full understanding of chemical reactivity traces back to the basic understanding of the influence of the surrounding solvent on the electronic transition. The solvation dynamics study of a newly created ion or a dipole in polar liquids is now a well established method for obtaining molecular level information about the response of solvent molecules (which has contributions from both orientational and translational motions) around the probe.[2] The uniqueness of solvation dynamics as a probe is that it allows, at least partly, for discrimination between the local and global contributions. There have been extensive studies on solvation dynamics in different heterogeneous media and restricted environments such as micelles, reverse micelles, lipids, proteins, DNA, and so forth.[2,15] The other common examples of restricted environment, which have been studied widely, are the cavities of the α-, β-, and γ-cyclodextrins. Cyclodextrins (CDs) are a group of structurally related natural products formed during bacterial digestion of cellulose. These cyclic oligosaccharides consist of (α-1,4)-linked α-D-glucopyranose units and contain a somewhat lipophilic central cavity and a hydrophilic outer surface.[16,17] In the pharmaceutical industry, CDs have mainly been used as complexing agents to increase the aqueous solubility of poorly soluble drugs, and to increase their bioavailability and stability. CDs are also successful catalyzers of many chemical reactions. The solvation dynamics of a coumarin dye molecule (C-480) within the γ-CD ring has been studied both experimentally and by computer simulations.[18,19]

Several other studies on CD complexes with aromatic molecules using steady-state and nanosecond spectroscopy have been reported.[20] The aim of these studies are to control the photophysical and photochemical behavior of organic guests such as fluorescence and phosphorescence enhancement, excimer/exciplex formation, photocleavage, charge and proton transfer, energy hopping, and cis−trans photoisomerization. These reports reflect the effects of molecular restriction, due to the cavity size of the host and protection of the guest (from quenchers such as oxygen molecules and H-bonding interaction with the medium, water) provided by CD cavity and its low polarity relative to that of water, on the photophysical and photochemical properties of the encapsulated guest. One cannot predict the effect of CD on the absorption and emission properties of dyes upon encapsulation, as the static and dynamic interactions are specific to the system being studied, which might change greatly in the excited state.

Received: May 2, 2011
Revised: August 2, 2011
Published: August 02, 2011

In recent years, there is tremendous interest to investigate the use of room temperature ionic liquids (RTILs) as solvent for many systems due to their unique properties, such as, low vapor pressure, high thermal stability, wide liquidous temperature range, wide electrochemical window, and as "designer solvents" because their physical properties can be varied predictably by incorporation of appropriate functional groups.[21−23] Due to these properties, RTILs have been successfully used in many applications, which include replacing traditional organic solvent in organic and inorganic synthesis,[24] solvent extraction with crown ethers,[25] liquid−liquid extractions with supercritical fluid CO_2,[26−28] electrochemical reactions,[29] and as a medium for enzyme reactions.[30] Interestingly, owing to the high solubility power of RTILs, a variety of additive compounds, including CDs and their derivatives can be dissolved in the RTILs[31a] to provide additional selectivity and resolution for separations that otherwise are not possible.[31b] Ionic liquids (ILs) are also recognized as green solvents for carbohydrate processing.[31c] Carbohydrates are only sparingly soluble in common organic solvents as well as in weakly coordinating ILs, such as 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$). ILs that contain the dicyanamide anion, in contrast, dissolve approximately 200 g L^{-1} of glucose, sucrose, lactose, and CD.[31d]

The addition of CDs to media containing IL gives rise to several interesting phenomena. For example, supramolecular controlled pseudo-LCST (lower critical solution temperature) effect was observed in CD-complexed poly-ILs.[32] Application of ILs to CD-containing systems requires an understanding of the interaction between CDs and ILs. There are many reports on the formation of inclusion complexes between CDs and ILs.[33−36,31a] Gao et al. have reported the formation of a 1:1 (host:guest) inclusion complex between 1-butyl-3-methylimidazolium hexafluorophosphate and β-CD.[33]

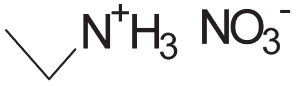
It is important to know the dynamics of any guest molecule in the CD cavity as well as the effect of the solvent molecules on the host−guest system. The rotational dynamics of the guest may be followed by fluorescence anisotropy decay using a fluorescent probe such as coumarin-153 (C-153). There are many reports in the literature on the formation of large linear nanotube aggregates of CDs in aqueous solution.[37,38] In these aggregates, CDs are connected by linear surfactants and also by aromatic guest molecules, e.g., diphenyl hexatriene (DPH) or diphenyl oxazole (DPO).[36,37] Roy et al. have reported the formation of the linear aggregate taking C-153 as an aromatic guest, and they have also reported the temperature dependence of anisotropy decay and solvation dynamics of C-153 in γ-CD aggregates.[39]

In this work we have used C-153 as an aromatic guest, but in place of water we have taken ethylammonium nitrate (EAN) as the solvent. Due to the limited solubility of CDs in ILs, to best of our knowledge, no such study in neat IL has been reported. EAN can dissolve CDs to almost the same extent as water. We have compared the temperature dependency of anisotropy decay and the solvation dynamics of C-153 in a γ-CD−EAN system with that reported by Roy et al. in a γ-CD−water system.[39] Since the increase in solvation time on going from pure water to water containing CDs is of the order of 100−1000 times,[39] and the extended hydrogen bonding between water and CD molecules are responsible for slowing down the solvent relaxation, so we want to see what will happen if we take EAN as a solvent in which ionic interactions are present between the cation and anion of the IL (EAN).

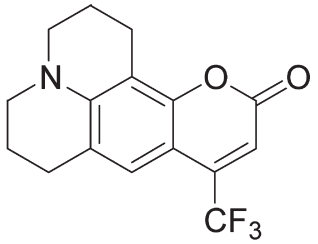
The combination of EAN and γ-CD can be useful in many ways. CDs are extensively used in separations due to their unique ability to form inclusion compounds with other smaller hydrophobic molecules, while EAN is a novel ionic solvent, liquid at room temperature, suitable for use as selective solvent for the isolation of analytes containing proton donor functional groups (alcohols, amines, phenols, carboxylic acids, etc.) by liquid−liquid distribution. These solvents form immiscible solvent pairs with nonpolar aliphatic and aromatic hydrocarbons, ethers and alkyl halide solvents (e.g., methylene chloride, chloroform). So combination of both γ-CD and EAN can provide additional selectivity and resolution for separations that otherwise are not possible.[40]

It is also known that if common detergents with long hydrophobic alkyl chains associate with a small protein to such an extent that their displacement upon dilution is difficult, then addition of a CD is necessary to remove the associated detergent from the protein and enable it to refold to its native conformation. The room-temperature liquid salt EAN has been used to enhance the recovery of denatured-reduced hen egg white lysozyme (HEWL). EAN has the ability to prevent aggregation of the denatured protein. The use of EAN as a refolding additive is advantageous because the renaturation is a one-step process.[41] So the combination of these two can be quite interesting for protein−detergent systems. Furthermore, the EAN−CD combination could be useful for many high-temperature organic reactions due to the higher boiling point of EAN compared to that of water.

Scheme 1. Structure of EAN and C-153



Ethylammonium Nitrate (EAN)



Coumarin 153 (C-153)

2. EXPERIMENTAL SECTION

2.1. Materials. The C-153 (laser grade), exciton, and γ-CD were used as received. EAN was prepared by the reaction of equimolar amounts of ethylamine and nitric acid as described by Evans et al.[42] Water was removed by rotary evaporation followed by lyophilization. The obtained EAN was recrystallized from acetonitrile. The structures of C-153 and EAN are shown in Scheme 1.

2.2. Sample Preparation. The final concentration of probe molecule C-153 in all the measurements was kept at 2×10^{-5} M. C-153 was initially dissolved in methanol, the requisite amount of which was transferred to a cuvette. Methanol was removed under vacuum, and then the required amount of γ-CD and EAN was added to the cuvette in nitrogen atmosphere in a globebox. The mixture was allowed to equilibrate for 6 h.

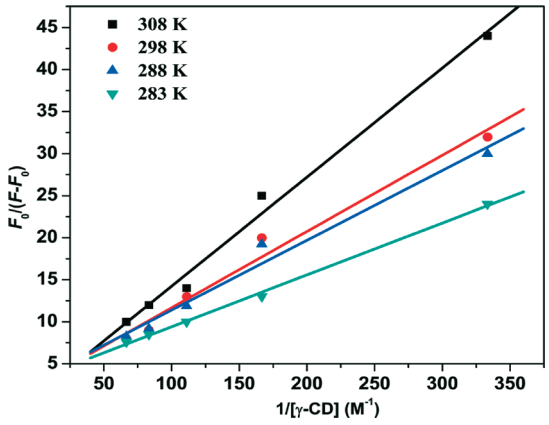


Figure 1. Determination of binding constant of C-153 with γ-CD using a Benesi Hildebrand plot: variation of $F_0/(F - F_0)$ of C-153 versus $1/[\gamma\text{-CD}]$ in EAN at different temperatures.

2.3. Instrumentation. The absorption and fluorescence spectra were collected using a Shimadzu (model no.UV-2450) spectrophotometer and a Hitachi (model no.F-7000) spectrofluorimeter respectively. For steady-state experiments, all the samples were excited at 410 nm. The time-resolved fluorescence setup is described in our earlier publication in detail.[43] Briefly, the samples were excited at 408 nm using a picosecond laser diode (IBH, Nanoled), and the signals were collected at magic angles (54.7°) using a Hamamatsu microchannel plate photomultiplier tube (3809U). The instrument response function of our setup is ~90 ps. The same setup was used for anisotropy measurements. For the anisotropy decays, we used a motorized polarizer on the emission side. The emission intensities at parallel $I_{\parallel}(t)$ and perpendicular $I_{\perp}(t)$ polarizations were collected alternatively until a certain peak difference between parallel $I_{\parallel}(t)$ and perpendicular $I_{\perp}(t)$ decay was reached. The analysis of the data was done using IBH DAS, version 6, decay analysis software. The same software was also used to analyze the anisotropy data. For viscosity measurements we used a Brookfield DV-II+ Pro (viscometer). The desired temperature was maintained by circulating water using a Neslab Thermostat (RTE7).

3. RESULTS AND DISCUSSION

3.1. Steady State Emission Spectra. At 298 K the emission maximum of C-153 in neat water and neat EAN was found to be 550 and 548 nm respectively. With the addition of γ-CD to a solution containing 20 μM of C-153 the emission intensity changes by 13% and the emission maximum was blue-shifted only by 3 nm (at 15 mM γ-CD). To account for this small change in fluorescence intensity and emission maximum we have to consider

(1) the binding constant of C-153 with γ-CD (distribution of C-153 in EAN and γ-CD),
(2) whether EAN forms any inclusion complex with γ-CD, and
(3) whether there is any nanotube aggregate formation of γ-CD linked by C-153 taking place.

3.2. Binding of C-153 with γ-CD in EAN. The fluorescence intensity of C-153 in EAN increases with the addition of γ-CD. This dependence of fluorescence enhancement on the γ-CD concentration was used to study quantitatively the interaction between C-153 and γ-CD. The binding constant and the stoichiometries of C-153/γ-CD complexes at various temperatures have been determined by means of a modified Benesi Hildebrand equation.[44a]

$$\frac{F_0}{F - F_0} = \frac{1}{A} + \frac{1}{AK[\text{CD}]^n} \quad (1)$$

where K is the binding constant, F_0 is the initial fluorescence intensity of free C-153, F is the maximum fluorescence intensity of the C-153−γ-CD inclusion complexes at the CD concentration [CD], A is a constant, and n is the number of binding sites. Figure 1 shows the plot of $F_0/(F - F_0)$ versus $1/[\gamma\text{-CD}]$ in pure EAN solution at different temperatures. The linearity of the plots of $F_0/(F - F_0)$ versus $1/[\gamma\text{-CD}]$ obtained reflects the formation of 1:1 complex between C-153 and γ-CD. The equilibrium is given by

$$\text{C-153} + \gamma\text{-CD} \overset{K}{\rightleftharpoons} [\text{C-153}-\ \gamma\text{-CD}] \quad (2)$$

The binding constant of C-153 with γ-CD decreases with increase in temperature (Table 1). With increase in temperature from 283 to 308 K the binding constant decreases from 52 M^{-1} to 10 M^{-1}. We have also calculated the fraction of C-153 bound to γ-CD. This fraction decreases from 0.44 to 0.13 with increase in temperature from 283 to 308 K. The K_a values were used to calculate the thermodynamic parameters by the classical method of plotting ln K_a against $1/T$ (i.e., the Van't Hoff method[44b]). In this case, the corresponding enthalpy ΔH^0 and entropy ΔS^0 are obtained from the slope and intercept of the graph ($R = 0.962$). We have obtained $\Delta H^0 = -44.73$ kJ mole^{-1} and $\Delta S^0 = -124.75$ J mol^{-1}K^{-1}. The results indicate that the formation of complex with γ-CD is favored by enthalpic factors.

3.3. Association Constant of EAN and γ-CD: Competitive Fluorescence Method. We have used the competitive fluorescence method to determine the association constant of EAN with γ-CD.[45] With the addition of EAN to a solution containing 7 μM of C-153 in aqueous solution of 40 mM γ-CD, the emission intensity increases (Figure 2). This observation is in contrast with the observation of He et al.[46] They have reported decrease in fluorescence intensity with the addition of 1-hexyl-2,3-dimethylimidazolium chloride to an aqueous solution of β-CD containing 2-(*p*-aminophenyl)-3,3-dimethyl-5-carboethoxy-3*H*-indole due to the formation of a 1:1 inclusion complex between 1-hexyl-2,3-dimethylimidazolium chloride and β-CD. So there is no such complex formation occurring between EAN and γ-CD. This can be attributed to the fact that due to the absence of a long hydrophobic chain that can be incorporated by γ-CD, complex formation does not occur between EAN and γ-CD.

3.4. Steady State and Time-Resolved Anisotropy Decay. The steady state emission spectra and the low binding constants of the probe molecule clearly indicate that only some of the probe molecules are incorporated in the hydrophobic cavity of the γ-CD. The position of the probe molecule can be more accurately predicted by the steady state and time-resolved fluorescence anisotropy. Since the fluorescence anisotropy decay of the organic dye molecules is directly related to the reorientation dynamics of excited molecule, it is the best suited technique for the investigation of molecular dynamics near the site of dye molecule. Time resolved fluorescence

Table 1. Binding Constants of C-153 with γ-CD at Different Temperatures

temperature (K)	binding constant K (M^{-1})	fraction of bound C-153 in 15 mM γ-CD
283	52	0.44
288	37	0.36
298	28	0.30
308	10	0.13

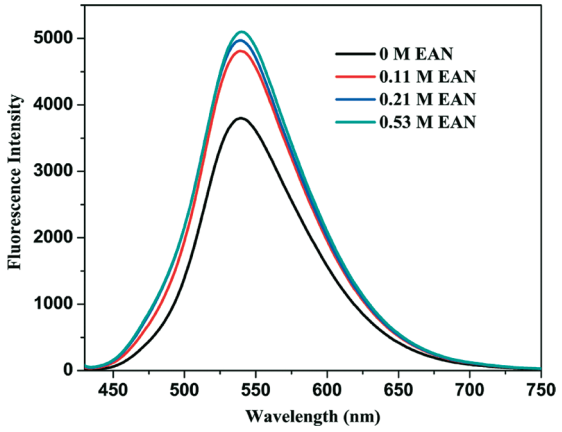


Figure 2. Determination of the association constant of EAN and γ-CD using the competitive fluorescence method by observing the change in emission spectrum of C-153 in water containing 40 mM γ-CD with the addition of EAN.

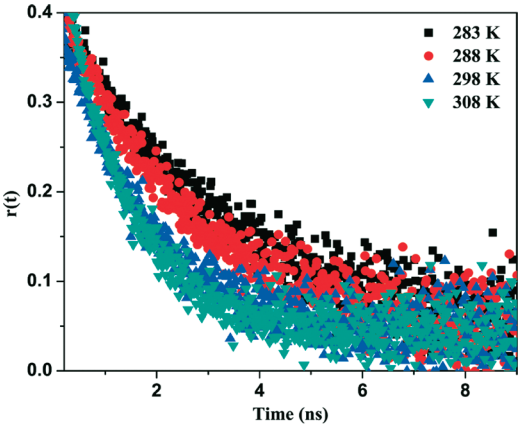


Figure 3. Time resolved fluorescence anisotropy decay of C-153 in neat EAN at different temperatures.

anisotropy $r(t)$ is calculated using the following equation:

$$r(t) = \frac{I_{||}(t) - GI_{\perp}(t)}{I_{||}(t) + 2GI_{\perp}(t)} \quad (3)$$

where G is the correction factor for detector sensitivity to the polarization direction of emission, and $I_{||}(t)$ and $I_{\perp}(t)$ are fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively.

Table 2. Anisotropy Decay Parameters of C-153 in EAN at Different Temperatures

temperature (K)	$r(0)_{EAN}$	$\tau_{rot,EAN}$ (ns)	viscosity (cP)[a]
283	0.36	3.08	51
288	0.36	2.48	41
298	0.36	1.68	28
308	0.38	1.23	18

[a] Error in experimental data of ±5%.

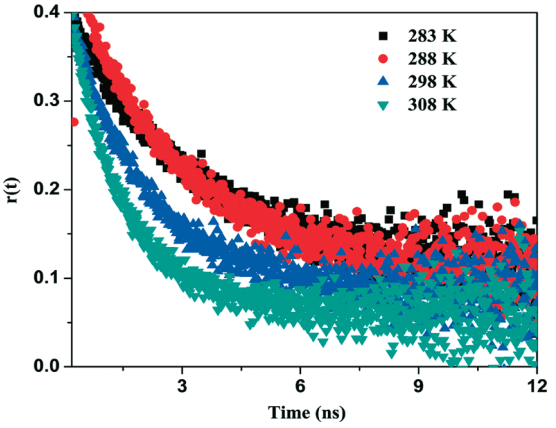


Figure 4. Time-resolved fluorescence anisotropy decay of C-153 in EAN containing 15 mM γ-CD at different temperatures.

The steady state anisotropy of C-153 in EAN and in the solution containing 15 mM γ-CD was found to be 0.086 and 0.136, respectively, at 298 K. The high steady state anisotropy suggests that the microenvironment of C-153 in 15 mM γ-CD is more rigid compared to that of neat EAN. We have studied time-resolved fluorescence anisotropy decay to know whether the formation of nanotube aggregate occurs, but before looking at the EAN−γ-CD system we will discuss the anisotropy decay in neat EAN. We studied the change in rotational relaxation time of C-153 in EAN with change in temperature from 283 to 308 K at four different temperatures (Figure 3). Anisotropy decays were found to be exponential at all temperatures. The anisotropy results are summarized in Table 2. The rotational relaxation time decreases from 3.08 to 1.23 ns with increase in temperature from 283 to 308 K. This can be accounted for by considering the change in viscosity with increase in temperature.

With the addition of 15 mM γ-CD to EAN we observed a distinct residual anisotropy that was not present in the case of neat EAN (Figure 4). The residual anisotropy does not decay over 13 ns at 298 K, which is much larger than the lifetime of C-153 (3.12 ns). Figure 5 represents the time-resolved fluorescence anisotropy decay of C-153, showing comparative decay of $r(t)$ in neat EAN and EAN containing 15 mM γ-CD at 283 and 288 K. Following the Stokes−Einstein formula, where the rotational time constant (τ_R) is related to viscosity (η) and the volume (V) of the C153:γ-CD complex as[47]

$$\tau_R = \frac{\eta V}{k_B T} \quad (4)$$

dx.doi.org/10.1021/jp2040532 |J. Phys. Chem. B 2011, 115, 10500–10508

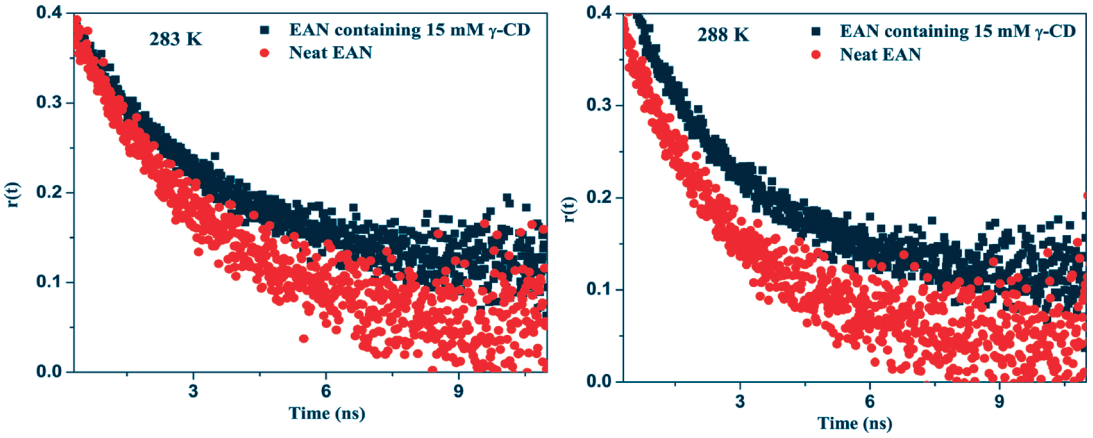


Figure 5. Time-resolved fluorescence anisotropy decay of C-153, showing comparative decay of $r(t)$ in neat EAN and EAN containing 15 mM γ-CD at 283 and 288 K.

Table 3. Anisotropy Decay Parameters of C-153 in EAN Containing 15 mM γ-CD at Different Temperatures Fitted by the Proposed Model (eq 5)

temperature (K)	$r(0)_{\gamma\text{-CD}}$	$\tau_{\text{rot},\gamma\text{-CD}}$ (ns)	viscosity (cP)[a]
283	0.37	22.42	55
288	0.39	21.62	44
298	0.40	19.64	30
308	0.40	16.23	22

[a] Error in experimental data of ±5%.

We have calculated the C-153:γ-CD complex volume at 298 K. A 13 ns rotational time constant (τ_R) corresponds to a volume of 1782 Å^3. The linear aggregate of γ-CD is an ellipsoid with semiaxes a, b, and c and volume $V = 4\pi abc/3$.[39] In this case, $a = b = 9$ Å, while the length is $2c$. Thus, from the observed rotational time constant (τ_R) and corresponding viscosity we have calculated the length of aggregate $2c \sim 10$ Å, which corresponds to a complex that contains almost one γ-CD. So we can say that, unlike the water−γ-CD system, aggregate formation does not take place in the case of the EAN−γ-CD system.

Finally, since we have obtained the exact distribution of the C-153 in EAN containing 15 mM γ-CD, the anisotropy decay of C-153 in EAN containing 15 mM γ-CD was fitted by our proposed model equation

$$r(t) = r(0)_{\text{EAN}} \cdot f_{\text{EAN}} \cdot \exp\left(\frac{-t}{\tau_{\text{rot, EAN}}}\right) + r(0)_{\gamma\text{-CD}} \cdot f_{\gamma\text{-CD}} \cdot \exp\left(\frac{-t}{\tau_{\text{rot, }\gamma\text{-CD}}}\right) \quad (5)$$

where $r(0)_{\text{EAN}}$ and $r(0)_{\gamma\text{-CD}}$ are the initial anisotropies in neat EAN and γ-CD, respectively, f_{EAN} and $f_{\gamma\text{-CD}}$ are the fractions of C-153 molecules distributed in EAN and γ-CD, respectively, and $\tau_{\text{rot,EAN}}$ and $\tau_{\text{rot},\gamma\text{-CD}}$ are the rotational relaxation times of C-153 in neat EAN and γ-CD, respectively. The fitted parameters are given in Table 3. The rotational relaxation time of C-153 in γ-CD $\tau_{\text{rot},\gamma\text{-CD}}$ was found to be 22.42 ns at 283 K. With an increase in temperature from 283 to 308 K, the $\tau_{\text{rot},\gamma\text{-CD}}$ decreased from 22.42 to 16.23 ns, which can be accounted for by considering the change in viscosity with increase in temperature. So, we can say that these high values of rotational relaxation times of C-153 in γ-CD $\tau_{\text{rot},\gamma\text{-CD}}$ are responsible for the observed residual anisotropy.

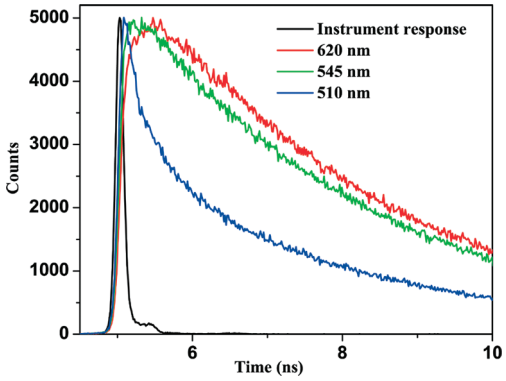


Figure 6. Fluorescence decay of C-153 in EAN containing 15 mM γ-CD at different wavelengths at 283 K.

Finally, we have performed fluorescence anisotropy measurements as a function of γ-CD concentration, which is another test of aggregation. We have not observed any considerable change either in the anisotropy decays or in the rotational relaxation time of C-153 in γ-CD, which once again indicates that the aggregate formation does not take place in the case of the EAN−γ-CD system.

3.5. Solvation Dynamics. To study solvent relaxation dynamics, we collected the time-resolved decays monitored at different wavelengths for all the systems. The fluorescence decays of C-153 in EAN containing 15 mM γ-CD showed the dependence on the emission wavelength at all the temperatures. At the red edge of emission spectra, the observed decay consists of a clear rise (growth) followed by usual decay, and at the blue end of emission spectra, a faster decay is observed, which is a clear indication of the solvation dynamics. The representative decays of C-153 in EAN containing 15 mM γ-CD monitored at three different wavelengths at 283 K are shown in Figure 6. The red edge and blue edge decay profiles were best fitted by biexponential and triexponential functions, respectively. The time-resolved emission spectra (TRES) were constructed by the following procedure of Fleming and Maroncelli.[1a,48] The TRES at a given time t, $S(\lambda;t)$, is obtained by the fitted decays, $D(t;\lambda)$,

dx.doi.org/10.1021/jp2040532 |J. Phys. Chem. B 2011, 115, 10500–10508

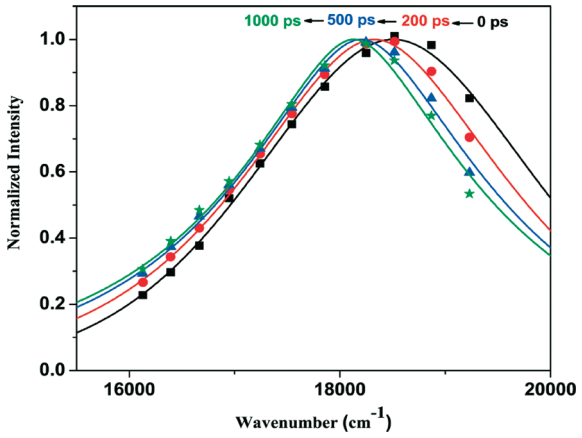


Figure 7. TRES of C-153 in EAN containing 15 mM γ-CD at 288 K.

by relative normalization to the steady-state spectrum $S_0(\lambda)$, as follows:

$$S(\lambda;t) = D(t;\lambda)\frac{S_0(\lambda)}{\int_0^\infty D(t;\lambda)dt} \quad (6)$$

The representative TRES plot of C-153 in EAN containing 15 mM γ-CD at 288 K is shown in Figure 7. Each TRES was fitted by "log-normal line shape function", which is defined as

$$g(\nu) = g_0 \exp\left[-\ln 2\left(\frac{\ln[1 + 2b(\nu - \nu_p)/\Delta]}{b}\right)^2\right] \quad (7)$$

where g_0, b, ν_p and Δ are the peak height, asymmetric parameter, peak frequency, and width parameter, respectively. The peak frequency evaluated from the log-normal fitting of TRES was then used to construct the decay of the solvent correlation function $C(t)$, which is defined as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (8)$$

$\nu(0)$ is the frequency at "zero-time", as calculated by the full method of Fleming and Maroncelli.[48] $\nu(\infty)$ is the frequency at "infinite time", which may be taken as the maximum of the steady-state fluorescence spectrum if solvation is more rapid than the population decay of the probe. $\nu(t)$ is determined by taking the maxima from the log-normal fits as the emission maximum. In most of the cases, however, the spectra are broad, so there is some uncertainty in the exact position of the emission maxima. Therefore, following Petrich et al.[49−51] we have considered the range of the raw data points in the neighborhood of the maximum to estimate an error for the maximum obtained from the log-normal fit. Depending on the width of the spectrum (i.e., zero-time, steady state, or TRES), we have determined the typical uncertainties as follows: zero time ≈ steady-state (110 cm^{-1}) < time-resolved (200 cm^{-1}) emission. We used these uncertainties to compute error bars for $C(t)$. Finally, in generating $C(t)$, the first point was obtained from the zero time spectrum. The second point was taken at the maximum of the instrument response function, which, having a full width at half-maximum of ≤100 ps, was taken to be 100 ps. Finally the time dependence of the

Table 4. Decay Parameters of $C(t)$ of C-153 (Excluding the Missing Component) in EAN Containing 15 mM γ-CD at Different Temperatures

temperature (K)	τ_i (a_i) (ps)	$\langle\tau_s\rangle$ (ps)
283	226 (13%), 490 (13%)	93
288	179 (4%), 408 (17%)	77
298	176 (11%), 341 (11%)	57

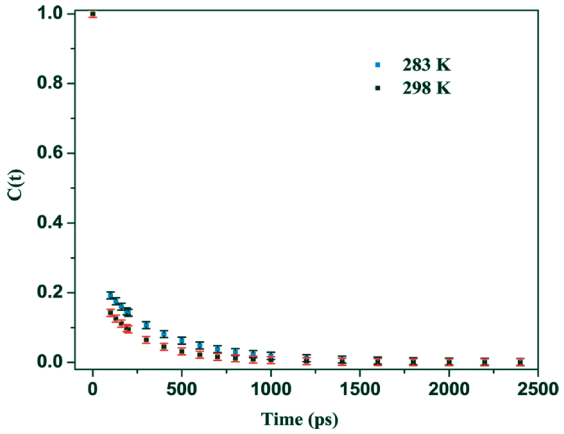


Figure 8. Decay of solvent correlation function $C(t)$ of C-153 in EAN containing 15 mM γ-CD at 283 and 298 K.

calculated $C(t)$ values was fitted by a biexponential function because χ^2 (autocorrelation function) lies close to 1, which indicates the goodness of the fit. The biexponential functions is as follows

$$C(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (9)$$

where τ_1, τ_2 are the solvent relaxation time constants, and a_1 and a_2 are normalized pre-exponential factors. The decay parameters of $C(t)$ are summarized in Table 4. The $C(t)$ versus time plots of 15 mM γ-CD in EAN are shown in Figure 8. The average solvation time is calculated as

$$\tau_{av} = a_1\tau_1 + a_2\tau_2 \quad (10)$$

First, we are going to discuss the important features of solvation dynamics in different systems. Water seems to be by far the "fastest" solvent studied so far: simulations predict that well over half of the solvation response for atomic solutes is inertial, happening on a time scale of about 20 fs,[52,53] and the remaining solvation occurs in the range of ≤50 ps. This latter component arises due to the diffusive motion of hydrogen-bonded water molecule clusters. The increase in solvation time on going from pure water to water containing CDs is on the order of 100−1000 times.[39]The extended hydrogen bonding between water and CD molecules is responsible for slowing down the solvent relaxation. The dynamic exchange model has often been used to explain bimodal solvent relaxation.[39]Recent computer simulations[54,3b] also support this fact. These studies[55] showed that the hydrogen bonding between water molecules and surfactant is much stronger than the hydrogen bond between the two water molecules. So these two types of water molecules are responsible for the slow and fast component of the solvation

dynamics. It should be noted that solvation dynamics in RTILs are vastly different from that in the isopolar conventional solvents such as methanol, acetonitrile, and so on.[55,56] Solvation in RTILs takes place because of the motion of the ions around an excited dye, whereas in water, methanol, and acetonitrile, that is, in polar solvents, solvation takes place as the solvent molecules reorient themselves around an excited dye. Recent ultrafast studies suggest that the difference is less striking than originally thought.[57,58a] Chapman and Maroncelli[59] showed that ionic solvation is slower compared to the pure solvent and dependent on the viscosity of the medium. Bart et al.[60] showed that ionic solvation is slow and biphasic in nature. Samanta et al.[61] ascribed that the fast component is due to the anions and the slow component is attributed to large-scale rearrangement of the ions around the photoexcited system. Petrich and coworkers observed that the polarizability of the cation is responsible for the fast component.[50] Song observed a similar phenomenon regarding fast components using the Debye−Huckel dielectric continuum model.[62] Halder et al.[63] suggested that translational motion of ions may not be the predominant factor in the short-time solvation of ionic fluids. According to Maroncelli et al.,[58b−e] the fast component arises because of the translation adjustment of the ions within the solvation structure present at the time of solute excitation. While Shim et al. have shown that the short component is due to the translational motion of the anions,[64] Kobrak and Znamenskiy, on the other hand, have demonstrated that collective cation−anion motion is responsible for the fast component.[65]Simulation studies also suggest that solvation dynamics in RTIL involves collective motion of cations and anions.[66]According to present theory of Kashyap and Biswas,[67] the fast component of the solvation response function originates from the rapid orientational relaxation involving the dipolar species, whereas the relaxation of the ion dynamic structure factor via ion translation produces the observed slow nonexponential component.

Halder et al.[63] have reported that the average solvation time of C-153 in neat EAN is 26 ps. We have used their data for the comparison with the EAN−γ-CD system, because we are unable to detect the solvation dynamics for neat EAN with our instrumental setup. The average solvation time of C-153 in EAN containing 15 mM γ-CD at 283 K is 93 ps with components of 226 ps (13%) and 490 ps (13%), whereas the average solvation time of C-153 in EAN containing 15 mM γ-CD at 298 K is 57 ps with components of 176 ps (11%) and 341 ps (11%). So the average solvation time decreases from 93 ps at 283 K to 57 ps at 298 K. We can also say that the increase in average solvation time on going from neat EAN to EAN containing γ-CD is very small (< 3 times) compared to the increase in solvation time on going from pure water to water containing γ-CD (100−1000 times). This observation is well supported by our earlier report[68] on IL micelles, where with micelle formation by $C_{12}E_8$ and $C_{14}E_8$ in $bmimBF_4$ the average solvation time increases by a factor of 1.57 and 1.22, respectively, at 4 times the critical micelle concentration (CMC). Recently we have also observed only a 4.65-fold increase in solvation time in a 1-butyl-3-methylimidazolium octyl sulfate (bmimOs)−EAN micelle at almost 3 times the CMC compared to the solvation time of neat EAN.[69] So the little increase in average solvation time on going from neat EAN to EAN containing γ-CD indicates that the movement of the cation and anion of the RTIL (EAN) is not affected with the addition of γ-CD.

4. CONCLUSION

We can conclusively state that there was no inclusion complex formation between EAN and γ-CD. This can be attributed to the absence of any long hydrophobic chain on either the cation or the anion of the EAN. The absence of this inclusion complex can be useful in simultaneous enantioseparations by capillary electrophoresis.[70a,b] Huang et al.[70a] have shown that compared with alkylimidazolium-based ILs and alkylpyridinium-based ILs, tetraalkylammonium-based ILs are more potent. The long-chain ILs were found to be useless in improving enantioseparations of β-agonists. They have shown that short-chain tetraalkylammonium-based ILs are more effective, because they are relatively more hydrophilic and less likely to occupy the hydrophobic cavity of chiral selectors (CDs). On the other hand, short-chain tetraalkylammonium-based ILs are less conductive, so that they can be used in high concentrations. So we can say that this combination of γ-CD and EAN fulfill all the requirements for the simultaneous enantioseparation of β-agonists by capillary electrophoresis. We have also shown that unlike the water−γ-CD system,[39] there is no aggregate formation taking place between the CD molecules in case of the EAN−γ-CD system. The increase in average solvation time on going from neat EAN to EAN containing γ-CD is very small (< 3 times) compared to the increase in solvation time on going from pure water to water containing γ-CD (100−1000 times), which is consistent with our earlier report on IL micelles.[66,67] The small increase in solvation time can be attributed to the fact that the movement of the cation and anion of the RTIL (EAN) is not affected by the addition of γ-CD. This behavior of CDs in an RTIL (EAN) may be helpful in the field of material synthesis and reaction control in the presence of both RTIL (EAN) and CDs. Combination of both γ-CD and EAN can provide additional selectivity and resolution for separations that otherwise are not possible (vide supra).[40,41,70]

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ACKNOWLEDGMENT

N.S. is thankful to the Department of Science and Technology (DST) and the Board of Research in Nuclear Sciences (BRNS), Government of India, for generous research grants. V.G.R., C.G., and R.P. are thankful to CSIR for research fellowships. S.S. is thankful to BRNS for an SRF. We are thankful to Ms. Udita Brahmachari for checking the English of this manuscript.

REFERENCES

(1) (a) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221. (b) Maroncelli, M.; Mac Innis, J.; Fleming, G. R. *Science* **1989**, *243*, 1674. (c) Jimenez, R.; Fleming, G. R.; Kumar, P. V.; Maroncelli, M. *Nature* **1994**, *369*, 471.

(2) (a) Nandi, N.; Bhattacharyya, K.; Bagchi, B. *Chem. Rev.* **2000**, *100*, 2013. (b) Nandi, N.; Roy, S.; Bagchi, B. *J. Chem. Phys.* **1995**, *102*, 1390. (c) Bagchi, B. *Chem. Rev.* **2005**, *105*, 3197. (d) Bhattacharyya, K. *Acc. Chem. Res.* **2003**, *36*, 95.

(3) (a) Pal, S.; Bagchi, B.; Balasubramanian, S. *J. Phys. Chem. B* **2005**, *109*, 12879. (b) Balasubramanian, S.; Pal, S.; Bagchi, B. *Phys. Rev. Lett.* **2002**, *89*, 115505.

(4) Mandal, D.; Sen, S.; Bhattacharyya, K.; Tahara, T. *Chem. Phys. Lett.* **2002**, *359*, 77.
(5) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.
(6) Rossky, P. J.; Simon, J. D. *Nature* **1994**, *370*, 263.
(7) Lundgren, L. S.; Heitz, M. P.; Bright, F. V. *Anal. Chem.* **1995**, *67*, 3775.
(8) Zhang, J.; Bright, F. V. *J. Phys. Chem.* **1991**, *95*, 7900.
(9) Mukherjee, P.; Crank, J. A.; Halder, M.; Armstrong, D. W.; Petrich, J. W. *J. Phys. Chem. A* **2006**, *110*, 10725.
(10) Adhikary, R.; Barnes, C. A.; Petrich, J. W. *J. Phys. Chem. B* **2009**, *113*, 11999.
(11) Sarkar, N.; Das, K.; Datta, A.; Das, S.; Bhattacharyya., K. *J. Phys. Chem.* **1996**, *100*, 10523.
(12) Levinger, N. E. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 118.
(13) Sen, P.; Ghosh, S.; Sahu, K.; Mondal, S. K.; Roy, D.; Bhattacharyya, K. *J. Chem. Phys.* **2006**, *124*, 204905.
(14) Hazra, P.; Chakrabarty, D.; Sarkar, N. *Chem. Phys. Lett.* **2003**, *371*, 553.
(15) (a) Sarkar, N.; Datta, A.; Das, S.; Bhattacharyya, K. *J. Phys. Chem.* **1996**, *100*, 15483. (b) Kumbhakar, M.; Nath, S.; Mukherjee, T.; Pal, H. *J. Chem. Phys.* **2004**, *121*, 6026. (c) Willard, D. M.; Riter, R. E.; Levinger, N. E. *J. Am. Chem. Soc.* **1998**, *120*, 4151.
(16) (a) Saenger, W. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E., MacNicol, D. D., Eds.; Academic Press: New York, 1984; Vol. 2, p 231. (b) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1978; Chapter 3. (c) Szetli, J. *Chem. Rev.* **1998**, *98*, 1743. (d) Li, S.; Purdy, W. C. *Chem. Rev.* **1992**, *92*, 1457.
(17) Uekama, K.; Hirayama, F.; Irie, T. *Chem. Rev.* **1998**, *98*, 2045.
(18) Vajda, S.; Jimenez, R.; Rosenthal, S. J.; Fidler, V.; Fleming, G. R.; Castner, E. W., Jr. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 867.
(19) Nandi, N.; Bagchi, B. *J. Phys. Chem.* **1996**, *100*, 13914.
(20) (a) Bortolus, P.; Monti, S. In *Adv. Photochem.*; Neckers, D. C., Volman, D. H., von Bunau, G., Eds.; John Wiley & Sons: New York, 1996; Vol. 21, p 1. (b) Monti, S.; Kohler, G.; Grabner, G. *J. Phys. Chem.* **1993**, *97*, 13011. (c) Douhal, A.; Amat-Guerri, F.; Acuña, A. U. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1514. (d) Douhal, A. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 448. (e) Douhal, A.; Fiebig, T.; Chachisvilis, M.; Zewail, A. H. *J. Phys. Chem. A* **1998**, *102*, 1657. (f) García-Ochoa, I.; Diez López, M. A.; Viñas, M. H.; Santos, L.; Martínez-Ataz, E.; Amat-Guerri, F.; Douhal, A. *Chem.—Eur. J.* **1999**, *5*, 897. (g) Douhal, A. *Chem. Rev.* **2004**, *104*, 1955. (h) Zhong, D. P.; Douhal, A.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 14052. (i) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325. (j) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516. (k) Born, M.; Ritter, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 309.
(21) Forsyth, S. A.; Pringle, J. M.; MacFarlane, D. R. *Aust. J. Chem.* **2004**, *57*, 113.
(22) Rodgers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792.
(23) Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem.* **2000**, *72*, 2275.
(24) Anna, M. M.; Gallo, V.; Mastrorilli, P.; Nobile, C. F.; Romanazzi, G.; Suranna, G. P. *Chem. Commun.* **2002**, 434.
(25) Dietz, M. L.; Dzielawa, J. A. *Chem. Commun.* **2001**, 2124.
(26) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *399*, 28.
(27) Blanchard, L. A.; Brennecke, J. F. *Ind. Eng. Chem. Res.* **2001**, *40*, 287.
(28) Kazarian, S. G.; Briscoe, B. J.; Welton, T. *Chem. Commun.* **2000**, 2047.
(29) Quinn, B. M.; Ding, Z.; Moulton, R.; Bard, A. J. *Langmuir* **2002**, *18*, 1734.
(30) Laszlo, J. A.; Compton, D. L. *Biotechnol. Bioeng.* **2001**, *75*, 181.
(31) (a) Zheng, Y.; Xuan, X.; Wang, J.; Fan, M. *J. Phys. Chem. A* **2010**, *114*, 3926. (b) Armstrong, D. W.; He, L.; Liu, Y. S. *Anal. Chem.* **1999**, *71*, 3873. (c) Zakrzewska, M. E.; Lukasik, E. B.; Lukasik, R. B. *Energy Fuels* **2010**, *24*, 737. (d) Liu, Q.; Janssen, M. H. A.; Rantwijk, F. V.; Sheldon, R. A. *Green Chem.* **2005**, *7*, 39.
(32) Amajjahe, S.; Ritter, H. *Macromolecules* **2008**, *41*, 3250.
(33) Gao, Y. A.; Li, Z. H.; Du, J. M.; Han, B. X.; Li, G. Z.; Hou, W. G.; Shen, D.; Zheng, L. Q.; Zhang, G. Y. *Chem.—Eur. J.* **2005**, *11*, 5875.
(34) Gao, Y.; Zhao, X.; Dong, B.; Zheng, L.; Li, N.; Zhang, S. *J. Phys. Chem. B* **2006**, *110*, 8576.
(35) Amajjahe, S.; Choi, S.; Munteanu, M.; Ritter, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3435.
(36) (a) Amajjahe, S.; Ritter, H. *Macromolecules* **2008**, *41*, 716. (b) He, Y.; Shen, X. *J. Photochem. Photobiol., A* **2008**, *197*, 253.
(37) (a) Okada, M.; Harada, A. *Org. Lett.* **2004**, *6*, 361. (b) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456. (c) Nepogodiev, S. A.; Stoddart, J. F. *Chem. Rev.* **1998**, *98*, 1959.
(38) (a) Li, G.; McGown, L. B. *Science* **1996**, *264*, 249. (b) Agbaria, R. A.; Gill, D. *J. Phys. Chem.* **1988**, *92*, 1052. (c) Agnew, K. A.; McCarley, T. D.; Agbaria, R. A.; Warner, I. M. *J. Photochem. Photobiol. A* **1995**, *91*, 205.
(39) Roy, D.; Mondal, S. K.; Sahu, K.; Ghos, S.; Sen, P.; Bhattacharyya, K. *J. Phys. Chem. A* **2005**, *109*, 7359.
(40) Armstrong, D. W.; He, L.; Liu, Y. S. *Anal. Chem.* **1999**, *71*, 3873.
(41) Summers, C. A.; Flowers, R. A. *Protein Sci.* **2000**, *9*, 2001.
(42) Evans, D. F.; Yamauchi, A.; Roman, R.; Casassa, E. Z. *J. Colloid Interface Sci.* **1982**, *88*, 89.
(43) (a) Hazra, P.; Sarkar, N. *Chem. Phys. Lett.* **2001**, *342*, 303. (b) Hazra, P.; Sarkar, N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1040. (c) Hazra, P.; Chakrabarty, D.; Sarkar, N. *Chem. Phys. Lett.* **2002**, *358*, 523. (d) Hazra, P.; Chakrabarty, D.; Sarkar, N. *Langmuir* **2002**, *18*, 7872.
(44) (a) Indirapriyadharshini, V. K.; Karunanity, P.; Ramamurthy, P. *Langmuir* **2001**, *17*, 4056.(b) Atkins, P.; De Paula, J. *Physical Chemistry*, 8th ed.; W. H. Freeman and Company: New York, 2006; p 212.
(45) Park, J. W.; Song, H. J. *J. Phys. Chem. B* **1989**, *93*, 6454.
(46) He, Y.; Chen, Q.; Xu, C.; Zhang, J.; Shen, X. *J. Phys. Chem. B* **2009**, *113*, 231.
(47) (a) Quitevis, E. L.; Marcus, A. H.; Fayer, M. D. *J. Phys. Chem.* **1993**, *97*, 5762. (b) Wittouck, N. W.; Negri, R. M.; De Schryver, F. C. *J. Am. Chem. Soc.* **1994**, *116*, 10601. (c) Krishna, M. G. M.; Das, R.; Periasamy, N.; Nityananda, R. *J. Chem. Phys.* **2000**, *112*, 8502. (d) Dutta, G. B. *J. Phys. Chem. B* **2003**, *107*, 10546. (e) Sen, S.; Sukul, D.; Dutta, P.; Bhattacharyya, K. *J. Phys. Chem. A* **2001**, *105*, 7495.
(48) Fee, R. S.; Maroncelli, M. *Chem. Phys.* **1994**, *183*, 235.
(49) Bose, S.; Adhikary, R.; Mukherjee, P.; Song, X.; Petrich, J. W. *J. Phys. Chem. B* **2009**, *113*, 11061.
(50) Headley, L. S.; Mukherjee, P.; Anderson, J. L.; Ding, R.; Halder, M.; Armstrong, D. W.; Song, X.; Petrich, J. W. *J. Phys. Chem. A* **2006**, *110*, 9549.
(51) Mukherjee, P.; Crank, J. A.; Sharma, P. S.; Wijeratne, A. B.; Adhikary, R.; Bose, S.; Armstrong, D. W.; Petrich, J. W. *J. Phys. Chem. B* **2008**, *112*, 3390.
(52) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 5044.
(53) Bader, J. S.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501.
(54) (a) Balasubramanian, S.; Bagchi, B. *J. Phys. Chem. B* **2001**, *105*, 12529. (b) Pal, S.; Balasubramanian, S.; Bagchi, B. *J. Chem. Phys.* **2002**, *117*, 2852. (c) Pal, S.; Balasubramanian, S.; Bagchi, B. *J. Phys. Chem. B* **2003**, *107*, 5194.
(55) Kahlow, M. A.; Kang, T. J.; Barbara, P. F. *J. Chem. Phys.* **1988**, *88*, 2372.
(56) (a) Maroncelli, M. *J. Mol. Liq.* **1993**, *57*, 1. (b) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.
(57) Arzhantsev, S.; Jin, H.; Baker, G. A.; Maroncelli, M. *J. Phys. Chem. B* **2007**, *111*, 4978.
(58) (a) Jin, H.; Baker, G. A.; Arzhantsev, S.; Dong, J.; Maroncelli, M. *J. Phys. Chem. B* **2007**, *111*, 7291. (b) Ito, N.; Arzhantsev, S.; Heitz, M.; Maroncelli, M. *J. Phys. Chem. B* **2004**, *108*, 5771. (c) Ingram, J. A.; Moog, R. S.; Ito, N.; Biswas, R.; Maroncelli, M. *J. Phys. Chem. B* **2003**, *107*, 5926. (d) Arzhantsev, S.; Ito, N.; Heitz, M.; Maroncelli, M. *Chem. Phys. Lett.* **2003**, *381*, 278. (e) Ito, N.; Arzhantsev, S.; Maroncelli, M. *Chem. Phys. Lett.* **2004**, *396*, 83.
(59) Chapman, C. F.; Maroncelli, M. *J. Phys. Chem.* **1991**, *95*, 9095.

(60) (a) Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1994**, *98*, 10819. (b) Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1994**, *98*, 3295.
(61) (a) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 4447. (b) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 6670.
(62) Song, X. *J. Chem. Phys.* **2009**, *131*, 044503.
(63) Halder, M.; Headley, L. S.; Mukherjee, P.; Song, X.; Petrich, J. W. *J. Phys. Chem. A* **2006**, *110*, 8623.
(64) (a) Shim, Y.; Duan, J. S.; Choi, M. Y.; Kim, H. J. *J. Chem. Phys.* **2003**, *119*, 6411. (b) Shim, Y.; Choi, M. Y.; Kim, H. J. *J. Chem. Phys.* **2005**, *122*, 44511. (c) Shim, Y.; Jeong, D.; Manjari, S.; Choi, M. Y.; Kim, H. J. *Acc. Chem. Res.* **2007**, *40*, 1130.
(65) Kobrak, M. N.; Znamenskiy, V. *Chem. Phys. Lett.* **2004**, *395*, 127.
(66) (a) Kobrak, M. N. *J. Chem. Phys.* **2006**, *125*, 64502. (b) Jeong, D.; Shim, Y.; Choi, M. Y.; Kim, H. J. *J. Phys. Chem. B* **2007**, *111*, 4920. (c) Bhargava, B. L.; Balasubramanian, S. *J. Chem. Phys.* **2006**, *125*, 219901. (d) Huang, X. H.; Margulis, C. J.; Li, Y. H.; Berne, B. J. *J. Am. Chem. Soc.* **2005**, *127*, 17842. (e) Liu, X.; Zhou, G.; Zhang, S.; Wu, G.; Yu, G. J. *J. Phys. Chem. B* **2007**, *111*, 5658. (f) Ghatee, M. H.; Ansari, Y. *J. Chem. Phys.* **2007**, *126*, 154502. (g) Kashyap, H. K.; Biswas, R. *J. Phys. Chem. B* **2008**, *112*, 12431.
(67) Kashyap, H. K.; Biswas, R. *J. Phys. Chem. B* **2010**, *114*, 254.
(68) Seth, D.; Chakraborty, A.; Setua, P.; Sarkar, N. *J. Phys. Chem. B* **2007**, *111*, 4781.
(69) Rao, V. G.; Ghatak, C.; Pramanik, R.; Sarkar, S.; Sarkar, N. *Chem. Phys. Lett.* **2010**, *499*, 89.
(70) (a) Huang, L.; Lin, J. M.; Yu, L.; Xu, L.; Chen, G. *Electrophoresis* **2009**, *30*, 1030. (b) Francois, Y.; Varenne, A.; Juillerat, E.; Villemin, D.; Gareil, P. *J. Chromatogr., A* **2007**, *1155*, 134.