Solvation Dynamics of Coumarin 480 in Bile Salt−Cetyltrimethylammonium Bromide (CTAB) and Bile Salt−Tween 80 Mixed Micelles

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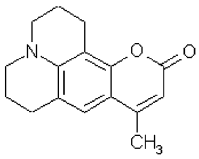
We have reported the retardation of solvation dynamics of Coumarin 480 (C-480) in the Stern layer of the cetyltrimethylammonium bromide (CTAB)−sodium deoxycholate (NaDC) and Tween 80−NaDC mixed micelles compared to pure water using picosecond time-resolved emission spectroscopy. The slow solvation dynamics in the Stern layer of the mixed micelles is due to the water molecules confined in the Stern layer, counterions, and interactions of the counterions with the headgroups of the surfactant. The rotational relaxation time of C-480 in these mixed micelles is also investigated. The rotational relaxation times are retarded in the Stern layer of the mixed micelles.

1. Introduction

There are mainly two types of water molecules present in nature, bulk water and the water in the immediate vicinity of biomolecules. Many aspects of structure and dynamics of bulk water are reasonably understood, but the same is not true for water found in interfacial or restricted environments (such as the surface of the proteins, micelles, or inside the pool of a reverse micelles). Since the most important biological processes occur in organized and restricted environments, the dynamics of the water molecules in theses environments have been studied by various techniques such as solvation[1−4] and dielectric relaxation.[5] Fleming et al.[6,7] have observed the solvation time of bulk water is very fast (<1 ps) using Coumarin 343 and Coumarin 480 (C-480, Scheme 1) as probes. But the dynamics of water in the restricted environments are bimodal, consisting of one subpicosecond component (comparable to bulk water) and another nanosecond slow component. Bagchi et al.[8,9] proposed a "dynamic exchange model" for reverse micelles and proteins to explain the slow solvation dynamics. Fleming et al.[7] first reported slow solvation of water molecules in the cyclodextrin cavity. Since then such studies were reported for micelles,[10] reverse micelles and microemulsions,[4,11−14] DNA,[15a] poly(ethylene glycol) and crown ethers,[15b] and unimolecular micelles.[15c] Recently, we have reported the slow solvation in the Stern layer of TX-100−bile salt (sodium deoxycholate, NaDC) mixed micelles using C-480 as a probe.[16] There are some simulation studies using reverse micelles[17] and micelles[18] as model systems.

Bile salt represents the class of amphiphilic potential biosurfactant synthesized in the liver and stored in the gallbladder.[19] Bile salt is different from other surfactants. It has a hydrophobic steroidal skeleton and hydrophilic moiety comprising hydroxyl groups, carboxylate anions, and sodium cation. But like ordinary surfactants, it does not have polar headgroups or a nonpolar alkyl chain. The polarity is much smaller than SDS micelles, but the microvisocity of bile salt is much higher.[20] In bile salt, the hydroxyl groups are present in the concave face and hydrophobic groups in the convex side. Thus, bile salt molecules get planar polarity, which helps in their aggregation.

SCHEME 1. Structure of Coumarin 480



Bile salt aggregates are involved in a variety of biologically important functions such as lipid, lecithin and cholesterol solubilization, billiary secretion, and regulation of cholesterol metabolism.[19,21−22] The vital bioactivities of bile salts are found at concentrations much above the critical micelle concentration (cmc). At low concentrations (∼10 mM), they form primary structures with low aggregation numbers. At high concentrations (∼60 mM), this primary structure produces a secondary structure or rodlike super grown micelles.[23,24] The aggregation behavior of bile salt can be explained with the help of Small's primary/secondary aggregation model.[19] Primary aggregations are formed by a small number of monomers (2−10) and can incorporate hydrophobic molecules within their core. At high concentrations, these primary aggregates associated together via hydrogen bonds between the hydroxyl groups and side chain groups to form large secondary structures. From small angle neutron scattering study,[23,24] the structure of the secondary aggregates resembles an elongated rod with a center hydrophilic core filled with water and ions. In case of NaDC, the length of the rod is about 32 Å and radius is 8 Å.

Mixtures of surfactant solutions usually form mixed micelles aggregates. Their properties are remarkably different from those of the individual components.[25,26] Like micelles, the core of the mixed micelles is essentially dry and contains the hydrocarbon chain. At the periphery, there is a "wet" shell containing headgroups of both the surfactants and counterions. This is the Stern layer. Mixed micellar aggregation can be used for various commercial applications and in various industrial formulations. In recent years, a number of studies involving bile salt and other surfactants have been published.[16,27−29] Most of the biological functions of the bile salts depend on the formation of the mixed species involving bile salts and biological lipids.[27]

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In our previous work,[16] we have reported the solvation dynamics of bile salt (NaDC) and Triton-X 100 mixed micelles using C-480 as a probe. The solvation time of C-480 in pure NaDC is also reported (3.37 ns). In this paper we report the solvation dynamics of C-480 in the Stern layer of mixed micelles of bile salt with another neutral surfactant, Tween 80 (polyoxyethylene sorbitan monooleate), and bile salt with a cationic surfactant, CTAB (cetyltrimethylammonium bromide). We also report here how the solvation dynamics of C-480 is affected in the Stern layer of 2:1 CTAB:NaDC (∼7 mM), 1:2 CTAB:NaDC (∼9 mM) and 1:3 Tween 80:NaDC (∼0.5 mM), 3:1 Tween 80: NaDC (∼1.5 mM) mixed micelles as well in pure Tween 80 (∼1.0 mM) micelle.

2. Experimental Section

Coumarin 480 (Laser grade from Exciton), NaDC (Sigma), Tween 80, and CTAB (Aldrich) were used as received. The solutions were prepared using literature procedures.[28,29] The concentration of C-480 was kept at 5×10^{-5} M. A Shimadzu spectrophotometer (model no. UV1601) and a Spex Fluorolog-3 (model no. FL3-11) spectrofluorimeter were used for absorption and fluorescence measurements, respectively. The excitation wavelength for the steady-state experiment was 408 nm. The fluorescence spectrum was corrected for the spectral sensitivity of the instruments.

For picosecond time-correlated single-photon counting measurements we used a picosecond laser diode (IBH, UK) at 408 nm. The signal was detected at the magic angle (54.7°) polarization using a Hamamatsu MCP PMT (3809U). The time resolution of our experimental setup was ∼85 ps. For anisotropy measurements we used the same setup. The analysis of the decay and anisotropy data was done by IBH DAS6 decay analysis software. All the decays were fitted with a biexponential function because the χ^2 was close to 1.2 for the biexponential fit, which indicates a good fit. For other types of fitting, χ^2 is much greater than 2. The temperature was kept constant (298 ± 1 K) for all measurements. The time-resolved emission spectrum (TRES) is constructed using the method of Maroncelli and Fleming[30] and described in our earlier publication.[31]

3. Results and Discussion:

3.1. Steady-State Absorption and Emission Spectra. The absorption peak of C-480 in pure water is at 392 nm. However, on addition of surfactant there is almost no change in the absorption spectrum. The absorption spectra of C-480 in different mixed micellar compositions are shown in Figure 1 and results are summarized in Table 1. The emission peak of C-480 in pure water is at 490 nm. But in a mixed micellar surface the emission maxima are blue-shifted to ∼480 nm. The emission spectra are shown in Figure 1 and results are summarized in Table 1. The emission peak of C-480 in CTAB−NaDC mixed micelles is at around 477 nm and in Tween 80−NaDC mixed micelles is at around 479 nm, whereas in pure Tween 80 it is at 481 nm. The emission maximum of C-480 in methanol is 477 nm. So, the emission maxima in the mixed micelles are close to that of methanol. It indicates that the polarity of the mixed micelles resembles that of methanol. The blue shift in the emission spectra of C-480 indicates that the probe molecules are moving from polar aqueous phase to the relatively nonpolar surface of mixed micelles. Moreover, the peak position of C-480 in nonpolar media like *n*-heptane is around 410 nm. In the mixed micelles the intensity of the emission spectra is much lower at around 410 nm. This indicates that very few probe molecules are residing in the hydrocarbon core.

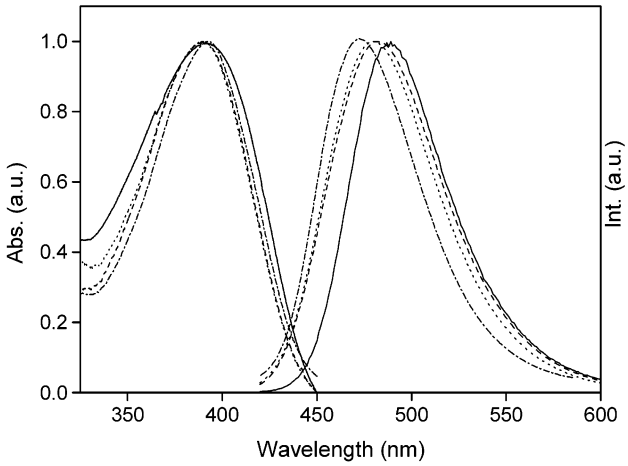

Figure 1. Steady-state absorption and emission spectra of C-480 in water and mixed micelles. Solid lines are for water, dashed lines are for pure Tween 80, dotted lines are for 1:3 Tween 80:NaDC mixed micelle, and dashed−dotted lines are for 2:1 CTAB:NaDC mixed micelle.

TABLE 1: Steady State Absorption and Emission Spectra of C-480 in Pure Tween 80 and Different Compositions of Mixed Micelles

composition	λ_{abs}(max)/nm	λ_{em}(max)/nm
pure Tween 80	389(±2)	481(±1)
Tween 80:NaDC (3:1)	389(±2)	479(±1)
Tween 80:NaDC (1:3)	389(±2)	479(±1)
CTAB:NaDC (1:2)	390(±2)	477(±1)
CTAB:NaDC (2:1)	392(±2)	477(±1)
water	392(±2)	490(±1)

3.2. Time-Resolved Fluorescence Anisotropy Measurements. In solvation dynamics measurement the location of the probe molecules is very important because it predicts the dynamics. We can predict the location of the probe molecules using time-resolved fluorescence anisotropy measurements. The anisotropy decay ($r(t)$) is given by

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) - 2GI_{\perp}(t)} \quad (1)$$

where $I_{\parallel}(t)$ and $I_{\perp}(t)$ are fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. The G factor for our case is 0.6. The representative anisotropy decays of C-480 in pure water, 1:2 CTAB:NaDC mixed micelles, and 1:3 Tween 80:NaDC mixed micelles are shown in Figure 2. The fluorescence anisotropy decays were fitted with a biexponential function in most cases and are shown in Table 2. The intial anisotropy value $r(0)$ is also shown in Table 2. The rotational relaxation of C-480 in pure water was fitted with a single-exponential function, and the anisotropy decay time is 125 ps.[16] The time constant of the anisotropy decay of C-480 in water measured by us was relatively large in comparison to the time constant reported by another group.[15c] This may arise due to the higher instrument response in our setup (∼ 85 ps). From Table 2 it is revealed that in all the mixed micelles and in pure Tween 80 micelles the rotational relaxation time consists of two components, one picosecond and another nanosecond component. As for example, in 1:3 Tween 80:NaDC mixed micelles the rotational relaxation is biexponential, having a time constant of 185 ps and 1.97 ns, respectively. For the 1:2 CTAB:NaDC system, the rotational relaxation is also biexponential, having time constants of 355 ps and 3.87 ns, respectively. A similar type of bimodal rotational relaxation in micelles

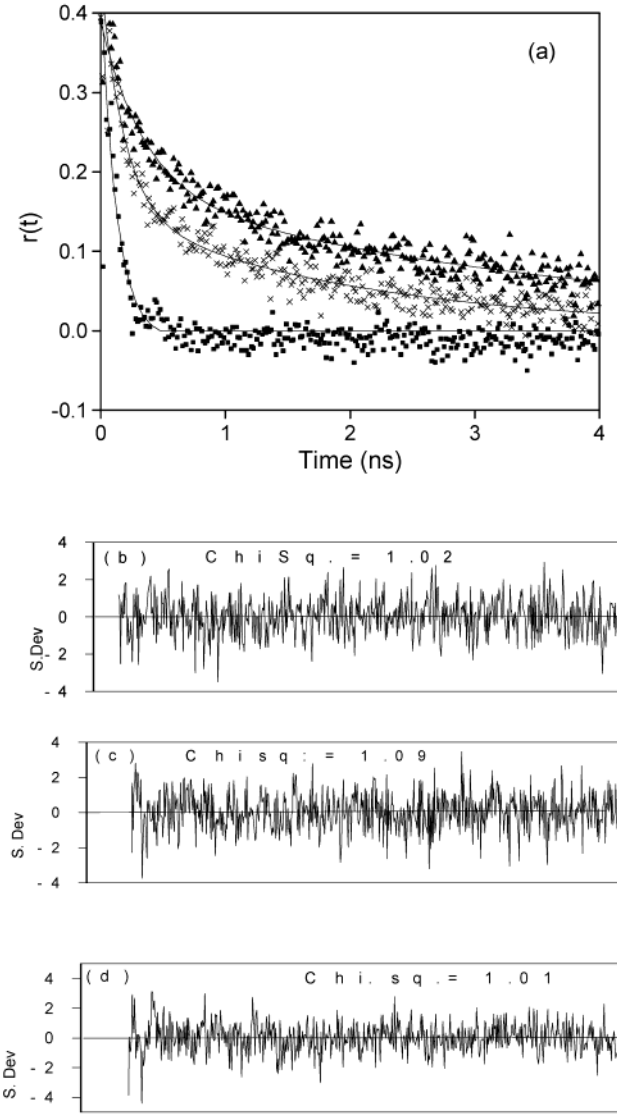

Figure 2. (a) Decay of fluorescence anisotropy ($r(t)$) of C-480 in pure water (■), in 1:3 Tween 80:NaDC (×), and in 1:2 CTAB:NaDC (▲) mixed micelles. The error in the experimental data is ±10%. (b−d) Standard deviations for the best fitted results for 1:3 Tween 80:NaDC, 1:2 CTAB:NaDC mixed micelles, and pure water, respectively.

TABLE 2: Initial Anisotropy Values (r_0) and Rotational Relaxation Time (τ_r) of C-480 in Pure Water, Pure Tween 80 Micelles, and Mixed Micelles

composition	r_0	a_{1r}	τ_{1r} (ns)	a_{2r}	τ_{2r} (ns)	$\langle\tau_r\rangle^{a,b}$ (ns)
pure Tween 80	0.40	0.70	0.150	0.30	1.50	0.555
Tween 80:NaDC (3:1)	0.40	0.65	0.221	0.35	1.95	0.826
Tween 80:NaDC (1:3)	0.39	0.64	0.185	0.36	1.97	0.828
CTAB:NaDC (1:2)	0.39	0.54	0.355	0.46	3.87	1.97
CTAB:NaDC (2:1)	0.40	0.57	0.324	0.43	3.23	1.57
pure water[c]	0.40	0.40	0.125			0.125

[a] $\langle\tau_r\rangle = a_{1r}\tau_{1r} + a_{2r}\tau_{2r}$. [b] Error in experimental data ±10%. [c] From ref 16.

was reported by several groups.[32] Both of the components of rotational relaxation time in mixed micelles and pure Tween 80 micelle are slower compared to the rotational relaxation time of C-480 in water (125 ps). This fact strongly suggests that probe molecules are residing at the micellar surface. This conjecture was also supported by Fayer et al.[32a] The average rotational relaxation times in pure Tween 80, CTAB, and NaDC are 555, 610, and 547 ps, respectively. So, the average rotational relaxation times in mixed micelles are much slower compared

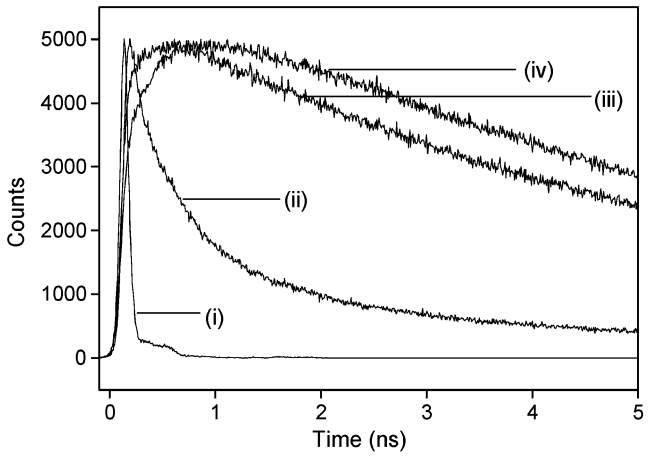

Figure 3. Fluorescence decays of C-480 in 2:1 CTAB:NaDC mixed micelle at (i) instrument response function (IRF), (ii) 435 nm, (iii) 480 nm, and (iv) 570 nm. The error in the experimental data is ±5%.

to pure micelles. The slow rotational relaxation time in mixed micelles may arise due to the high viscosity of the mixed micelles compared to pure micelles.[33] The average rotational relaxation time in 1:2 CTAB:NaDC micelles is 1.97 ns, which is higher compared to the rotational relaxation time (1.57 ns) in 2:1 CTAB:NaDC micelles. These data suggest that there are more close-packed structures in the mixed micelle in the presence of high NaDC concentration. Various model such as "wobbling-in-a-cone" and the two-step model have been used to explain the rotational relaxation in mixed micelles and micelles.[32] There are various motions responsible for fluorescence depolarization in a micelles and mixed micelles, such as wobbling of the probe in a cone, translational motion of the probe along the surface of the spherical micellar aggregates, and overall tumbling of the micelles and mixed micelles.[32]

3.3. Solvation Dynamics. In all the mixed micelles and in pure Tween 80 micelles, wavelength dependence fluorescence decays are observed. Moreover, the decay at long wavelength exhibits a distinct growth on the nanosecond time scale, indicating that the guest dipole is gradually solvated with time, thus lowering its energy and shifting to the longer wavelength. Representative decays of C-480 in 2:1 CTAB:NaDC mixed micelles at 435, 480, and 570 nm are shown in Figure 3. A few dye molecules (if any) in the hydrocarbon core do not show any wavelength dependence decays and the dynamics in the bulk water is too fast (310 fs)[7] to be detected by our setup (time resolution ~85 ps). So, the probe molecules residing in the Stern layer of the mixed micelles are responsible for the observed time-dependent Stokes' shift. The solvation dynamics is quantitatively measured with the help of solvation time correlation function $C(t)$, which is defined as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \tag{2}$$

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ are the peak frequencies at time zero, t, and infinity, respectively. The peak emission frequency was evaluated from the time-resolved emission spectra (TRES). A representative TRES for 1:2 CTAB:NaDC mixed micelle is shown in Figure 4. The decay characteristics of $C(t)$ for all the mixed micelles and pure Tween 80 are shown in Figure 5. The decay characteristics of $C(t)$ are summarized in Table 3. It is revealed from Table 3 that the solvation time in the mixed micelles and in pure Tween 80 micelle is slowing down compared to the solvation time of C-480 in pure water.[7] The

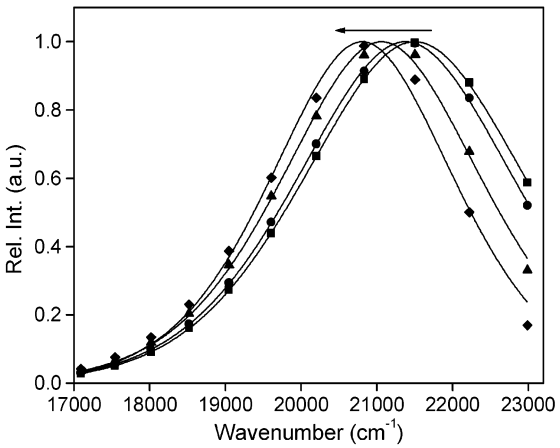

Figure 4. Time-resolved emission spectra of C-480 in 1:2 CTAB: NaDC mixed micelles at (i) 0 (■), (ii) 200 (●), (iii) 1000 (▲), and (iv) 3000 (◆) ps.

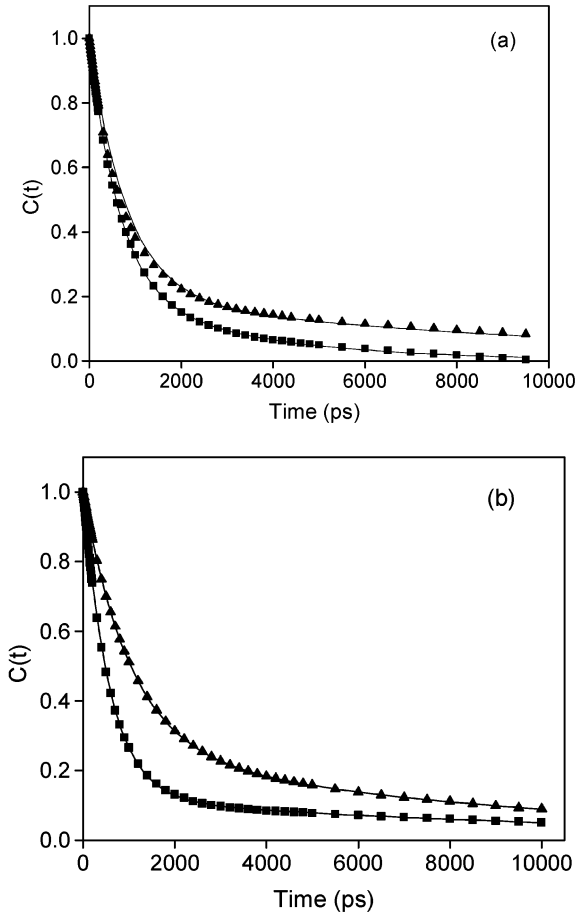

Figure 5. Decay of the solvent correlation function ($C(t)$) of C-480 in (a) pure and mixed micelles of Tween 80 and NaDC, (■) for pure Tween 80, and (▲) for 3:1 Tween 80:NaDC, and (b) mixed micelles of CTAB and NaDC, (■) for 2:1 CTAB:NaDC, and (▲) for 1:2 CTAB: NaDC.

solvation dynamics in the mixed micelles are relatively slower compared to the solvation dynamics of C-480 in γ-cyclodextrin,[7] as the solvation time in γ-CD is 480 ps. But the solvation times in mixed micelles are relatively faster than the water molecules in the core of the reverse micelles.[4,11−14,31]

3.3.1. Solvation Dynamics in Tween 80:NaDC Mixed Micelles. We had earlier reported the solvation dynamics in the pure NaDC micelle.[16] The solvation time of NaDC micelle was 3.37 ns, which is very close to the solvation time reported by

TABLE 3: Decay Characteristics of $C(t)$ of Coumarin 480 (C-480) in Pure Tween 80 and in Different Mixed Micelles

composition	$\Delta\nu$ (cm^{-1})[a]	a_1	τ_1 (ns)	a_2	τ_2(ns)	$\langle\tau\rangle$[b,c](ns)
pure Tween 80	439	0.78	0.641	0.22	3.22	1.21
Tween 80:NaDC(3:1)	681	0.80	0.676	0.20	8.72	2.28
Tween 80:NaDC(1:3)	600	0.79	0.797	0.21	9.10	2.54
CTAB:NaDC (2:1)	899	0.87	0.566	0.13	9.77	1.76
CTAB:NaDC (1:2)	898	0.72	0.993	0.28	8.32	3.04

[a] $\Delta\nu = \nu_0 - \nu_\infty$. [b] $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$. [c] Error in experimental data ±5%.

Bhattacharyya et al.[34] Now on addition of Tween 80 to NaDC the mixed micelles are formed. The stability of the mixed micelles formed by addition of Tween 80 to the ionic NaDC micelles is explained from the thermodynamic standpoint. From Table 3 it is revealed that in all the mixed micelles of Tween 80−NaDC system and in pure Tween 80, $C(t)$ consist of two components, one picosecond component and another nanosecond component. In Table 3 we have reported the weighted average ($\langle\tau\rangle$) of the solvation time to compare the results in the mixed micelles. In micelles or biomolecules the bimodal solvation dynamics is usually explained with the help of the dynamic exchange model of Bagchi et al.[8,9] In this model, they assume a dynamic exchange between the "free" and "bound" water molecules. The existence of two types of water molecules in micelles was reported by Balasubramanian et al.[18c] The energetics of the exchange depends on the strength and number of hydrogen bonds among the bound water molecules and biomolecules/micelles. The relative population of the slow component increases due to the increase in strength of the hydrogen bond. This can explain the solvation dynamics in relatively two different time scales. So, it is justifiable to take the weighted average for reporting the solvation time. With addition of Tween 80 to NaDC, average solvation time decreases. For 1:3 Tween 80:NaDC, the average solvation time is 2.54 ns, whereas for 3:1 Tween 80:NaDC the average solvation time is 2.28 ns. We have also determined the solvation time of Tween 80 as 1.21 ns. This is very close to the solvation time of C-480 in another neutral micelle, Triton X-100.[10] A Tween 80 molecule consists of several polyoxyethyelene groups, and water molecules can bind with the oxygen atom of these polyoxyethyelene groups. This may be a possible reason for the slow dynamics in Tween 80. Recently, Shirota et al.[15b] measured the solvation dynamics of Coumarin 153 in poly(ethylene glycol)s and attributed the fast dynamics to the cooperative motion arising for the local dynamics of the ethylene oxide part of the poly(ethylene glycol)s. Similar contribution of poly(ethylene oxide) may be responsible for the slow solvation dynamics in Tween 80. In the mixed micelles the polar headgroups of the surfactants, counterions, and water molecules are responsible for solvation. But polar headgroups reside at the one end of the long alkyl chain and mobility will be much slower because chain dynamics are quite slow (∼100 ns).[35] So, counterions and water molecules contribute to the solvation dynamics in mixed micelles. The fast component of $C(t)$ may arise due to the water molecule present in the Stern layer. Recently, Balasubramanian et al.[18c] carried out a molecular simulation study and showed that hydrogen bonds between water molecules and polar headgroups of the micelles are 13 times stronger than the hydrogen bond between two tagged water molecules. Na^+ may also contribute to the slow component. There are several reports of the slow ionic solvation. Huppert et al.[36] examined how the slow solvation in the molten salt was contributed by the translational motion of the Na^+ ions. Chapman et al.[37] also verified the role of ions in the slow dynamics. The interaction of the counterions

with the polar headgroups may retard the solvation time. The average solvation time in mixed micelles is less compared to that in pure NaDC. The most probable explanation is the removal of the Na^+ ions from the Stern layer of the mixed micelles as we increased the concentration of Tween 80. Balasubramanian et al.[18d] executed a detailed molecular dynamics simulations study with cesium pentadecafluorooctanoate (CsPFO) in water and showed that the observed slow dynamics in the micellar surface was contributed by the interaction of the cesium ion with the polar headgroup and the orientational motion of the water molecules played a secondary role. Moreover, with the increase in bile salt concentration, the number of the water molecules in the Stern layer bound to hydroxyl groups via hydrogen bonds and to the carboxylate and sodium ions via electrostatic force increased, which may be a possible cause for the retardation of solvation time.

Though we have observed the slow dynamics in the Stern layer of the mixed micelles, a substantial portion of the dynamics, i.e., less that 85 ps, is missed due to the limited time resolution of our instrument. The steady-state Stokes' shift in pure Tween 80, $\sim$1950 cm^{-1}, is larger compared to that in nonpolar solvent. We have also calculated "time zero" spectrum using the procedure of Fee and Maroncelli.[38] This indicates a total value of Stokes' shift $\sim$2150 cm^{-1}. The observed spectral shift is 439 cm^{-1}. Thus for pure Tween 80 we are missing $\sim$80% of the spectral shift. For Tween 80:NaDC mixed micelles one should observe a total shift of $\sim$1850 cm^{-1} (from steady-state spectra) or $\sim$2100 cm^{-1} (from time zero spectrum). Thus, we are missing $\sim$70% of the total spectral shift. The results are reasonable because Fleming et al. pointed out that contribution of the slow relaxation in the solvation dynamics is expected to be 5−20%.[39]

3.3.2. Solvation Dynamics in NaDC:CTAB Mixed Micelles. Table 3 reveals that $C(t)$ for 2:1 CTAB:NaDC mixed micelle consists of two components of 0.566 and 9.77 ns time scale with 0.87 and 0.13 relative amplitudes. But for 1:2 CTAB:NaDC mixed micelles, the solvation times and relative amplitudes are as follows: $\tau_1 = 0.993$ ns ($a_1 = 0.72$) and $\tau_2 = 8.32$ ns ($a_2 = 0.28$). The average solvation time also increases (from 1.76 to 3.04 ns) in mixed micelles containing more NaDC. The solvation time of C-480 in pure CTAB micelles was already reported.[10a] It consisted of two components with time constant of 285 ps (40%) and 600 ps (60%), and the average solvation time was 474 ps. So, solvation dynamics of C-480 in mixed micelles is slower compared to that in pure CTAB micelles. Moreover, with the increase in NaDC concentration the decay time of the fast component of $C(t)$ increases with decrease in relative amplitude. We ascribe the fast component of solvation time due to the water molecules present in the Stern layer of the mixed micelles. Molecular dynamics simulation by Balasubramanian et al.[18d] also suggests that the dynamics in the Stern layer is slow compared to bulk water. The slow component may arise due to the counterions, interaction of counterions with headgroups. NaDC molecules have a polar face (made up with hydroxy groups and carboxylate groups) and a nonpolar face made up of the hydrocarbon segments of the steroid backbone. Mazer et al.[40] showed that a large fraction of the polar face remains exposed to the hydrocarbon elements, between the polar groups. Now insertion of the bile salt molecules (only the negatively charged carboxylate ions in the headgroup region) between cationic CTAB micelles would decrease the average area per surfactant molecules, due to the mutual attraction between the opposite charges, and give a somewhat larger contribution to the core volume than that of surfactant. So, an increase in NaDC concentration causes more close-packed or more oraganized mixed micelles.[33] Almgren et al.[33] also support this conjecture. Moreover, addition of bile salt causes major portions of water molecules in the Stern layer bound to hydroxyl groups and to carboxylate sodium ions. So, the mobility of the water molecules in the Stern layer of the mixed micelles is relatively slower with increasing NaDC concentration. For this reason, the decay time of the fast component of $C(t)$ increases with an increase in NaDC concentration in micelles. The anisotropy data also supports this fact. The rotational relaxations in CTAB−NaDC mixed micelles are slower than for the Tween 80−NaDC mixed micelles. The rotational relaxation time also increases with increase in NaDC concentration in the case of CTAB−NaDC mixed micelles. Almgren et al.[33] also showed that the viscosity of the mixed micelles increases dramatically with an increase in the NaDC concentrations. It may also retard the solvation time and rotational relaxation time. The addition of bile salt molecules shields the probe molecules from the aqueous environments; consequently, the relative amplitudes of the fast component decrease with an increase in NaDC concentration. A similar type of shielding is also observed by Almgren et al.[33] For CTAB−NaDC mixed micelles we observed $\sim$1650 cm^{-1} (from steady-state spectra) or $\sim$1900 cm^{-1} (from time zero spectrum) as the total spectral shift. The observed Stokes' shift in these systems was $\sim$900 cm^{-1}. Thus, in these systems we are missing $\sim$50% of the total spectral shift.

Coumarin binds preferentially to micelles. Due to the dipole moment change upon excitation, its optimum location in the Stern layer of the micelles and mixed micelles and its prefer distance from the nonpolar aliphatic core may change. The slow nanosecond component may correspond to the velocity change of such a process. The rotational diffusion of Coumarin in micelles and mixed micelles is double exponential and a slow time constant appears on the nanosecond time scale. The slow component of the solvent correlation function is even larger. It suggests that the monitored change in the solvation dynamics may be due, in part, to the motion of the probe with respect to the micelle and mixed micelle and by the segmental dynamics of the corresponding ionic part.

4. Conclusions

In this present work, we have observed retardation of solvation time of C-480 in the Stern layer of Tween 80−NaDC and CTAB−NaDC mixed micelles. The solvation time in pure Tween 80 is 1.21 ns, whereas in pure NaDC it is 3.37 ns.[16,34] The water molecules in the Stern layer and the counterions are responsible for solvation in mixed micelles. With the increase in bile salt concentration in mixed micelles, the contribution of the Na^+ increases, leading to a relatively slow solvation dynamics in Tween 80−NaDC mixed micelles. The addition of the bile salt in the CTAB micelles causes more closely packed mixed micelles. So, the mobility of the water molecules is retarded. Thus solvation time increases with increase in NaDC concentrations in the case of CTAB−NaDC mixed micelles. Moreover, dynamics observed in the Stern layer of the mixed micelles using C-480 is several time slower compared to ultrafast solvation of the same probe in pure water (310 fs).[7] We have also observed slow rotational relaxation in the mixed micelles and micelles compared to pure water.

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