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Tuning the Probe Location on Zwitterionic Micellar System with Variation of pH and Addition of Surfactants with Different Alkyl Chains: Solvent and Rotational Relaxation Studies

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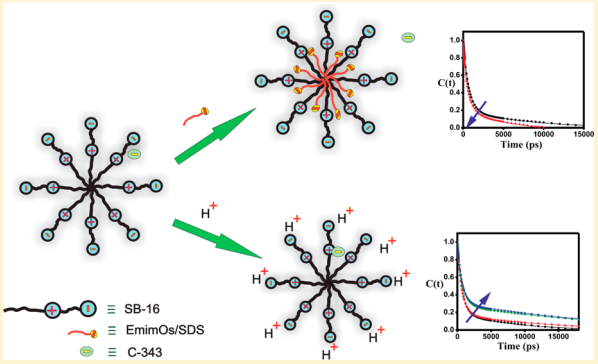
Supporting Information

ABSTRACT: In this manuscript, we have modulated the location of an anionic probe, Coumarin-343 (C-343) in a zwitterionic (*N*-hexadecyl-*N*,*N*-dimethylammonio-1-propanesulfonate (SB-16)) micellar system by three different approaches. The effect of addition of the surfactant sodium dodecyl sulfate (SDS) and the room temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium octylsulfate (EmimOs) and *N*,*N*-dimethylethanol hexanoate (DAH), to the micellar solution has been studied. The effect of pH variation has been studied as well using solvent and rotational measurements. Migration of the anionic probe, C-343, from the palisade layer of SB-16 micelle to the bulk water has been observed to varying extents with the addition of SDS and EmimOs. The effect is much more pronounced in the presence of SDS and can be ascribed to the presence of the long alkyl (dodecyl) chain on SDS which can easily orient itself and fuse inside the SB-16 micelle and facilitate the observed migration of the probe molecule. This phenomenon is confirmed by faster solvation and rotational relaxation of the investigated probe molecule. The analogous fusion process is difficult in case of EmimOs and DAH because of their comparatively smaller alkyl (octyl and hexanoate) chain. However, the direction of C-343 migration is reversed with the decrease of pH of the SB-16 micellar medium. An increase in the average solvation and rotational relaxation time of the probe in acidic medium has been observed. Since experimental conditions are maintained such that the probe molecules and the zwitterionic SB-16 micelles remain oppositely charged, the observed results can be attributed to the increased electrostatic interaction (attractive) between them. Temperature dependent study also supports this finding.



1. INTRODUCTION

Surfactants have the ability to form micellar structures above the critical micelle concentration (CMC) and have been the subject of great interest due to their unusual physicochemical properties.[1−3] The micellar matrix can be controlled by adjusting variables such as water content, surfactant concentration, and obviously temperature. These organized assemblies play an important role in many applications such as nanomaterial synthesis,[4−6] drug delivery,[7] separation,[8] pharmaceutical formulations, and also other dispersant technologies.[8] They are also useful as solubilizing and emulsifying agents, flow field regulators, membrane mimetic media, and nanoreactors for enzymatic reactions.[3,9] Zwitterionic surfactants, whose hydrophilic polar head consists of both positive and negative charges, are interesting in several aspects. They exhibit pH dependent behavior and high foam stability and produce less skin-irritation compared to positively or negatively charged surfactants.[10] In spite of being well-known, very few articles have been published on zwitterionic surfactants. Their micelles have no net charge, but unlike other nonionic micelles, they can easily bind with both cations and anions[11−13] following the Hofmeister series and Pearson's hard−soft classification.[13−16] Interactions between ions and sulfobetaine have been well studied by Okada and co-workers using partition and ion-pair models.[15] They included the ionic potential term in the Poisson−Boltzmann equation in their partition model, whereas in the ion pair model, they considered the inner and outer potentials of zwitterionic micelle. Added ions change zwitterionic surfaces, affecting both the packing and surface charges, which should modulate properties of these surfaces. Because of these useful characteristics, zwitterionic surfactants are often combined with cationic and anionic surfactants for many industrial applications. A mixture of zwitterionic and ionic surfactants is very important due to their interesting rheological behavior. To further increase the utility of the zwitterionic micelles, we have investigated the effect of pH also, along with surfactants and surfactant like room temperature ionic liquids (RTILs).

RTILs are receiving much attention due to their unusual properties.[17,18] They are environmentally benign, nontoxic green solvents, with melting points below room temperature.[19] Substituted imidazolium ions are the most popular cationic components of the RTILs which are frequently used in

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combination with anions like $[BF_4]^-$, $[PF_6]^-$, and $[(CF_3SO_2)_2N]^-$. RTILs are also termed as "designer solvents" as one can easily modify their properties by changing the constituent ions.[20] Several chemical reactions have been carried out in RTILs with efficiency. RTILs have negligible vapor pressure and also recycled easily. ILs contain a long hydrophobic chain and a charged hydrophilic part, which draws much attention due to their structural similarity with ionic surfactants and their ability to form micellar aggregates. Nowadays, in order to investigate the physical and chemical properties of RTILs, several physical, photophysical, and ultrafast spectroscopic studies have been carried out on the RTILs.[21−28]

Studies on combinations of surfactants with ionic liquids are also becoming an attractive topic[29,30] as physicochemical properties of the surfactants can be modulated in such combinations. Formation of micelles with altered and desired physicochemical properties within aqueous IL solutions is both exciting and useful. Pandey et al. have shown the effect of addition of RTILs on aqueous surfactant solutions.[31−34] ILs with longer alkyl chain-lengths facilitate the micellization process, i.e., behave as cosurfactants, and depending on the concentration can act as cosolvents as well. Modification of physicochemical properties of aqueous surfactant solutions upon addition of IL is bound to advance their applications in various fields.

Many important biological reactions and fundamental processes take place at interfaces like membranes, which provide a restricted environment where the properties of the solvents change in a drastic manner. Various studies show that the structure of the water at interfaces is different from that in the bulk;[35,36] hence, the understanding of solvation dynamics in micelles and other confined media is essential for the better understanding of chemical reaction such as electron and charge transfer process in these organized assemblies. There have been extensive studies on solvation dynamics in different heterogeneous media such as micelles, reverse micelles, lipids, proteins, DNA, etc.[36−39] A lot of studies have shown that the motion of water molecules inside the micelles differ from that in the bulk.[40−44] By measuring the microviscosity inside reverse micelles of varying size using a molecular probe, Hasegawa et al. showed that the viscosity of water in small micelles is greater than that in bulk water.[40] Recently, several groups have studied dynamics of such water molecules by using many different techniques, which include dielectric relaxation,[45,46] solvation dynamics,[47−49] NMR relaxation dispersion (NMPD),[50,51] and intermolecular water−solute NOE studies.[52,53]

Time-dependent fluorescence Stokes Shift is a very powerful technique which can be used to characterize dynamical features of solvent.[54−58] This spectroscopic technique monitors the solvent reorganization process by using spontaneous electronic perturbation of a solvochromic fluorescence probe with a detection time of 10^{-13}−10^{-15} s (temporal response depends on the spectroscopic technique and the light source). Bhattacharrya and co-workers extensively studied the water dynamics in aqueous micellar solution.[58] They found that slowest solvation component of micellar solutions is 2−3 times slower than the bulk water. Pal et al. also observed the similar trend in case of protein hydration.[59] The solvation dynamics in neutral, cationic, and anionic micelles are different. In brief, the neutral TX-100 [hydrophobic part is poly(ethylene oxide)] micellar solution shows a quite large nanosecond solvation component with respect to cationic (cetyl trimethyl ammonium bromide, CTAB) and anionic (sodium dodecyl sulfate, SDS) micellar solutions. Here we reveal the water dynamics in the zwitterionic micellar system.

In this work, we showed that the surfactant−IL or surfactant−surfactant mixture can be used as a drug delivery vehicle using steady-state and time-resolved measurements. We used zwitterionic SB-16 micelles as a drug carrier with C-343 as the model drug molecule. So, our aim is to release this probe molecule from that organized assembly and also penetration of the probe molecule whenever needed. In this respect three methods have been employed; addition of an anionic surfactant (SDS) having a long alkyl chain, addition of RTIL (1-ethyl-3-methylimidazolium octylsulfate, EmimOs) having a comparatively smaller alkyl chain, and decreasing the pH of the solution. Our first goal, i.e., release of the probe molecules from the organized assembly, has been fulfilled by the addition of the IL (EmimOs) and surfactant (SDS) and our second goal i.e., penetration of the probe molecules being fulfilled by simply changing the pH of the micellar system. We showed that all methods are equally applicable depending on the direction of movement of the probe molecule. We also used *N*,*N*-dimethylethanol hexanoate (DAH) as a protic IL to see the effect of −OH moiety. Solvation experiments have also been done which give us the solute−solvent interaction, i.e., how quickly the solvent dipoles rearrange around a solute dipole created in a polar liquid. So, our aim was to choose solute molecules in such a way which shows a nearly zero dipole moment at the ground state but is very large in the excited state, so in our study we used C-343.

2. EXPERIMENTAL SECTION

2.1. Materials. SB-16 and SDS were purchased from Sigma-Aldrich and used as received. EmimOs (>99% purity) and H_2SO_4 were procured from Merck Chemicals and used as received. DAH (>99% purity) was obtained from Bioniqs. Coumarin-343 (laser grade, Exciton) was also used as received.

2.2. Sample Preparation. An aqueous SB-16 solution was prepared by taking the appropriate amount of SB-16 in doubly distilled deionized water (Milli-Q water) so that the final concentration of the solution was 28 mM. The probe (C343) solution was prepared in methanol. The appropriate volume of probe solution was taken in a 2 mL volumetric flask, methanol was evaporated using stream of nitrogen gas, and then 2 mL of the SB-16 solution (28 mM) was added to the same volumetric flask. The final concentration of probe molecules (C343) was kept at 4.43×10^{-5} M throughout the experiment. The required amounts of SDS, EmimOs, and DAH were added directly to the SB-16 solution. The pH of the solution has been changed from 7.0 to 4.8 by the addition of H_2SO_4. The structures of SDS, EmimOs, C343, and the zwitterionic surfactant (SB-16) are shown in Scheme 1.

2.3. Instrumentation. The absorption and fluorescence spectra were recorded using Shimadzu (model no. UV-2450) spectrophotometer and Hitachi (model no. F-7000) spectrofluorimeter. For steady-state experiments, all samples were excited at 408 nm. The details of the time-resolved setup are described in our earlier publication.[60] In brief, the samples were excited at 408 nm using a picosecond laser diode (IBH, Nanoled), and the signals were collected at the magic angle of 54.7° using a Hamamatsu microchannel plate photomultiplier tube (3809U), where the instrument response was 100 ps. The decay analysis was done by IBH DAS, version 6 software. All of the long and short wavelength decays were fitted biexponen-

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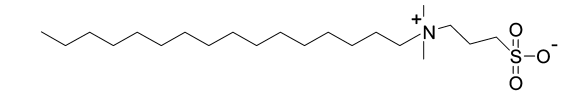
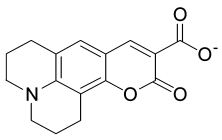
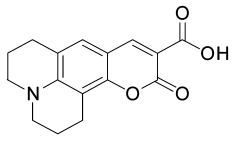
Scheme 1



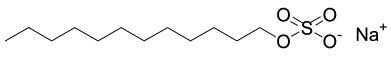
N-hexadecyl-N,N-dimethylammonio-1-propanesulfonate (SB-16)



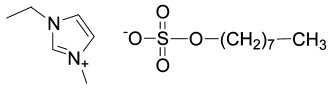
C-343, anionic form



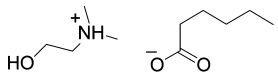
C-343, neutral form



Sodium dodecyl sulfate (SDS)



1-ethyl-3-methylimadazolium octylsulfate (EmimOs)



N,N-Dimethylethanolammonium Hexanoate (DAH)

tially by considering χ^2 becomes close to 1, indicating a good fit. For the anisotropy decays, we used a motorized polarizer in the emission side. The emission intensities at parallel and perpendicular polarizations were collected alternately, until a certain peak difference was reached between them. The peak differences depend on the tail matching of the parallel and perpendicular decays. The analysis of the data was done by IBH DAS, version 6 decay analysis software. For viscosity measurements, we used a Brookfield DV-II + Pro (Viscometer).

3. RESULTS AND DISCUSSION

3.1. Steady-State Studies. The absorption and emission spectra were taken in both neat water and SB- 16 micelles. Depending on the solution pH, the probe C-343 can exist in different prototropic forms (anionic and neutral) in water. At basic and neutral pH, C-343 mainly exists in the anionic form, but at acidic pH (pH <4), it exists in the neutral protonated form.[61,62] The absorption and emission spectra in the presence of different additives are illustrated in Figures 1−3. The absorbance peak of C-343 at 423 nm in neat water implies that our investigated probe exists in its anionic form under experimental condition[63] (The absorption and emission spectra in neat water are not shown here.) A gradual red shift in the absorption maximum is observed with the addition of EmimOs and SDS (Figures 1a and 2a). The emission peak of C-343 in neat water was found to be 490 nm, which is well supported by earlier reports.[61−63] In SB-16 micellar solution this peak shifts to 476 nm. This 14 nm shift in emission spectrum suggests that the environment experienced by the dye within the micelles differs from that in bulk water. When we added the external additives (SDS, EmimOs) or decreased the pH of the micellar medium for modulating the location of the dye, the isosbestic point is not observed in the absorption as well as the fluorescence emission spectra, suggesting that the observed shifts do not arise from two different forms of the dye, such as protonated and deprotonated, either in the ground or excited states. On addition of 10 mM EmimOs to a solution of C-343 in SB-16 micelles, the emission maximum of C-343 exhibits a marked red shift from 476 to 488 nm (Figure 1b). This red shift by 12 nm indicates the transfer of the C-343 molecules toward the bulk water. On increasing the concentration of EmimOs to 20 mM, the emission spectra of C-343 was red-shifted to 491 nm which remained unchanged on further addition of EmimOs. This bathochromic shift of the emission spectra of the dye with the increase in EmimOs concentration indicates an increase in the micropolarity around the probe molecules. We also obtained similar results on the addition of anionic surfactant (SDS), but the effect was more pronounced. With the addition of 10 mM SDS to 28 mM SB-16 micellar solution, the emission maximum of C-343 dye shifted from 476 to 491 nm (Figure 2b) which remained the same on further increase of the SDS concentration (up to 30 mM). However, in the case of pH-variation of the micellar system, we obtained some interesting results. With a gradual decrease in pH of the micellar system from neutral to pH 5.5 and 5.0, there is almost no change in the emission maxima, although at pH 4.8 a little change has occurred to this (Figure 3). So we can conclude that when we decrease the pH of the micellar system probe molecules are not migrating toward the bulk water, and our

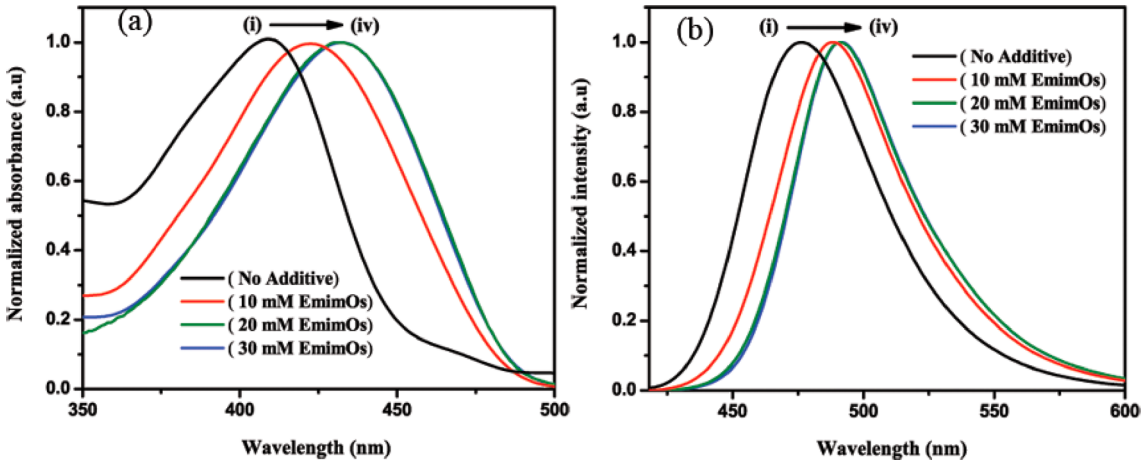


Figure 1. Absorption (a) and emission (b) spectra of C-343 (4.43×10^{-5} M) in 28 mM aqueous SB-16 in the presence of different amounts of EmimOs.

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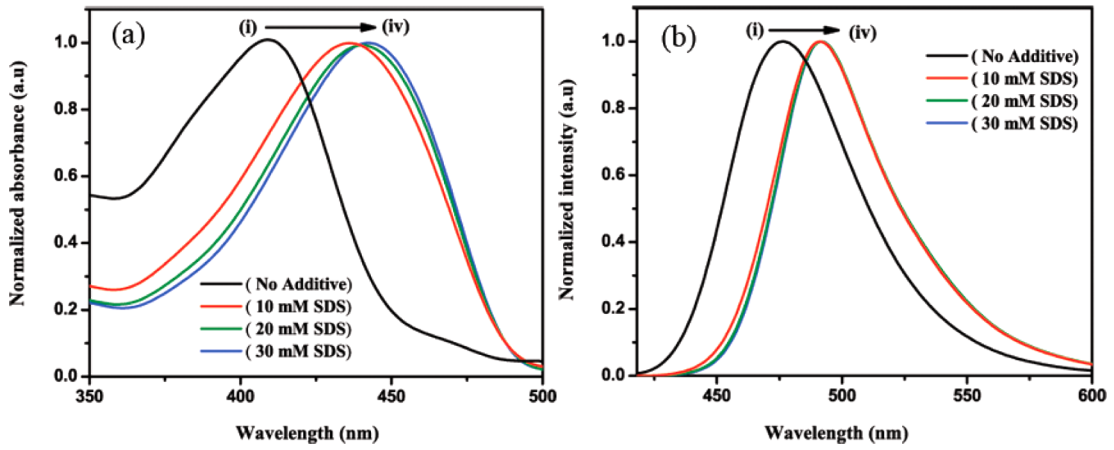

Figure 2. Absorption (a) and emission (b) spectra of C-343 (4.43×10^{-5} M) in 28 mM aqueous SB-16 in the presence of different amounts of SDS.

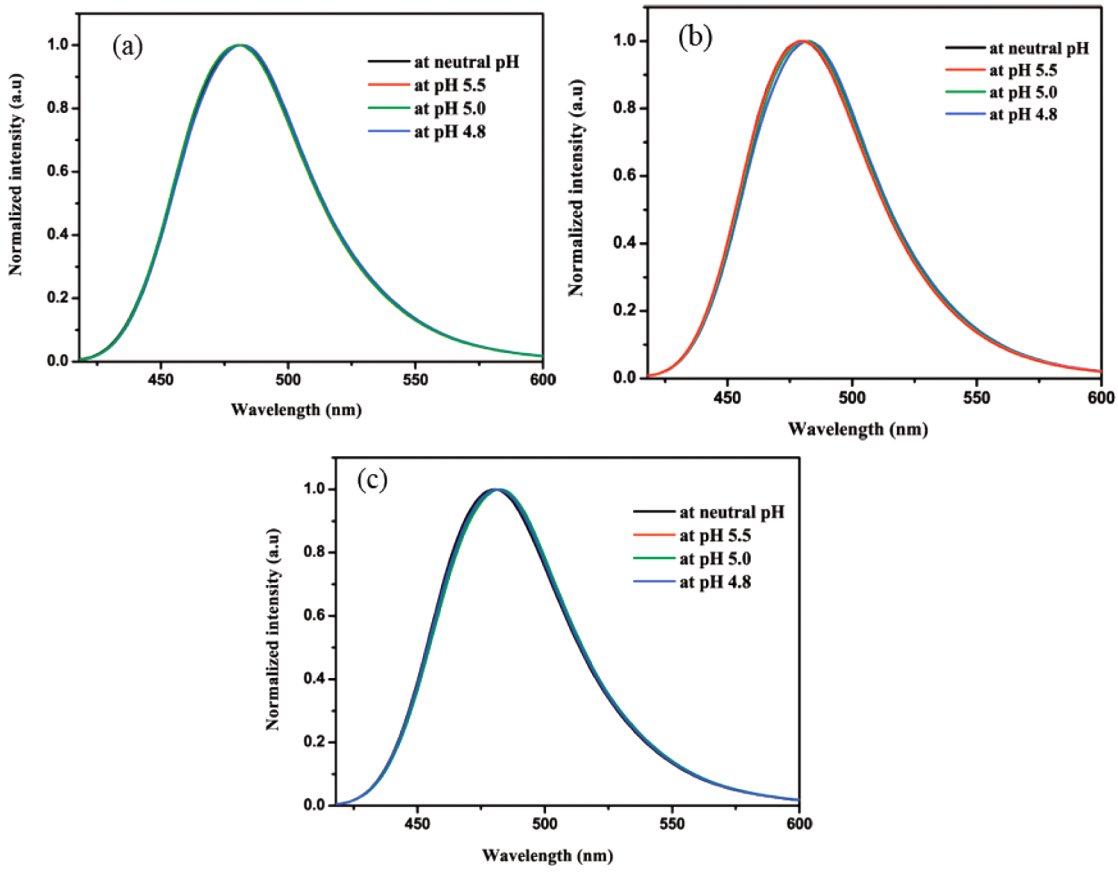

Figure 3. Emission spectra of C-343 (4.43×10^{-5} M) in 28 mM aqueous SB-16 at different pH values at 293 (a), 298 (b), and 303 K (c).

time-resolved data suggest that the movement is completely reversed compare to those of EmimOs and SDS addition (vide infra).

3.2. Time-Resolved Measurements. *3.2.1. Time-Resolved Anisotropy Measurements.* Time-resolved experiments were executed to investigate the microenvironment around the probe molecules in the SB-16 micellar system with an increase in the SDS and EmimOs concentration as well as a decrease in the pH of the micellar medium as discussed in the earlier section. The bathochromic shift of the emission spectra could be due to the gradual movement of the dye. If such a change does occur, the local environment, specially the water structure around the probe molecules, will also change quite significantly.

To further support these findings we have recorded time-resolved anisotropy decays. Time resolved anisotropy, $r(t)$, has been calculated by using the following equation:[64−69]

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

where G is the correction factor for detector sensitivity to the polarization direction of emission, whose value is 0.6 for our setup. $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the fluorescence decays, polarized parallel and perpendicular to the direction of polarization of the excitation light, respectively. Anisotropy decays of C-343 in the SB-16 micellar solution with various concentrations of EmimOs

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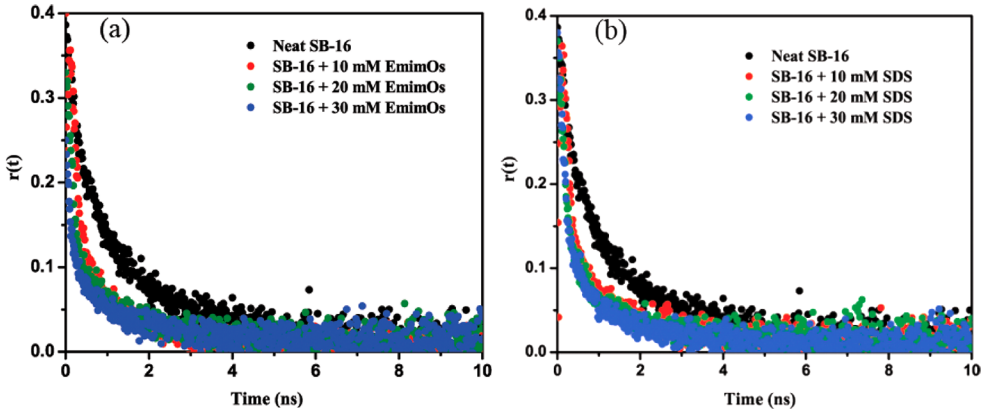

Figure 4. Time-resolved fluorescence anisotropy decays of C-343 in 28 mM aqueous SB-16 in the presence of different amounts of EmimOs (a) and SDS (b).

Table 1. Anisotropy Decay Parameters of C-343 in Neat SB-16, SB-16 and EmimOs, and SB-16 and SDS at 298 K

systems	a_{fast}	a_{slow}	τ_{fast} (ns)	τ_{slow} (ns)	$\langle\tau_{rot}\rangle$ (ns)[a]	viscosiy (cP)	R_0
SB-16 (28 mM) at neutral pH	0.39	0.61	0.21	1.37	0.91	0.91	0.39
SB-16 (28 mM) and EmimOs (10 mM)	0.62	0.38	0.17	1.60	0.71	0.94	0.37
SB-16 (28 mM) and EmimOs (20 mM)	0.73	0.27	0.14	1.36	0.47	0.95	0.33
SB-16 (28 mM) and EmimOs (30 mM)	0.64	0.36	0.11	0.99	0.41	0.97	0.25
SB-16 (28 mM) and SDS (10 mM)	0.72	0.28	0.15	1.44	0.51	1.04	0.38
SB-16 (28 mM) and SDS (20 mM)	0.76	0.24	0.18	1.50	0.49	1.07	0.37
SB-16 (28 mM) and SDS (30 mM)	0.74	0.26	0.16	1.27	0.44	1.09	0.39
SB-16 (28 mM) at pH 5.5	0.48	0.52	0.33	2.00	1.19	0.92	0.37
SB-16 (28 mM) at pH 5.0	0.47	0.53	0.32	2.02	1.22	0.91	0.38
SB-16 (28 mM) at pH 4.8	0.47	0.53	0.38	2.08	1.28	0.91	0.34
SB-16 (28 mM) and DAH (10 mM)	0.42	0.58	0.25	1.25	0.83	0.93	0.32

[a]Error in experimental data of ±5%.

and SDS are shown in Figure 4. The same decays of C-343 with a decrease in the pH of the SB-16 micellar system are shown in the Supporting Information (Figure S2) and with addition of DAH are also shown in the Supporting Information (Figure S3). The anisotropy decays in the micellar system were found to be biexponential in nature and are listed in Tables 1 and 2.

Table 2. Anisotropy Decay Parameters of C-343 in Neat SB-16 at Different Temperatures with Variation of pH

systems	a_{fast}	a_{slow}	τ_{fast} (ns)	τ_{slow} (ns)	$\langle\tau_{rot}\rangle$ (ns)[a]
SB-16 (28 mM) at neutral pH (293 K)	0.43	0.57	0.44	2.37	1.54
SB-16 (28 mM) at pH 5.5	0.45	0.54	0.51	2.48	1.56
SB-16 (28 mM) at pH 5.0	0.42	0.58	0.45	2.45	1.61
SB-16 (28 mM) at pH 4.8	0.50	0.50	0.62	3.00	1.81
SB-16 (28 mM) at neutral pH (303 K)	0.55	0.45	0.40	1.50	0.89
SB-16 (28 mM) at pH 5.5	0.51	0.49	0.37	1.93	1.13
SB-16 (28 mM) at pH 5.0	0.53	0.47	0.42	2.00	1.16
SB-16 (28 mM) at pH 4.8	0.53	0.47	0.45	2.10	1.22

[a]Error in experimental data of ±5%.

The average rotational relaxation time of C-343 at 298 K in 28 mM aqueous SB-16 solution was 0.91 ns with components 1.37 ns (61%) and 0.21 ns (39%), respectively. These values decreased to 0.71, 0.47, and 0.41 ns on addition of 10, 20, and 30 mM EmimOs, respectively. A similar trend was also observed with the addition of SDS where the average rotational relaxation time of C-343 decreased from its value in neat SB-16 micellar solution to 0.51, 0.49, and 0.44 ns with gradual addition of 10, 20, and 30 mM SDS, respectively. The decrease in rotational relaxation time upon addition of EmimOs and SDS is an indication of the movement of the C343 dye from micellar palisade layer to bulk water, which is further supported by solvation dynamics study. We have observed that this effect is much more pronounced in presence of SDS compared to that for the RTIL. This can be ascribed to the presence of the long alkyl (dodecyl) chain of SDS which can orient itself and easily fuse inside the SB-16 micelle and help to migrate the probe molecule (Scheme 2).[70] However, when we decreased the pH of the micellar system from pH 7 to pH 5.5, 5.0, and 4.8 at 298 K, the rotational relaxation time of the C-343 dye gradually increased from 0.91 to 1.19, 1.22, and 1.28 ns, respectively (Table 1); that is, the trend is completely opposite to that obtained in the previous two cases. Riter et al.[61] have reported that at neutral pH C-343 exists as an anionic species and it is converted to its neutral form beyond its pK_a value which is 4.6. From spectroscopic and crystallographic studies they have also reported that the protonation of the dye occurs on the carboxylic moiety. In the present case, since the pH of the solution was kept above 4.6 throughout the pH-variation study, the dye molecules remained in their anionic form. For the zwitterionic SB-16, the decrease in pH of the micellar solution makes it a positively charged species since the negative part of the surfactant molecules is neutralized by H^+ ions. It appears likely that with decreasing pH the electrostatic interaction between the oppositely charged dye molecules

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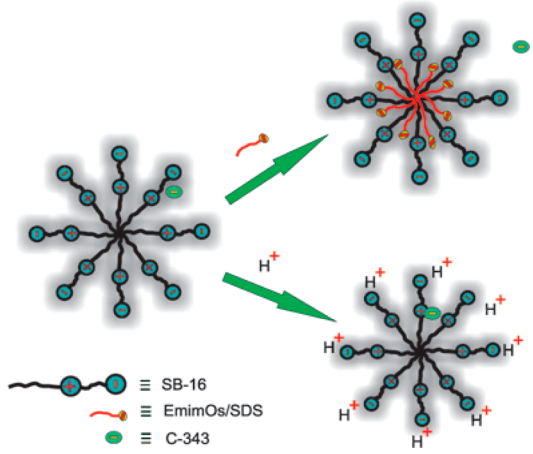
Scheme 2



and the surfactant will increase (Scheme 2). The increased interaction would impose restrictions on the movement of the probe. This line of reasoning is in fact supported by the observed anisotropy values. To confirm the type of interaction, we performed the temperature dependent study with variation of pH. The results are listed in Tables 1 and 2. At 293 K the average rotational relaxation time of C-343 increases from 1.54 to 1.56, 1.61, and 1.8 ns with pH 7.0, 5.5, 5.0, and 4.8. However, at 303 K the average rotational time also increases from 0.89 ns to 1.13, 1.16, and 1.22 ns with the same pH range.

From the above results it is clear that the increase in the rotational relaxation time with gradual decrease in pH is more pronounced at lower temperature than that of higher temperature. Hence we can say that the electrostatic interaction is the major contributor for increasing the anisotropy values of C-343 molecules with a gradual decrease in pH of SB-16 micellar solution. We also did the same experiment in the presence of protic IL, DAH (*N*,*N*-dimethylethanolammonium hexanoate (DAH)) to see is there any effect due to the presence of an −OH moiety. However, we did not get any increase in anisotropy values implying that this type of −OH group is unable to increase the rotational relaxation time of the C-343 probe molecules. There is a little decrease in anisotropy value with addition of 10 mM DAH. This may be due to the presence of a small hexanoate chain. Which suggests that a molecule possessing this type of small chain is unable to fuse inside SB-16 micellar system; hence, the effect is very little compare to those for EmimOs and SDS. The experimental data are shown Table 1.

3.2.2. Solvation Dynamics. Time resolved decays at different wavelengths for all systems have been performed to study the solvent relaxation dynamics. The decays at the red edge of the emission spectra were preceded by a growth in the nanosecond time scale, whereas decays at the blue edge occurred very rapidly. The fast decay at the blue end and the slow rise at the red end of the emission spectrum signify that solvent relaxation is taking place in our present system. Figure S4 (Supporting Information) shows the fluorescence transients

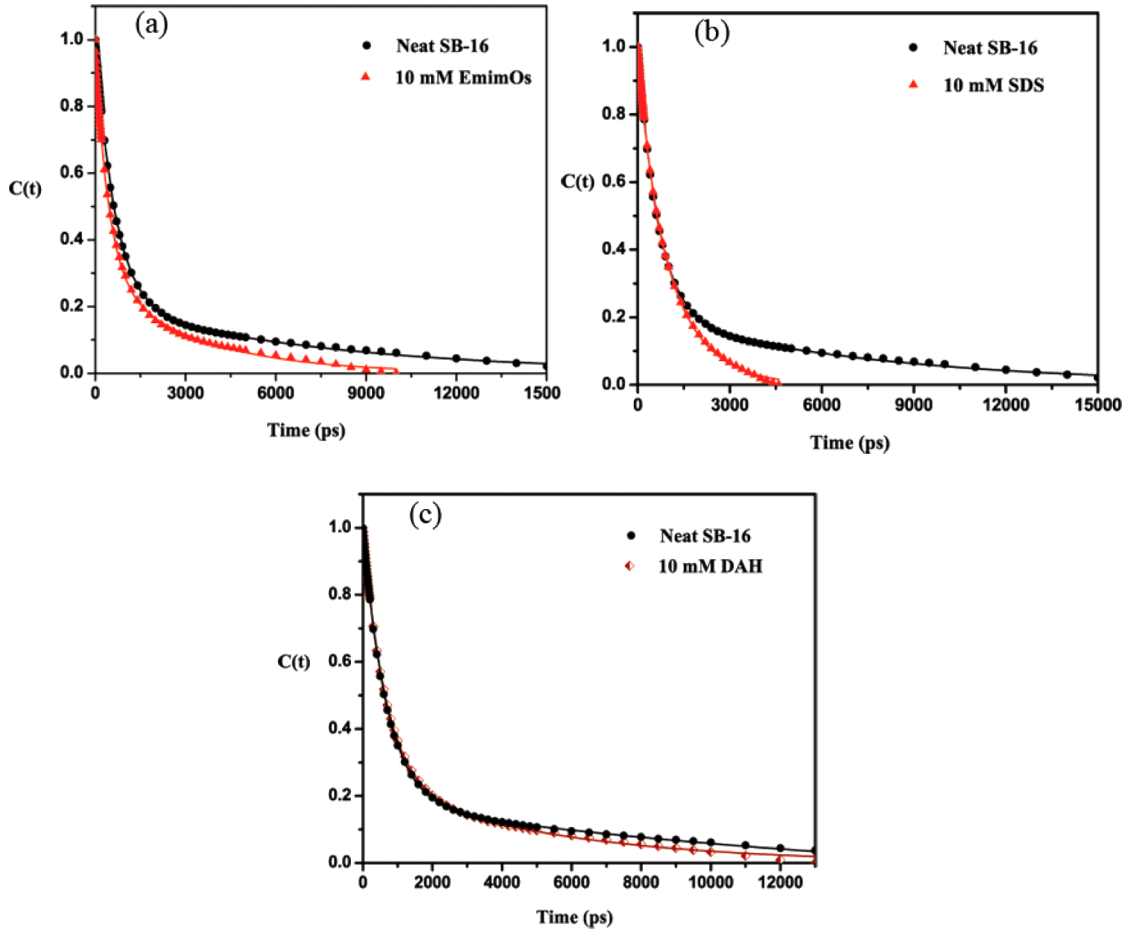


Figure 5. Decays of solvent response functions, $C(t)$, of C-343 in 28 mM SB-16 solution with addition of (a) EimOs, (b) SDS, and (c) DAH.

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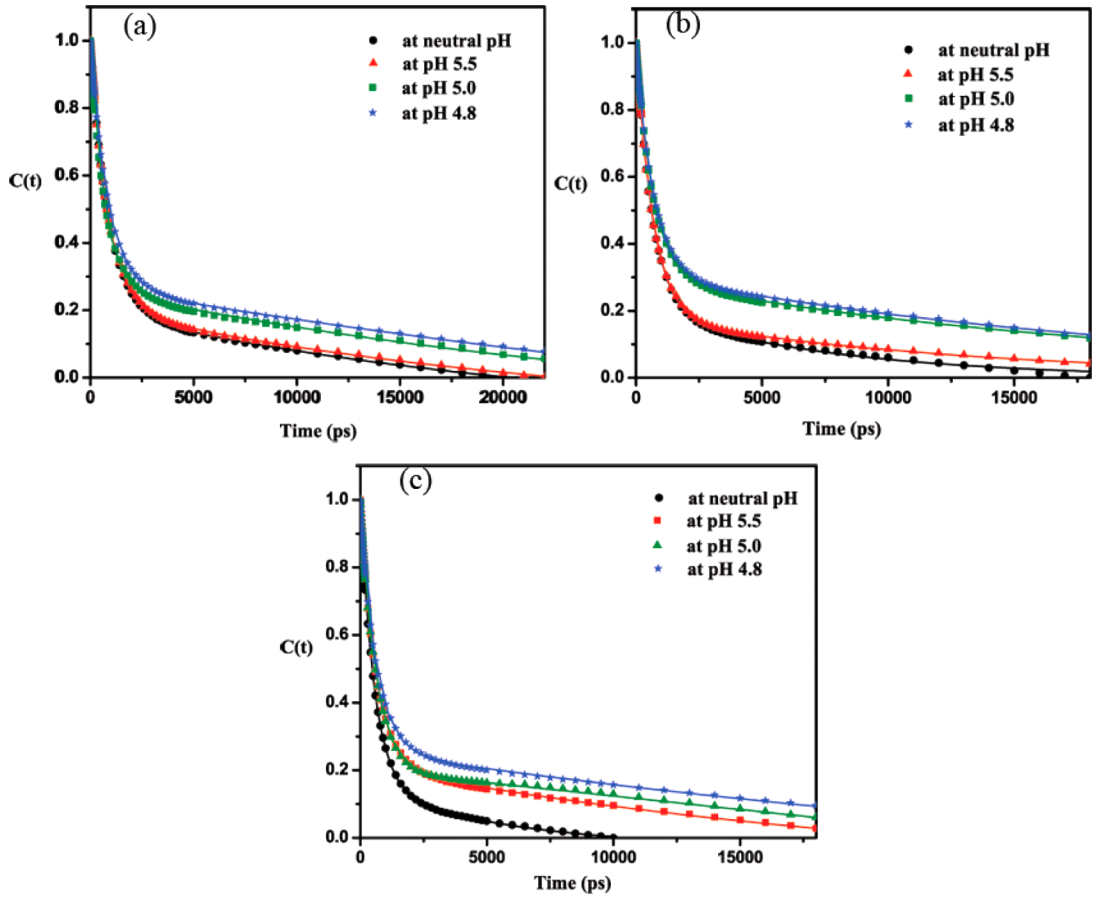

Figure 6. Decays of solvent response functions, $C(t)$, of C-343 in 28 mM SB-16 solution at 293 (a), 298 (b), 303 K (c).

for the C-343 dye in 28 mM SB-16 solution at different wavelengths. To construct the time-resolved emission spectra (TRES), we followed the literature procedure, described by Fleming and Maroncelli.[71,72] The TRES at given time t, $S(\lambda;t)$, is calculated by the fitted decays, $D(t;\lambda)$, by relative normalization to the steady-state spectrum, $S_0(\lambda)$, as follows:

$$S(\lambda;\, t) = D(t;\, \lambda)\frac{S_0(\lambda)}{\int_0^\infty D(t;\, \lambda)\, \mathrm{d}t} \tag{2}$$

Each TRES was fitted by a log-normal line shape function, which is defined as

$$g(\nu) = g_0 \exp\left[-\ln 2\left(\frac{\ln[1 + 2b(\nu - \nu_p)/\Delta]}{b}\right)^2\right] \tag{3}$$

where g_0, b, ν_p, and Δ are the peak height, asymmetric parameter, peak frequency, and width parameter, respectively. A representative TRES plot of C-343 in 28 mM aqueous SB-16 solution is shown in the Supporting Information (Figure S5).

By log-normal fitting of TRES, we obtained the value of peak frequency. The solvation dynamics was monitored by the solvent response function defined as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \tag{4}$$

where $\nu(0)$ is the frequency at "zero-time", as calculated by the literature method.[73,74] $\nu(\infty)$ is the frequency at "infinite time", which can be taken as the maximum of the steady-state fluorescence spectrum if solvation occurred more rapidly than the population decay of the probe. $\nu(t)$ is determined by taking the maxima from the log-normal fits as the emission maximum. The solvent response function $C(t)$ was fitted using the following biexponential decay function

$$C(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \tag{5}$$

where τ_1 and τ_2 are the two relaxation times with amplitudes a_1 and a_2, respectively. The $C(t)$ verses time plots are shown in Figures 5 and 6. The decay parameters of $C(t)$ are summarized in Tables 3 and 4. The average solvation time is calculated by

$$\tau_{av} = a_1\tau_1 + a_2\tau_2 \tag{6}$$

Table 3. Decay Parameters of $C(t)$ of C-343 in Neat SB-16, SB-16 and EmimOs, and SB-16 and SDS at 298 K

systems	a_{fast}	a_{slow}	τ_{fast} (ns)	τ_{slow} (ns)	$\langle\tau_s\rangle$ (ns)[a]
SB-16 (28 mM) at neutral pH	0.80	0.20	0.64	7.57	2.02
SB-16 (28 mM) and EmimOs (10 mM)	0.67	0.33	0.44	3.23	1.36
SB-16 (28 mM) and SDS (10 mM)	0.24	0.76	0.40	1.19	1.00
SB-16 (28 mM) at pH 5.5	0.81	0.19	0.65	11.44	2.70
SB-16 (28 mM) at pH 5.0	0.70	0.30	0.65	16.83	5.50
SB-16 (28 mM) at pH 4.8	0.66	0.34	0.64	16.25	5.94
SB-16 (28 mM) and DAH (10 mM)	0.75	0.25	0.64	5.09	1.75

[a]Error in experimental data of ±5%.

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Table 4. Decay Parameters of $C(t)$ of C-343 in Neat SB-16 at Different Temperatures with Variation of pH

systems	a_{fast}	a_{slow}	τ_{fast} (ns)	τ_{slow} (ns)	$\langle\tau_s\rangle$ (ns)[a]
SB-16 (28 mM) at neutral pH (293 K)	0.76	0.24	0.79	8.46	2.63
SB-16 (28 mM) at pH 5.5	0.75	0.25	0.79	10.41	3.19
SB-16 (28 mM) at pH 5.0	0.68	0.32	0.64	15.94	5.53
SB-16 (28 mM) at pH 4.8	0.67	0.33	0.77	17.00	6.12
SB-16 (28 mM) at neutral pH (303 K)	0.80	0.20	0.52	4.52	1.32
SB-16 (28 mM) at pH 5.5	0.75	0.25	0.57	7.00	2.17
SB-16 (28 mM) at pH 5.0	0.77	0.23	0.57	14.14	3.69
SB-16 (28 mM) at pH 4.8	0.76	0.24	0.57	14.00	3.79

[a]Error in experimental data of ±5%.

For comprehending the solvation dynamics process, a thorough understanding of the micellar structure and location of the probe within the micelle is necessary. The dielectric constant is an important tool for measuring the polarity of a solvent, which changes from bulk solvent to micellar solution with the probe in the palisade layer.[72] According to the molecular approach for the solvation relaxation process, which takes into account the solvent structures around the probe, it appears to be more logical to understand the results in micellar media, although it is more complicated than the homogeneous solution. Inside the micellar palisade layer, the movement of the water molecules is much more hindered than the bulk water molecules, hence it is expected that the solvation process inside the micelle should be slower than that in the bulk. The water molecules adjacent to the probe are much more restricted and difficult to rearrange than the water molecules somewhat away from the probe. So the slower solvation component arises from the response of the few restricted water molecules that are adjacent to the probe, and the collective response of the relatively large number of water molecules that are not in the vicinity of the probe gives rise to the faster solvation component.[75] From UV−visible spectra, fluorescence spectra, and also anisotropy values, one can conclude that the probe molecules reside inside the palisade layer of the micelles. The average solvation time of C-343 at 298 K in aqueous solution of 28 mM SB-16 was found to be 2.02 ns (Table 3), with components 0.64 ns (80%) and 7.57 ns (20%). The process becomes faster in the presence of both the surfactant (SDS) and the RTIL (EmimOs), and the effect is more pronounced in the case of SDS. With the addition of 10 mM EmimOs and SDS to 28 mM SB-16 solution, the average solvation time changes from 2.02 to 1.36 and 1.00 ns, respectively. The slow component of the solvation time of C-343 at 298 K in 28 mM SB-16 solution was found to be 7.57 ns with amplitude of 20%. With addition of 10 mM EmimOs, this value decreases from 7.57 to 3.23 ns and the amplitude changes from 20% to 33%, which clearly indicates that the strength of the hydrogen bonding decreases but the water penetration increases. On addition of 10 mM SDS to the 28 mM SB-16 solution, the slow component decreases from 7.57 to 1.19 ns and the amplitude increases from 20% to 76% which suggests that the strength of hydrogen bonding decreases while the water penetration increases abnormally. This is a manifestation of the movement of the probe molecules to the bulk water phase.

Now, considering the fast component of the solvation dynamics, the addition of 10 mM EmimOs to a 28 mM SB-16 solution it changes from 0.64 to 0.44 ns and the magnitude decreases from 80% to 67%. This change is clearly a manifestation of the movement of the probe molecules from the micellar palisade layer to the bulk solvent. The effect of addition of 10 mM SDS to a 28 mM SB-16 solution is more drastic since the fast component then changes to 0.40 ns with a magnitude of 24%. To see the effect of the −OH moiety, we performed a similar study with the addition of 10 mM DAH, as a protic IL. In that case, the average solvation time decreased from 2.02 to 1.75 ns, suggesting that the effect of DAH is similar compare to those for EmimOs and SDS, although the effect is much less compared to those for SDS and EmimOs. As a result, we can say that the efficiency of the movement of the probe solely depends on the chain length and follows the order SDS > EminOs > DAH, becasue SDS possesses a dedecyl chain, EmimOs, possesses an octyl chain, and DAH possesses a hexanoate chain.

Variation of pH also produced some interesting effects on the solvation dynamics of a 28 mM SB-16 solution at 298 K. Under ambient conditions and in neutral pH, SB-16 micellar solution exhibits two components, one is fast and the other is the slow components, which are 0.64 and 7.57 ns, with magnitudes of 80% and 20%, respectively. However, when we decrease the pH to 5.5, the slow component of solvation dynamics increases from 7.57 to 11.44 ns and the magnitude changes only 1%, which clearly indicates that the strength of the hydrogen bonding increases, whereas the penetration of water molecules remains same. At pH 5.0, the slow component further increases to 16.83 ns with a magnitude of 30%, and at pH 4.8 it is 16.25 ns with a magnitude of 34%, which implies that, beyond pH 5, the strength of the hydrogen bonding and the microfluidity remain constant. Although in all the cases the fast component remains almost same, the average solvation time increases from 2.02 ns at neutral pH to 5.94 ns at pH 4.8. As a consequence, we can conclude that with a gradual decrease in pH the anionic probe C-343 penetrates more and more to the palisade layer of the SB-16 micelle.

To further confirm the nature of the interaction between the probe molecules and the zwitterionic micellar system, we performed a temperature dependent study with variation of pH. Results are summarized in Table 4. At 293 K, the SB-16 micellar solution (pH 7) also exhibits two components, one is fast and the other is the slow components, which are 0.79 and 8.46 ns, with magnitudes of 76% and 24%, respectively. The process becomes slower with decreasing pH of the medium as mentioned before. At pH 5.5 the magnitudes of the fast and slow components remained almost same, but the solvation time of the slow component increased from 8.46 to 10.41 ns; hence, there was a little increase in average solvation time from 2.63 to 3.19 ns. At pH 5.0 and 4.8, the magnitudes of the slow components are 32% and 33% with solvation times of 0.64 and 0.77 ns. So, there are 8% and 9% increases of the magnitude of the slow component with 7.48 and 8.54 ns increments of solvation time compare to neat SB-16 micellar system at pH 7, suggesting that there is a huge increase in hydrogen bonding. At 303 K the effect is also similar but the increase is much less compared to the experimental data obtained at 298 K. At pH 7 the magnitudes of fast and slow components of the 28 mM SB-16 micellar solution are 80% and 20% with solvation times of 0.52 and 4.52 ns, respectively. Now with a decrease in pH value to 5.5, the magnitudes of the fast component decreased from 80% to 75% and the magnitudes of the slow component increased from 20% to 25%. The increase in the magnitude of the slow component implies that the penetration of the water

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molecules decreases. However, on going from pH 5.5 to 5.0 and 4.8, the magnitudes of the fast and slow components remained the same although the solvation time of the slow component increased by ∼7 ns which indicates that the strength of hydrogen bonding has increased.

4. CONCLUSION

In conclusion, we have thoroughly studied the influence of external additives such as SDS, EmimOs, and DAH and also the effect of pH in the zwitterionic micellar system using solvent and rotational relaxation studies. The study shows that the rotational relaxation time as well as solvation time become faster in the presence of such additives. However the effect is more pronounced in the case of SDS addition compared to those of EmimOs or DAH addition due to the presence of a dodecyl chain in SDS, which can reorient itself and easily fuse inside the SB-16 micelle, whereas this type of fusion is somewhat difficult when we added EmimOs or DAH due to its relatively smaller alkyl (octyl) or hexanoate chain (Scheme 2). So, in general we can say that the efficiency of the movement of the probe molecules solely depends on the chain length and follows the order SDS > EminOs > DAH. The effect of the decrease in pH of the SB-16 micellar system has also been studied. Since the zwitterionic micelles of SB-16 become positively charged under acidic conditions, their interaction with the probe molecules which are anionic under experimental conditions becomes stronger. This increased interaction with decreasing pH is supported by the results obtained from time-resolved studies. Therefore, this study reveals that the microenvironment of a dissolved solute can be modulated over a wide range in the zwitterionic micellar system by proper choice of additives (in our case SDS, EmimOs, and DAH) and also by the variation of pH, which can be used to modulate their physical and chemical properties over a wide range for different types of applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Anisotropy decays, time-resolved emission spectra, and fluorescence transients at different wavelengths. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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