
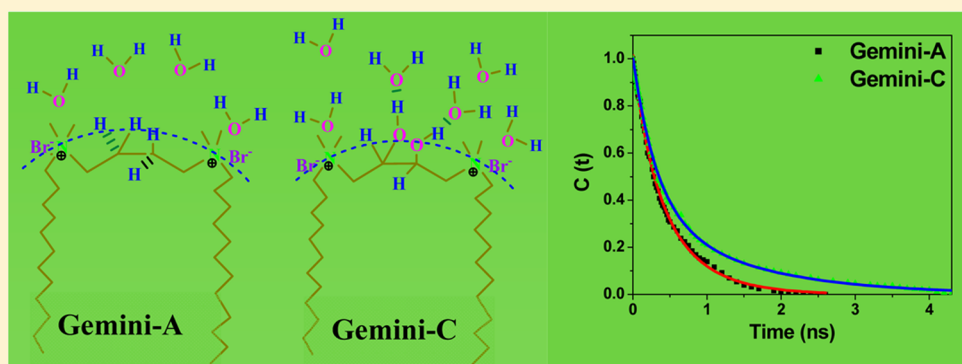


# Effect of Hydroxyl Group Substituted Spacer Group of Cationic Gemini Surfactants on Solvation Dynamics and Rotational Relaxation of Coumarin-480 in Aqueous Micelles

Amit K. Tiwari, Sonu, and Subit K. Saha\*

Department of Chemistry, Birla Institute of Technology and Science, Pilani 333 031, Rajasthan, India

 Supporting Information



**ABSTRACT:** The solvation dynamics and rotational relaxation of Coumarin 480 (C-480) have been investigated in the micelles of a series of gemini surfactants, 12-4(OH)<sub>n</sub>-12 ( $n = 0, 1$ , and  $2$ ), with increasing hydroxyl group substitution within the spacer group. Steady-state and time-correlated single photon counting (TCSPC) fluorescence spectroscopic techniques have been used to carry out such study. Steady-state and TCSPC fluorescence data support the location of probe molecule at the Stern layer. The solvation dynamics is found to be slower on hydroxyl substitution of spacer group due to the formation of hydrogen bonds between water molecules and hydroxyl group(s) of spacer group. Such kind of hydrogen bonding protects the probe molecule from its contact with water molecules and also results in restricted mobility of water molecules. The average rotational relaxation time increases on increasing number of substituted hydroxyl group on a spacer group. It is because of formations of more and more close packed micelles and larger extent of intermolecular hydrogen bonding interactions between C-480 and hydroxyl group(s). For micelles of each of 12-4-12 and 12-4(OH)-12, the slow rotational relaxation is dominated by the lateral diffusion of the fluorophore along the spherical surface of the micelle. However, for 12-4(OH)<sub>2</sub>-12, the slow rotational relaxation is mainly due to the rotational motion of the micelle as a whole. Because of high microviscosity of micelles of 12-4(OH)<sub>2</sub>-12 and greater extent of hydrogen bonding interactions with C-480, the relaxation time corresponding to the lateral diffusion of the fluorophore is very high in this case.

## 1. INTRODUCTION

The water molecule plays a central role in biological systems.<sup>1</sup> There are several techniques such as NMR relaxation dispersion,<sup>2</sup> dielectric relaxation<sup>3</sup> and solvation dynamics available<sup>4–7</sup> to study the properties of water molecules in various systems of molecular assemblies. Because of higher sensitivity toward time and length scale, solvation dynamics has been found to be one of the best techniques.<sup>4–7</sup> Maroncelli and co-workers<sup>8–11</sup> have studied the solvation dynamics using Coumarin-480 (C-480) and Coumarin-343 (C-343) as probes and reported very fast ( $<1$  ps) solvation process of bulk water with single solvation time.<sup>11</sup> However, in presence of self-organized systems, the solvation times for water get delayed. Vajda et al.<sup>12</sup> observed bimodal behavior of water in cyclodextrin. A dynamic exchange model has been proposed to explain such kind of bimodal behavior ('free' and 'bound') of water molecules associated with the self-organized systems.<sup>13</sup>

Micelles<sup>14–17</sup> and mixed micelles<sup>18–20</sup> have been very fascinating systems to study the solvation dynamics of water. The bimodal behavior of solvation dynamics of water molecules in the micelles of conventional surfactants are well studied.<sup>16,17</sup> Bhattacharyya and co-workers first reported the solvation dynamics of C-480 and 4-aminophthalimide (4-AP) in the micelles of conventional surfactants, i.e., Triton X-100 (TX), cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS). They did not observe much difference between the average solvation time using two probes in these micelles and concluded that the solvation dynamics in the micelles weakly dependent on the probe.<sup>16,17</sup> Their time-dependent Stokes' shift studies with C-480 first showed that the

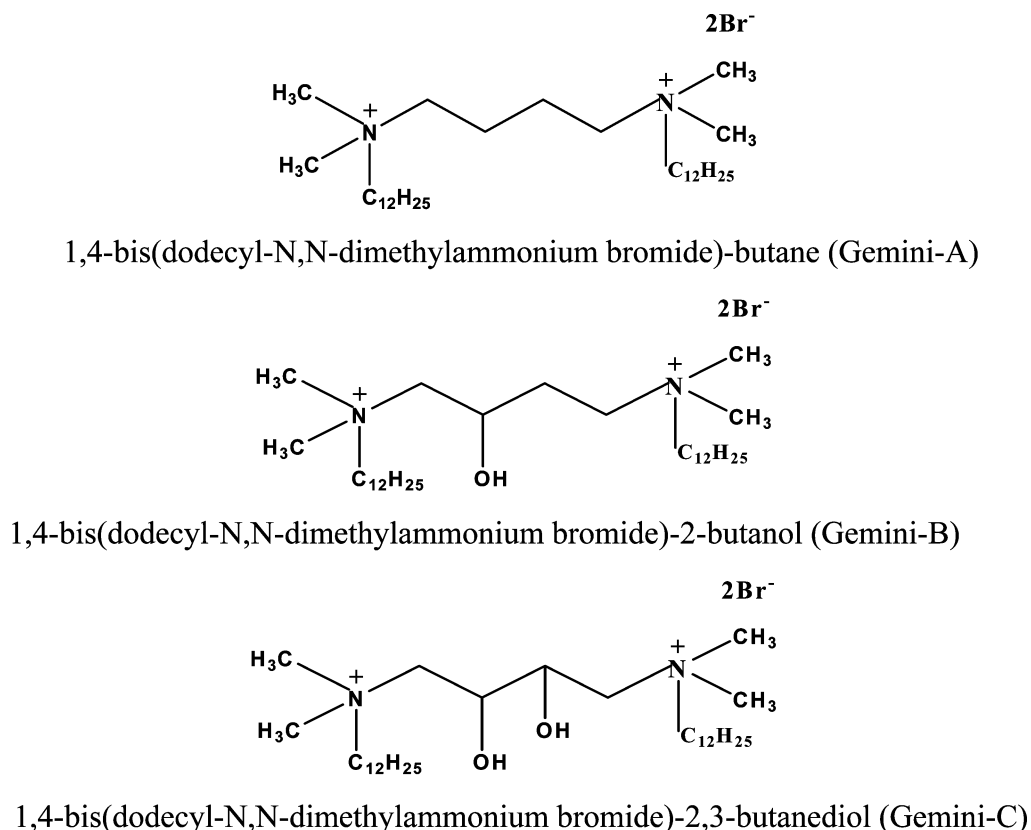
Received: July 15, 2013

Revised: March 8, 2014

Published: March 11, 2014



Scheme 1. Chemical Structure of Gemini Surfactants

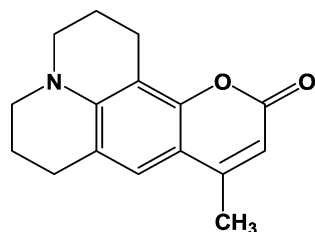


relaxation dynamics of water molecules in the Stern layer of micelles was much slower than that of ordinary bulk water.<sup>16</sup> Sarkar and co-workers have also studied solvation dynamics in various surfactant systems.<sup>18,21–23</sup> They have observed retardation of average solvation time of C-480 in the Stern layer of Tween 80-bile salt and CTAB-bile salt mixed micelles.<sup>18</sup> Hof and co-workers have studied the solvation dynamics in presence of phospholipid bilayer<sup>24–26</sup> and also investigated the structure and dynamics of fully hydrated liquid crystalline lipid bilayers composed of mixtures of cationic dioleoyltrimethylammonium propane (DOTAP) and neutral dioleoylphosphatidylcholine (DOPC) using different types of fluorescent dyes.<sup>27</sup> Hazra and co-workers have studied the solvation dynamics with C-153 in SDS dispersed single walled carbon nanotubes<sup>28</sup> and the dynamics of urea inside the reverse micelles of dioctyl-sulfosuccinate sodium salt (AOT) using C-343 as a probe.<sup>29</sup> Shiota and co-workers<sup>30</sup> have reported the solvation dynamics in the micelles of cationic and anionic surfactants with Coumarin-102 (Kodak's name of C-480) as a probe. The solvation dynamics in the aqueous micelles of anionic surfactant is found to be slower than that in the aqueous micelles of cationic surfactant. The slower solvation dynamics in anionic micelles as compared to cationic micelles is due to stronger hydrogen bonding interaction between the water molecule and the headgroup of surfactant in the former than that in the latter.<sup>30</sup>

Gemini surfactants generally show better surface active properties than their conventional counterparts.<sup>31–33</sup> These surfactants consist of two amphiphilic groups connected at the level of the headgroups by a spacer group of varied chemical nature such as rigid, flexible, hydrophobic or hydrophilic.<sup>34–36</sup> The effect of the chemical nature of the spacer group and the

concentration of gemini surfactants on the aggregation behavior in aqueous and nonaqueous media are well documented.<sup>37–41</sup> After having vast survey of literature, we realized that the micelles of gemini surfactants could also be very interesting systems to study the solvation dynamics of water molecules at the Stern layer or micelle-water interface. Because there are structural differences between the conventional and gemini surfactants and the presence of a spacer group of varying chemical nature in the latter controls the aggregation behavior.<sup>34–36</sup> Depending on the chemical nature of the spacer group of gemini surfactants, a difference in solvation dynamics is expected as compared to conventional surfactants. In the present work, we have studied the effect of the spacer group of gemini surfactants containing varying number of hydroxyl groups on the solvation dynamics. The structures of the investigated gemini surfactants are shown by Scheme 1 (denoted as Gemini-A, Gemini-B and Gemini-C, respectively hereafter). Except the spacer group, chemical nature of other parts of all three gemini surfactants are identical. C-480 has been used as a solvation dynamics probe (Scheme 2). It has ability to form the hydrogen bond. Several basic centers present in C-480 are responsible to form hydrogen bonds. Different groups have studied the hydrogen bonding ability of C-480 in ground and excited states in polar and nonpolar solvents, experimentally and theoretically.<sup>42–47</sup> Chudoba et al.<sup>44</sup> have reported that the hydrogen bond between C-480 and chloroform ( $\text{CHCl}_3$ ) is significant in the electronic ground state and this bond is cleaved within 200 fs after the excitation of probe molecules. Palit et al.<sup>46</sup> have also reported the cleavage of hydrogen bond upon excitation of probe in hydrogen donating solvents. In contrast to this, Zhao and co-worker<sup>47</sup> on the basis of theoretical study have reported that intermolecular

Scheme 2. Chemical Structure of Coumarin-480



Coumarin-480 (C-480)

hydrogen bonds between C-480 and hydrogen donating solvents, strengthen the early time of photoexcitation to the excited state.

Present work also demonstrates the effect of hydroxyl substituted spacer group of gemini surfactants on the bimodal behavior of rotational relaxations of C-480.<sup>48,49</sup> This study provides with better picture about the microenvironment around the probe. To our knowledge, this kind of study on the effects of substituted spacer groups of gemini surfactants on solvation dynamics and rotational relaxation at the Stern layer or micelle-water interface has not been reported. The spacer group being present at the micelle-water interface and the aggregation behavior of gemini surfactants is tuned by changing the chemical nature of the spacer group, the study of dynamics of water molecules and rotational relaxation of a molecule at the Stern layer or micelle-water interface has practical and fundamental importance.

## 2. MATERIALS AND METHODS

**2.1. Materials.** The procedures for the syntheses of Gemini-A, Gemini-B, and Gemini-C surfactants used in this study are reported in the literature.<sup>50</sup> The structures of synthesized compounds were confirmed by FT-IR and <sup>1</sup>H NMR data (Table S1, Supporting Information). C-480 was obtained from the Exciton (laser grade) and was used as received. The concentration of C-480 was kept at 5  $\mu$ M. Triple distilled water was used for the preparation of aqueous solutions. All solvents used were of spectroscopic grades and were procured from Spectrochem Chemical Company, India. The lamp profile in case of time-correlated single-photon counting (TCSPC) measurement was recorded by using aqueous solution of Ludox as a scatterer. Ludox was procured from Aldrich Chemical Co., WI, and was used as received.

**2.2. Methods.** The aqueous solutions of gemini surfactants were prepared with constant concentration of C-480. First, 0.05 mL of a stock solution of C-480 (1 mM) in methanol was added to the volumetric flask and then kept for a few hours for complete evaporation of methanol. After the evaporation of methanol, the required volume of the aqueous solution of a gemini surfactant was added to the volumetric flask and the final volume was adjusted to 10 mL using water. The concentration of C-480 in final solution was 5  $\mu$ M. The concentrations of all three gemini surfactants were chosen to be  $\sim$ 15 times higher than their respective cmc to ensure that the probe molecules were completely micellized.

The absorption spectra were recorded using a Jasco V-630 UV–visible spectrophotometer. Steady-state fluorescence measurements were performed using a Horiba Jobin Yvon Fluoromax-4 scanning spectrofluorimeter. The excitation and emission slit widths used for the fluorescence measurements

were 3 nm each. The excitation wavelength ( $\lambda_{ex}$ ) was 375 nm to obtain fluorescence spectra. The fluorescence spectra have been corrected for spectral sensitivity of the instruments. The steady-state fluorescence anisotropy measurements were performed with the same steady-state spectrofluorimeter fitted with a polarizer attachment and details are available elsewhere.<sup>4,51</sup>

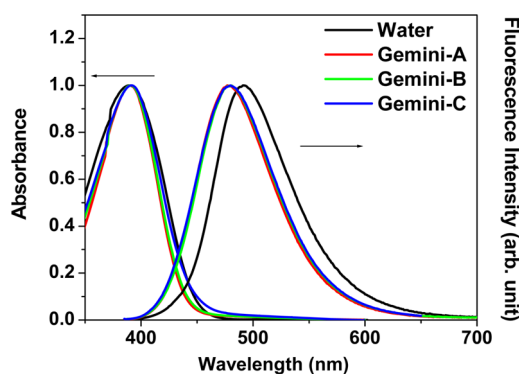
The excited singlet state lifetimes were estimated from intensity decays using Horiba Jobin Yvon Fluorocube-01-NL picoseconds TCSPC experimental setup. A picosecond diode laser of 375 nm (NanoLED 375L, IBH, U.K.) was used as a light source. The fluorescence signals were detected at magic angle (54.7°) polarization using a TBX photon detection module (TBX-07C). The instrument response function of this laser system is  $\sim$ 165 ps. The decays were analyzed using IBH DAS-6 decay analysis software. The goodness of fits was analyzed by  $\chi^2$  criterion and visual inspection of the residuals of the fitted function to the data. The same setup was used for time-resolved anisotropy measurements.

The conductivity measurement was performed using direct reading Eutech Instruments combined pH and conductometer, model PC 510. The detailed method of measuring the conductivity has been given in our earlier publication.<sup>52</sup> The dynamic light scattering (DLS) measurements were carried out with a Zetasizer, model Nano ZS (ZEN 3600, Malvern Instruments, U.K.). Samples were filtered prior to the measurements with 0.22- $\mu$ m filter (Durapore, PVDF). The wavelength of the laser light was 632.8 nm and the scattering angle was 173°. The FT-IR spectra were recorded in ABB Boman MB 300 instruments and <sup>1</sup>H-NMR spectra were recorded with a Bruker-avance instrument. All spectroscopic, conductivity, and DLS measurements were carried out at  $298.15 \pm 1$  K temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. UV–Visible Absorption and Steady-State Fluorescence Spectra.

Figure 1 represents the absorption and



**Figure 1.** Normalized absorption and steady-state fluorescence spectra of C-480 in pure water and in the micelles of Gemini surfactants.  $\lambda_{ex}$  = 375 nm.

fluorescence spectra of C-480 in pure water and in the micelles of Gemini-A, Gemini-B, and Gemini-C surfactants in aqueous media. The full width at half maxima (fwhm) for absorption spectra of C-480 in the micelles of Gemini-A, Gemini-B, and Gemini-C are 4049, 4410, and 4627  $\text{cm}^{-1}$ , respectively, and for fluorescence spectra are 3343, 3355, and 3506  $\text{cm}^{-1}$ , respectively. The experimental concentrations of all three gemini surfactants were chosen to be  $\sim$ 15 times higher than their respective cmc. The cmc values of Gemini-A and Gemini-

B have been estimated by conductometric measurements at 298.15 K following Williams's method (Supporting Information, Figure S1 and Note 1).<sup>53</sup> The cmc value of Gemini-C determined using same method has been reported in our earlier publication.<sup>54</sup> The absorption and fluorescence peak maxima of C-480 in pure water and in solutions of each of the three gemini surfactants at a concentration of  $\sim 15$  times of cmc along with the cmc values are listed in Table 1. The cmc values available in the literature are given in the parentheses. The estimated cmc values are well corroborated with the reported values.<sup>55</sup>

**Table 1. Cmc of Surfactants, Total Concentration of Surfactants Taken for the Present Study, Peak Maxima of Absorption and Steady-State Fluorescence Spectra of C-480 in Water and Micelles**

system	cmc (mM)	[surfactant] (mM)	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{fl}}$ (nm) <sup>a</sup>
water	—	—	389	489
methanol	—	—	390	475
cyclohexane	—	—	362	408
Gemini-A	1.17 (1.17 <sup>b</sup> )	18	390	477
Gemini-B	0.96 (0.94 <sup>b</sup> )	15	390	478
Gemini-C	0.78 <sup>c</sup> (0.87 <sup>b</sup> )	12	391	479

<sup>a</sup> $\lambda_{\text{ex}} = 375$  nm. <sup>b</sup>Reference 55. <sup>c</sup>Reference 54.

An absorption peak maximum of C-480 in pure water is found at 389 nm and mostly remains unchanged in the presence of micelles of gemini surfactants. Chakrabarty et al.<sup>23</sup> also did not observe much change in the absorption spectra of C-480 in the micelles and mixed micellar system of conventional cationic surfactants. It could be due to the structurally constrained nature of C-480.<sup>42</sup> We have observed that C-480 has an emission peak maximum at 489 nm in pure water, which is well corroborated with the literature value.<sup>16,23</sup> In presence of the micelles of gemini surfactants, blue shifts in the emission peak maxima of C-480 have been observed. The emission peak maxima of C-480 in the micelles of Gemini-A, Gemini-B, and Gemini-C are found to be at 477, 478, and 479 nm, respectively. These results indicate that the probe molecule is facing less polar environment in the micelles than that in the pure water. This conclusion is based on the fact that the emission peak maxima of C-480 in methanol and cyclohexane are found to be at 475 and 408 nm, respectively. These peak maxima values are close to reported values.<sup>42,43</sup> The way it is reported in the literature, the resemblance of emission peak maxima of C-480 in gemini micelles with the peak maximum in methanol indicates that the polarity of the microenvironment of C-480 in micelles is similar to that of methanol.<sup>16</sup> Thus, following the method of comparison available in the literature,<sup>16</sup> we can also state that probe molecules are neither residing in the core of the micelles nor in the bulk, but residing somewhere in between core and bulk i.e., at the Stern layer. Because if probe resides in the core of the micelle then emission peak maximum is expected to be at  $\sim 408$  nm; if it resides in the bulk then peak should appear at  $\sim 489$  nm.<sup>16</sup>

To further support our above-mentioned discussion on the microenvironment of C-480 in the micelles, the micropolarity expressed in equivalent scale of  $E_{\text{T}}(30)$ <sup>56,57</sup> which is an empirical solvent polarity parameter has been determined. This micropolarity has been estimated by comparing the fluorescence behavior of C-480 in micellar systems to that in

different compositions of dioxane-water mixture.<sup>58</sup> The fluorescence energies of C-480 at peak maximum ( $\epsilon_{\text{max}}^{\text{fl}}$ ) have been calculated in dioxane-water mixture of various compositions and are plotted against  $E_{\text{T}}(30)$  (Figure S2). The  $\epsilon_{\text{max}}^{\text{fl}}$  values are corrected for the  $\lambda^2$  factor. Using this plot and the  $\epsilon_{\text{max}}^{\text{fl}}$  value of C-480 in each kind of micelles, the micropolarities in terms of  $E_{\text{T}}(30)$  have been calculated and given in Table 2 along with  $\lambda_{\text{max}}^{\text{fl}}$  and  $\epsilon_{\text{max}}^{\text{fl}}$  values. It is

**Table 2. Micropolarity Expressed in Equivalent Scale of  $E_{\text{T}}(30)$  and Microviscosity of Micelles**

surfactant	$\lambda_{\text{max}}^{\text{fl}}$ (nm)	$\epsilon_{\text{max}}^{\text{fl}}$ (cm <sup>-1</sup> )	$E_{\text{T}}(30)$ (kcal mol <sup>-1</sup> )	anisotropy	microviscosity (cP)
Gemini-A	477	20 722	54.43	0.022	15.1
Gemini-B	478	20 687	55.02	0.035	27.2
Gemini-C	479	20 670	55.33	0.040	30.9

noteworthy that for all three micelles, the  $E_{\text{T}}(30)$  values are close to that of methanol (55.4 kcal mol<sup>-1</sup>). This experiment further supports that the probe molecules are mostly located at the Stern layer.<sup>16,23</sup>

**3.2. Fluorescence Lifetime Study.** Excited singlet state lifetimes of C-480 have been determined in pure water, methanol and cyclohexane and also in aqueous micellar solutions of three different gemini surfactants. All decays are found to be triexponential in presence of micelles and monoexponential in presence of pure solvents. The fluorescence decay of C-480 at 460 nm in Gemini-A micelles along with the best fit and residuals are shown by representative Figure S3. Without giving much emphasis on the multi-component decays, the average lifetime ( $\langle t \rangle$ ) values have been calculated using eq 1 to compare the microenvironment of micelles with the homogeneous solvents.

$$\langle t \rangle = \sum a_i \tau_i \quad (1)$$

where  $a_i$  is the pre-exponential factor of the  $i$ th component and  $\tau_i$  is the lifetime of the  $i$ th component.

The average lifetimes with  $\chi^2$  values are listed in Table 3. The lifetime of C-480 in pure water is 5.89 ns, which is very close to the reported value.<sup>43</sup> The average lifetime values of C-480 in the micellar media of Gemini-A and Gemini-B are close to that in methanol and quite different from that in cyclohexane. This value in Gemini-C is different from that in methanol, but close to that in pure water. This could be because of the fact that the micropolarity at the Stern layer of Gemini-C is higher than that of other two geminis as a result of presence of more number of hydroxyl groups on the spacer group of Gemini-C.

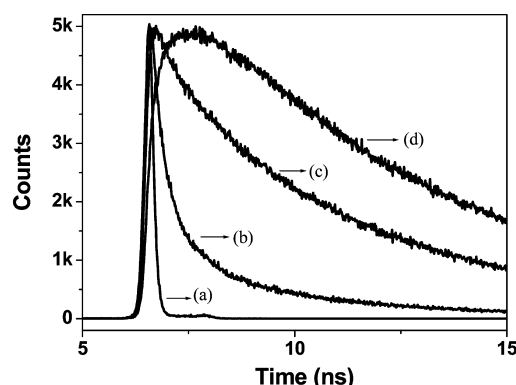
**3.3. Study on Solvation Dynamics.** C-480 shows time-dependent Stokes' shifts in the emission spectra in micelles. The fluorescence decays of C-480 in the micelles of each of the three gemini surfactants are observed at several wavelength (15 nm intervals) across the range of its emission spectrum (415–580 nm) by exciting the sample at 375 nm. The wavelength dependent fluorescence decay characteristics of C-480 in the micelles of Gemini-A are shown by Figure 2 as a representative one. It has been observed in each case of micellar system that toward the blue edge of the fluorescence spectrum of C-480 the decay is very fast, but toward the red edge of the spectrum initially there is a rise (or growth) in the decay followed by a slow decay, and the growth is clearly resolvable (Figure 2). The rapid decay at a short wavelength generally corresponds to the fluorescence from the unsolvated dipoles created at the excited



Table 3. Excited State Lifetime<sup>a</sup> of C-480 in Various Homogeneous and Micellar Media

system	$a_1^b$	$\tau_1$ (ns)	$a_2^b$	$\tau_2$ (ns)	$a_3^b$	$\tau_3$ (ns)	$\langle\tau_{\text{avg}}\rangle$ (ns)	$\chi^2$
water	1.00	5.89	—	—	—	—	5.89	1.09
cyclohexane	1.00	3.13	—	—	—	—	3.13	1.12
methanol	1.00	4.90	—	—	—	—	4.90	1.01
Gemini-A	0.03	2.60	0.84	5.69	0.13	1.48	5.05	1.01
Gemini-B	−0.01	2.77	0.84	5.76	0.17	1.73	5.11	1.05
Gemini-C	0.12	3.04	−0.04	2.70	0.92	5.84	5.62	1.08

<sup>a</sup> $\lambda_{\text{ex}} = 375$  nm,  $\lambda_{\text{em}} = 475$  nm. <sup>b</sup>All pre-exponential factors ( $a$ ) are normalized.



**Figure 2.** Time resolved fluorescence decay of C-480 in the micelles of Gemini-A at (a) instrument response function, (b) 415 nm, (c) 460 nm, and (d) 580 nm.  $\lambda_{\text{ex}} = 375$  nm. [Gemini-A] = 18 mM.

state without undergoing any relaxation process. But in the present case a significant contribution from the solvated dipoles is also expected. Because our TCSPC setup does not allow us to study the initial fast relaxation processes of entirely unsolvated dipoles. However, a decay occurs at a long wavelength corresponds to the relaxation of the solvated dipoles created at the excited state followed by the fluorescence emission, and is thus delayed by relaxation time.<sup>4,7</sup> So this wavelength-dependent dynamics of C-480 clearly indicates that the probe molecule undergoes solvation at the Stern layer which leads to a time-dependent Stokes' shift in the emission spectra. It is noteworthy that the solvation of the solute if present in the bulk water is too fast to be measured by our instrument (time resolution  $\sim 165$  ps). It is expected that the few solute molecules present in the core of the micelles will not exhibit any time-dependent Stokes' shift in the emission spectra.<sup>16</sup>

To study the solvation dynamics of C-480 at the Stern layer, we have calculated the solvent correlation function,  $C(t)$  which is defined in eq 2 and explained by Fleming and Maroncelli:<sup>10</sup>

$$C(t) = \frac{v(t) - v(\infty)}{v(0) - v(\infty)} \quad (2)$$

Here  $v(t)$ ,  $v(\infty)$ , and  $v(0)$  are the peak frequencies at time  $t$ , infinity and zero, respectively. To evaluate the peak frequencies, the time-resolved emission spectra (TRES) have been constructed following the method of Fleming and Maroncelli<sup>10</sup> collecting the decay profiles at various wavelengths across the entire range of an emission spectrum. To deconvolute the instrument response function, each decay profile was fitted to a triexponential function to have  $\chi^2$  value in between 1 and 1.2 using decay analysis software (DAS 6). The impulse response function,  $I(\lambda, t)$  was calculated using those best fitted decay

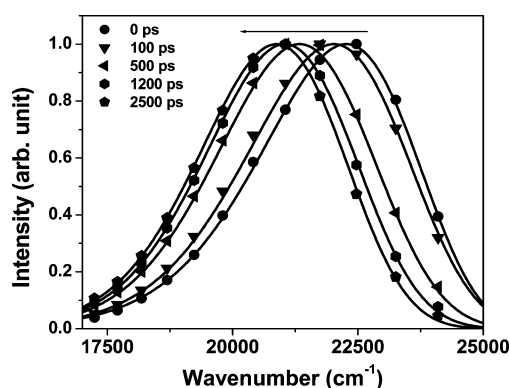
profiles. To construct the TRES, a set of  $H(\lambda)$  values was calculated using eq 3:

$$H(\lambda) = \frac{F(\lambda)}{\sum a_i(\lambda)\tau_i(\lambda)} \quad (3)$$

Here  $F(\lambda)$  is the steady-state intensity,  $a_i(\lambda)$  is the pre-exponential factor, and  $\tau_i(\lambda)$  is the decay time at that wavelength with  $\sum a_i(\lambda) = 1$ . The TRES at different times were constructed from the appropriately normalized intensity decay functions,  $I(\lambda, t)$  for various wavelengths and at various times using eq 4.

$$I'(\lambda, t) = H(\lambda) \times I(\lambda, t) = H(\lambda) \sum a_i(\lambda) \exp[-t/\tau_i(\lambda)] \quad (4)$$

The emission maximum at each time,  $v(t)$  was then obtained after fitting the spectrum to a log-normal function.<sup>10,14</sup> A representative TRES of C-480 in Gemini-A micelle is shown in Figure 3. The time constants of the observable solvation are



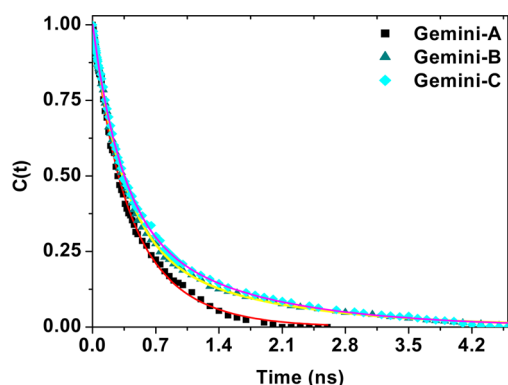
**Figure 3.** Time-resolved emission spectra (TRES) of C-480 in Gemini-A micelles.

obtained after fitting the plot of solvent correlation function,  $C(t)$  versus time. A biexponential function which is written as eq 5, has been used to obtain the solvent relaxation time constants.

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

where,  $\tau_1$  and  $\tau_2$  are the solvent relaxation time constants and  $a_1$  and  $a_2$  are normalized pre-exponential factors. The decay plots of  $C(t)$  versus time for micelles of all three gemini surfactants are shown in Figure 4. The decay parameters of C-480 in different micelles are listed in Table 4.

The solvation dynamics for C-480 is bimodal (fast and slow solvation components) in nature in all three micelles. Nandi et al.<sup>13</sup> studied the time dependent relaxation of biological water and according to them dynamic equilibrium between the "free" and "bound" water molecules are responsible for the bimodal



**Figure 4.** Decay of solvent correlation function  $C(t)$  of C-480 in micelles of gemini surfactants.

solvation dynamics. The “bound” water molecules are responsible for slower component. However, comparatively “free” water molecules are responsible for fast solvation. In the present systems, many factors could be responsible for solvation of dipole created at the excited state, and they are water molecules, counterions, headgroup and spacer groups of geminis. The polar headgroups of surfactant being attached to the long chain is expected to contribute to a very slow solvation dynamics (nanosecond time scale).<sup>16,59</sup> Similarly, the solvation due to the hydrophilic spacer group is also expected to be slow because of restricted mobility of the spacer group as it is connected with two hydrocarbon chains at their headgroups. Therefore, the water molecules and counterions are mostly responsible for the solvation dynamics. It has been reported that the hydrogen bond strength between two water molecules is much weaker than that between water molecules and polar headgroups of surfactant molecules.<sup>16,60,61</sup> Thus, water molecules hydrogen bonded with polar headgroups of surfactant molecules are responsible for slow component. However, the other type of water molecules contributes to the fast solvation dynamics. The time scale for the fast component (major component) of solvation dynamics at the Stern layer of present micelles is 233–334 ps (Table 4). This time scale is 3 orders of magnitude slower than that in bulk water.<sup>12</sup> Vajda et al.<sup>12</sup> have reported based on their fluorescence upconversion experiment that the solvation time of C-480 in bulk water is 310 fs. However, in the present micelles, the solvation dynamics occur on almost the same time scale as that in case of micelles of conventional surfactants.<sup>16</sup>

In the present study, we have observed that the time scales for both the solvation components and obviously the average solvation time increase on hydroxyl substitution of the spacer group of a gemini surfactant. Except spacer group, all other chemical parts (counterion, hydrophobic tail, headgroups) are same in the studied gemini surfactants. It means that the spacer group plays an important role in the solvation, because the effects of other components are expected to be same in all three micelles. The hydroxyl group(s) of a spacer group of gemini

surfactant forms hydrogen bond(s) with water molecules at the micelle-water interface and may protect the probe molecule from its contact with some of the water molecules. It could be the reason that there is a little increase in the solvation time scale of fast component in each case of Gemini-B and Gemini-C as compared to Gemini-A.

The mobility of water molecules those are hydrogen bonded with the hydroxyl group(s) of the spacer group and also with the probe molecule is expected to be restricted because of the restricted motion of the spacer group. Thus, some of these water molecules in addition to the water molecules hydrogen bonded with the polar headgroups may also be responsible for slow solvation dynamics. Counter ions generally contribute to the slow solvation dynamics. However, hydroxyl group(s) of the spacer group can also participate in hydrogen bond formation with the counterions ( $\text{Br}^-$ ) of the surfactant<sup>60</sup> and protect these ions from taking part in solvation process. The data in Table 4 show that the slow component becomes three times slower on hydroxyl substitution of the spacer group. Water molecules are protected from their contact with the probe molecule through hydrogen bonding interaction with the hydroxyl group(s) of the spacer group. While doing so the spacer group gets hydrated. Because of this kind of protection the solvation dynamics becomes slower. The greater extent of hydration of spacer groups of Gemini-B and Gemini-C as compared to Gemini-A is supported by the lower values of cmc of the former two surfactants than that of the third one (Table 1). A gemini surfactant with hydrophilic, flexible spacer has higher affinity toward micelle formation.<sup>62,63</sup> As a result of that such kind of gemini surfactants have lower cmc as compared to that of a gemini surfactant with rigid, hydrophobic spacer. According to Wang et al.<sup>63</sup> the hydrophilic spacer can easily be located at the micelle-water interface and therefore can be hydrated which leads to the reduction of the Coulombic repulsive interactions between the headgroups of a gemini surfactant molecule. Thus, Gemini-A is less active toward the micelle formation than that of Gemini-B and Gemini-C.<sup>55</sup> The lower value of cmc of Gemini-C as compared to that of Gemini-B could be because of greater extent of intermolecular hydrogen bonding between the former surfactant molecules than that between the latter surfactant molecules as in case of Gemini-C there are two hydroxyl groups in a spacer group. This fact probably could be supported by the hydrodynamic radii values of micelles of three surfactants determined by DLS method. The observed hydrodynamic radii of the micelles of Gemini-A, Gemini-B and Gemini-C with surfactant concentrations of 15 times of cmc are  $1.92 \pm 0.03$ ,  $1.87 \pm 0.03$  and  $1.62 \pm 0.03$  nm, respectively (Figure S4). The similar trend has also been reported in the literature for the micelles of these three surfactants at their cmc.<sup>55</sup> The higher values of hydrodynamic radii obtained in the present work as compared to the reported values are because of taking higher concentration of surfactant in this work. These values depict that the micelles are spherical in shape<sup>36,64,65</sup> and with

**Table 4.** Decay Characteristics of  $C(t)$  of C-480 in Different Micelles

surfactant	$a_1$	$\tau_1$ (ps)	$a_2$	$\tau_2$ (ps)	$\langle \tau_s \rangle^a$ (ps)	$\Delta v^b$ ( $\text{cm}^{-1}$ )	missing component (%)
Gemini-A	0.34	233	0.66	574	458	1354	16
Gemini-B	0.72	334	0.28	1704	718	1448	20
Gemini-C	0.64	330	0.36	1471	741	1470	15

$$^a \langle \tau_s \rangle = a_1 \tau_1 + a_2 \tau_2. \quad ^b \Delta v = v(0) - v(\infty).$$

increasing number of hydroxyl groups in the spacer group a micelle becomes progressively more and more close packed due to greater extent of hydrogen bonding interactions and does affect the cmc. It is noteworthy that because of greater extent of intermolecular hydrogen bonding and hydrogen bonding with C-480 molecules in case of Gemini-C micelles as compared to Gemini-B micelles, the water molecules may not be protected with the strength in same proportion in the former as it is in the latter. As a result of that the solvation time does not increase in the same proportion for Gemini-C micelles as it is observed for Gemini-B micelles with respect to solvation time in Gemini-A micelles.

Tamoto et al.<sup>30</sup> have studied the solvation dynamics of C-102 (or C-480) in presence of conventional anionic and cationic surfactants. The average solvation time reported by them in the micelles of dodecyltrimethylammonium bromide (DTAB), which is the conventional counterpart of the present studied gemini surfactants is found to be 260 ps. The higher average solvation time in presence of present gemini surfactants than that of DTAB is due to the effect of spacer group as discussed above.

The microviscosity values of environment around probe in three gemini micelles have been calculated (discussed latter) and given in Table 2. The trend in microviscosity and average solvation time has very close correlation. It infers that viscosity may also be leading to slow down the solvation dynamics.

**3.4. Time-Resolved Fluorescence Anisotropy (or Rotational Relaxation) Studies.** To get more information about the microenvironment around the probe, the time-resolved fluorescence anisotropy studies have been performed in water and micellar media. The time-resolved fluorescence anisotropy,  $r(t)$  has been calculated using eq 6:

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)} \quad (6)$$

Here  $G$  represents the correction factor for the detector sensitivity to the polarization detection of emission (the value of  $G$  for our instrument is  $\sim 0.6$ ),<sup>4,51</sup>  $I_{\parallel}(t)$  and  $I_{\perp}(t)$  are fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. The combined anisotropy decays of C-480 in water and in Gemini-A, Gemini-B, and Gemini-C micelles are shown by Figure 5. The anisotropy decay of C-480 is single exponential in water, however the decays are biexponential in nature in all three

micellar media. The biexponential anisotropy decay function can be represented as eq 7

$$r(t) = r_0[a_{1r}e^{-t/\tau_{1r}} + a_{2r}e^{-t/\tau_{2r}}] \quad (7)$$

where  $r_0$  is the limiting anisotropy to represent the inherent depolarization of the probe molecule,  $\tau_{1r}$  and  $\tau_{2r}$  are the fast and slow rotational relaxation components of the probe molecule in micellar media, respectively, and  $a_{1r}$  and  $a_{2r}$  are the relative amplitudes of two components, respectively. The average rotational relaxation time for the biexponential decay in micelles is calculated using eq 8:

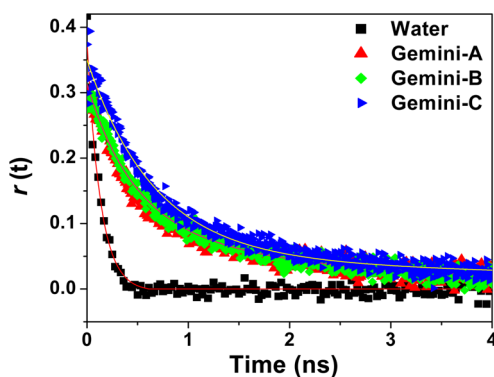
$$\langle \tau_r \rangle = a_{1r}\tau_{1r} + a_{2r}\tau_{2r} \quad (8)$$

All rotational relaxation parameters of C-480 in pure water and in micellar media are tabulated in Table 5. The rotational relaxation times in micellar media are longer than that in pure water. The relaxation time in pure water is found to be 132 ps which is very close to the reported value, i.e., 125 ps.<sup>23</sup> The slow anisotropy decay in micellar media as compared to pure water suggests that the microenvironment around the probe molecule in micelles is such that the random motion is restricted in comparison to pure water. There is an increasing tendency of average rotational relaxation time of C-480 in the micelles of gemini surfactants with increase in the number of substituted hydroxyl group(s) in the spacer group. As discussed above, with increasing number of substituted hydroxyl groups in the spacer group, the micelles become more and more close packed. As a result of that the microviscosity of environment around the probe molecule gradually increases which leads to gradual increase in the rotational relaxation time of C-480.

To support the fact that the microviscosity of environment around C-480 in micelles increases with increasing number of substituted hydroxyl groups of the spacer group, the microviscosity values in three micellar media with surfactant concentrations  $\sim 15$  times of their respective cmc have been calculated. For this purpose we have explored the viscosity dependent fluorescence properties of C-480. See Note 2 in the Supporting Information for detailed method of determination of microviscosity.<sup>66–68</sup> The microviscosity values of micelles along with the steady-state fluorescence anisotropy of C-480 are also tabulated in Table 2. The data in Table 2 support the fact that the microviscosity of the micelles increases with gradual increase in the number of substituted hydroxyl group of the spacer group of gemini surfactant as a result of increasing close packing of surfactant molecules. It is noteworthy that these microviscosity values are approximate because the possibility of increased anisotropy partly due to the hydrogen bonding interaction cannot be ruled out.<sup>69</sup>

The fluorescence anisotropy decay of C-480 in the micellar media is biexponential in nature. This biexponential anisotropy decay is not because of its different locations, but due to its various kinds of rotational motions.<sup>49</sup> For detailed explanation of the biexponential behavior of anisotropy decay as a result of different types of rotational motions, the model often used is the two-step and wobbling-in-a-cone model (see Note 3 in Supporting Information section).<sup>49</sup> On the basis of the two-step model,  $\tau_{2r}$  is related to the relaxation time corresponding to the rotational motion of micelle as a whole ( $\tau_m$ ) and the relaxation time corresponding to the lateral diffusion of the fluorophore ( $\tau_D$ ) as follows (eq 9):

$$\frac{1}{\tau_{2r}} = \frac{1}{\tau_D} + \frac{1}{\tau_m} \quad (9)$$



**Figure 5.** Decays of fluorescence anisotropy of C-480 in the pure water and in the micelles of gemini surfactants.

Table 5. Rotational Relaxation Parameters for C-480 in Different Micelles

system	$r_0$	$a_{1r}$	$\tau_{1r}$ (ps)	$a_{2r}$	$\tau_{2r}$ (ps)	$\chi^2$	$\langle\tau_r\rangle$ (ps)
water	0.38	$1.00 \pm 0.02$	$132 \pm 45$	—	—	1.06	132
Gemini-A	0.32	$0.64 \pm 0.02$	$372 \pm 62$	$0.36 \pm 0.02$	$1663 \pm 097$	1.04	837
Gemini-B	0.31	$0.67 \pm 0.03$	$438 \pm 70$	$0.33 \pm 0.01$	$1868 \pm 108$	1.03	910
Gemini-C	0.35	$0.80 \pm 0.02$	$652 \pm 68$	$0.20 \pm 0.01$	$3124 \pm 325$	1.11	1146

Table 6. Values of the Internal Motion of the Probe ( $\tau_e$ ), the Overall Rotation Motion of the Micelles ( $\tau_m$ ), Lateral Diffusion of the Probe ( $\tau_D$ ), Wobbling Diffusion Coefficient ( $D_w$ ), Cone Angle ( $\theta_o$ ), and the Order Parameter (|S|) Obtained from the Anisotropy Decays of C-480 in Different Micelles

surfactant	$\tau_e$ (ps)	$\tau_m$ (ps)	$\tau_D$ (ps)	$D_w \times 10^{-8}$ (s <sup>-1</sup> )	$\theta_o$ (deg)	S
Gemini-A	$479 \pm 62$	$6440 \pm 097$	$2242 \pm 097$	3.79	45.24	0.60
Gemini-B	$572 \pm 70$	$5950 \pm 108$	$2723 \pm 108$	3.46	47.24	0.57
Gemini-C	$824 \pm 68$	$3870 \pm 325$	$16206 \pm 325$	3.27	55.08	0.45

The detailed method<sup>70</sup> of calculation of  $\tau_m$  is discussed in the Supporting Information, Note 4. The values of  $\tau_m$  calculated at 298 K using estimated  $r_h$  values of three micelles given above and  $\tau_D$  values calculated using eq 9 are given in Table 6. For Gemini-A and Gemini-B,  $\tau_m$  values are much higher than the respective  $\tau_{2r}$ . So it can be stated that for these two micelles,  $\tau_{2r}$  are dominated by lateral diffusion. However, for Gemini-C,  $\tau_m$  value is close to the value of  $\tau_{2r}$ . Thus, slow rotational relaxation is mainly due to the rotational motion of the micelle as a whole. This is supported by very slow relaxation corresponding to the lateral diffusion of the fluorophore. The relaxation time corresponding to the lateral diffusion of the fluorophore in Gemini-C is much longer than that in Gemini-A and Gemini-B. The microviscosity of Gemini-C micelles is similar to that of Gemini-B micelles (Table 2). Therefore, the large extent of intermolecular hydrogen bonding interactions between C-480 and hydroxyl groups of the spacer group of Gemini-C must be the dominating factor for very high value of  $\tau_D$  in the micelles of it.

Two hydroxyl groups in the spacer group of Gemini-C might be contributing greater extent of hydrogen bonding interactions than that with one hydroxyl group in the spacer group of Gemini-B. The large extent of hydrogen bonding interactions in case of Gemini-C restrict the translational diffusion of the fluorophore. As a result of that the slow rotational relaxation is essentially dominated by the rotational motion of the micelle as a whole. This observation is in contrary to the results reported by Maroncelli and co-worker.<sup>71</sup> They have reported that rotational relaxation times correlate well with viscosity and not with solvent hydrogen bonding ability. Our argument is that in the present case the effect of hydrogen bonding interactions dominate over that of viscosity as hydroxyl groups are attached to the spacer group of gemini surfactants. The mobility of hydroxyl groups attached to the spacer group is more restricted than that of solvents. However, more clarity is required for the effect of viscosity and hydrogen bonding interactions on the rotational relaxation times in the future.

The fast motion has been modeled as restricted rotational diffusion. An effective relaxation time ( $\tau_e$ ) corresponding to the restricted rotational diffusion is related to the fast relaxation time ( $\tau_{1r}$ ) and slow relaxation time ( $\tau_{2r}$ ) as follows (eq 10):

$$\frac{1}{\tau_{1r}} = \frac{1}{\tau_e} + \frac{1}{\tau_{2r}} \quad (10)$$

The effective relaxation time,  $\tau_e$  can be considered to be a measure of the relaxation of the local structure of the micelle.<sup>70</sup>

The  $\tau_e$  values calculated using eq 10 are given in Table 6. The  $\tau_e$  values of C-480 in three different micelles are significantly different. The  $\tau_e$  value increases in presence of hydroxyl group and with increasing number of hydroxyl group in the spacer group of gemini surfactants. The hydrogen bonding interactions between the fluorophore and the hydroxyl group(s) of the spacer group of gemini molecules cause motions of the fluorophore molecule to be more strongly coupled to the motions of the micelle. As compared to Gemini-B, the extent of hydrogen bonding interactions could be greater in Gemini-C resulting in the local structure to take shorter relaxation time in the former than that in the latter. The values of order parameter, |S|, cone angle,  $\theta_o$ , and wobbling diffusion coefficient,  $D_w$ , introduced by the wobbling-in-a-cone model<sup>49</sup> (see Note 3 in the Supporting Information) are tabulated in Table 6. As the internal motion of the probe ( $\tau_e$ ) becomes slower with gradual increase in the number of hydroxyl group in the spacer group, wobbling diffusion coefficient,  $D_w$  becomes progressively smaller. The high value of |S| supports location of the probe molecule at the Stern layer.

It can be seen from the data in Table 6 that  $\theta_o$  and |S| values are not correlating well with the microviscosity and extent of hydrogen bonding interactions.  $\theta_o$  is higher and |S| is lower for Gemini-C as compared to other two micelles. To overcome this discrepancy spinning-in-equatorial-band model has been acquired in case of Gemini-C. This model is applicable when |S| < 0.5, which is the case for Gemini-C. According to this model, the rod-like probe molecule is aligned in such a way that the emission moment is perpendicular to the long axis<sup>70,72</sup> and |S| is related to  $\theta_o$  as follows (eq 11):

$$S^2 = [(1/2)(1 - \cos^2 \theta_o)]^2 \quad (11)$$

The cone angle,  $\theta_o$  calculated using eq 11 is coming out to be 71.56° which is different from that calculated using wobbling-in-a-cone model (Table 6). The  $\tau_e$  as well as  $D_w$  values are in favor of the fact that the hydrogen bonding interactions between the C-480 and the hydroxyl group(s) of the spacer group of gemini molecules cause restricted motions of C-480. However, unexpected values of  $\theta_o$  and |S| in case of Gemini-C indicating that the orientation of C-480 in this micelles must be different from that in other two micelles. The greater extent of hydrogen bonding interactions in Gemini-C micelles are responsible for this different orientation. In fact in case of Gemini-B also  $\theta_o$  is little higher and |S| is little lower as compared to Gemini-A. But the differences in these values are not as prominent as they are in case of Gemini-C, because in



case of Gemini-C the hydrogen bonding interactions are higher as compared to Gemini-B.

**3.5. Missing Components.** Since the time resolution of our instrument is low, most of the portion of dynamic Stokes shift is missed. The missing components for the studied systems have been calculated using the method given by Fleming and Maroncelli<sup>10</sup> (see Note 5 in the Supporting Information). The calculated missing components for Gemini-A, Gemini-B, and Gemini-C are 16, 20, and 15% of the total spectral shift (Table 4) those are comparatively lower than that of DTAB micellar system (43%).<sup>23</sup>

## 4. CONCLUSIONS

In the present work, we have studied the effect of the spacer group of gemini surfactants on solvation dynamics and rotational relaxation of C-480 at the Stern layer. Steady-state and TCSPC fluorescence study reveal that probe molecules are mostly residing at the Stern layer. Although the fast component of solvation has the same time scale as that in case of micelles of conventional surfactants, but the solvation is found to be slower on hydroxyl substitution of the spacer group. The increase in the solvation time could be due to the formation of hydrogen bonds between water molecules and hydroxyl group(s) of spacer group which results in protection of the probe molecule from its contact with some of the water molecules. Moreover, hydrogen bonding interactions between hydroxyl group(s) of the spacer group and water molecules may restrict the mobility of water molecules as well. The average rotational relaxation time of C-480 increases with increase in the number of substituted hydroxyl group(s) in the spacer group of surfactants. With increasing number of substituted hydroxyl group in the spacer group, the micelles become more and more close packed. As a result of that the microviscosity of environment around the probe molecule gradually increases which leads to gradual increase in the rotational relaxation time of C-480. The anisotropy decay is bimodal in nature. For Gemini-A and Gemini-B, the slow rotational relaxation is dominated by the lateral diffusion of the fluorophore. However, for Gemini-C, the slow rotational relaxation is mainly due to the rotational motion of the micelle as a whole. Exceptionally slow relaxation corresponding to the lateral diffusion of the fluorophore in Gemini-C as compared to Gemini-A and Gemini-B could be because of an additional factor, i.e., greater extent of hydrogen bonding interactions between hydroxyl groups of the spacer group of Gemini-C and C-480. The effective relaxation time,  $\tau_e$  significantly increase on hydroxyl substitution of the spacer group. The hydrogen bonding interactions between the fluorophore and the hydroxyl group(s) of the spacer group cause motions of the fluorophore molecule to be more strongly coupled to the motions of the micelle. There is an indication of different kind of orientation of C-480 in Gemini-C micelles as compared to other two micelles. This could be because of different extent of hydrogen bonding interactions in the former than that in other two micelles. Looking into the fact that properties of gemini surfactants can be tuned by changing chemical nature of spacer groups and they are being widely used as solubilizers in various applications, the study of dynamics of water molecules and rotational relaxation of a molecule has practical and fundamental importance.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

FT-IR and <sup>1</sup>H NMR data of the synthesized gemini surfactants, a brief note on the determination of cmc of gemini surfactants by conductivity method with a figure showing the plots, plots showing variation of the fluorescence energy at peak maximum of C-480 in dioxane-water mixture with  $E_T(30)$  of the dioxane-water mixture and the time-resolved fluorescence decay of C-480 at 460 nm in Gemini-A micelles along with the best fit and residuals, a size distribution graph for the micelles of gemini surfactants, a note on the method of determination of microviscosity, a plot of fluorescence anisotropy of C-480 as a function of volume percentages of glycerol-methanol mixture and a plot containing viscosity as a function of volume percentage of glycerol-methanol mixture, and brief notes on the wobbling-in-a-cone model, methods to compute the  $\tau_m$  and the percentage of missing component. These information are available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*(S.K.S.) Telephone: +91 1596 515279. Fax: +91 1596 244183  
E-mail: [sksaha@pilani.bits-pilani.ac.in](mailto:sksaha@pilani.bits-pilani.ac.in); [subitksaha@gmail.com](mailto:subitksaha@gmail.com).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

S.K.S. acknowledges the University Grants Commission (UGC) special assistance program (F.540/14/DRS/2007 (SAP-I)), Department of Science and Technology (DST) FIST program, Government of India and also the Aditya Birla Groups for financial support. A.K.T. acknowledges CSIR for financial support under senior research fellowship, and S. acknowledges the UGC for financial support under a junior research fellowship.

## ■ REFERENCES

- (1) Zhong, D.; Pal, S. K.; Zewail, A. H. Biological water: A critique. *Chem. Phys. Lett.* **2011**, 503, 1–11.
- (2) Denisov, V. P.; Peters, J.; Horlein, H. D.; Halle, B. Using Buried Water Molecules to Explore the Energy Landscape of Proteins. *Nat. Struct. Biol.* **1996**, 3, 505–509.
- (3) Telgmann, T.; Kaatz, U. Monomer Exchange and Concentration Fluctuations of Micelles. Broad-band Ultrasonic Spectrometry of the System Triethylene Glycol Monoethyl Ether/Water. *J. Phys. Chem. A* **2000**, 104, 1085–1094.
- (4) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic: New York, 1999.
- (5) Kahlow, M. A.; Jarzeba, W.; Kang, T. J.; Barbara, P. F. Femtosecond Resolved Solvation Dynamics in Polar Solvents. *J. Chem. Phys.* **1989**, 90, 151–158.
- (6) Silva, C.; Walhout, P. K.; Yokoyama, K.; Barbara, P. F. Femtosecond Solvation Dynamics of the Hydrated Electron. *Phys. Rev. Lett.* **1998**, 80, 1086–1089.
- (7) Bhattacharyya, K. Nature of Biological Water: A Femtosecond Study. *Chem. Commun.* **2008**, 2848–2857.
- (8) Chapman, C. F.; Fee, R. S.; Maroncelli, M. Measurements of the Solute Dependence of Solvation Dynamics in 1-propanol: The Role of Specific Hydrogen-bonding Interactions. *J. Phys. Chem.* **1995**, 99, 4811–4819.
- (9) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. Subpicosecond Measurements of Polar Solvation Dynamics: Coumarin 153 Revisited. *J. Phys. Chem.* **1995**, 99, 17311–17337.

- (10) Maroncelli, M.; Fleming, G. R. Picosecond Solvation Dynamics of Coumarin 153: The Importance of Molecular Aspects of Solvation. *J. Chem. Phys.* **1987**, *86*, 6221–6239.
- (11) Jimenez, R.; Fleming, G. R.; Kumar, P. V.; Maroncelli, M. Dynamics of Water. *Nature* **1994**, *369*, 471–473.
- (12) Vajda, S.; Jimenez, R.; Rosenthal, S. J.; Fidler, V.; Fleming, G. R.; Castner, E. W. Femtosecond to Nanosecond Solvation Dynamics in Pure Water and Inside the  $\gamma$ -Cyclodextrin Cavity. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 867–873.
- (13) Nandi, N.; Bagchi, B. Dielectric Relaxation of Biological Water. *J. Phys. Chem. B* **1997**, *101*, 10954–10961.
- (14) Maciejewski, A.; Kubicki, J.; Dobek, K. The Origin of Time-Resolved Emission Spectra (TRES) Changes of 4-Aminophthalimide (4-AP) in SDS Micelles. The Role of the Hydrogen Bond Between 4-AP and Water Present in Micelles. *J. Phys. Chem. B* **2003**, *107*, 13986–13999.
- (15) Kumbhakar, M. Effect of Ionic Surfactants on the Hydration Behavior of Triblock Copolymer Micelles: A Solvation Dynamics Study of Coumarin 153. *J. Phys. Chem. B* **2007**, *111*, 12154–12161.
- (16) Sarkar, N.; Datta, A.; Das, S.; Bhattacharyya, K. Solvation Dynamics of Coumarin 480 in Micelles. *J. Phys. Chem.* **1996**, *100*, 15483–15486.
- (17) Datta, A.; Mandal, D.; Pal, S. K.; Das, S.; Bhattacharyya, K. Solvation Dynamics in Organized Assemblies, 4-aminophthalimide in Micelles. *J. Mol. Liq.* **1998**, *77*, 121–129.
- (18) Chakraborty, D.; Hazra, P.; Chakraborty, A.; Sarkar, N. Solvation Dynamics of Coumarin 480 in Bile Salt-Cetyltrimethylammonium bromide (CTAB) and Bile Salt-Tween 80 Mixed Micelles. *J. Phys. Chem. B* **2003**, *107*, 13643–13648.
- (19) Dey, S.; Adhikari, A.; Mandal, U.; Ghosh, S.; Bhattacharyya, K. Solvation Dynamics in Ionic Liquid Swollen P123 Triblock Copolymer Micelle: A Femtosecond Excitation Wavelength Dependence Study. *J. Phys. Chem. B* **2008**, *112*, 5020–5026.
- (20) Das, A. K.; Mondal, T.; Mojumdar, S. S.; Bhattacharyya, K. Marcus-like Inversion in Electron Transfer in Neat Ionic Liquid and Ionic Liquid-Mixed Micelles. *J. Phys. Chem. B* **2011**, *115*, 4680–4688.
- (21) Chakraborty, D.; Hazra, P.; Chakraborty, A.; Sarkar, N. Dynamics of Solvation and Rotational Relaxation in Neutral Brij 35 and Brij 58 Micelles. *Chem. Phys. Lett.* **2004**, *392*, 340–347.
- (22) Chakraborty, D.; Hazra, P.; Sarkar, N. Solvation Dynamics of Coumarin 480 in TritonX-100 (TX-100) and Bile Salt Mixed Micelles. *J. Phys. Chem. A* **2003**, *107*, 5887–5893.
- (23) Chakraborty, D.; Chakraborty, A.; Seth, D.; Hazra, P.; Sarkar, N. Effect of Alkyl Chain Length and Size of the Headgroups of the Surfactant on Solvent and Rotational Relaxation of Coumarin 480 in Micelles and Mixed Micelles. *J. Chem. Phys.* **2005**, *122*, 184516–1–7.
- (24) Sykora, J.; Slavicek, P.; Jungwirth, P.; Barucha, J.; Hof, M. Time-Dependent Stokes Shifts of Fluorescent Dyes in the Hydrophobic Backbone Region of a Phospholipid Bilayer: Combination of Fluorescence Spectroscopy and Ab Initio Calculations. *J. Phys. Chem. B* **2007**, *111*, 5869–5877.
- (25) Sykora, J.; Jurkiewicz, P.; Epand, R. M.; Kraayenhof, R.; Langner, M.; Hof, M. Influence of the Curvature on the Water Structure in the Headgroup Region of Phospholipid Bilayer Studied by the Solvent Relaxation Technique. *Chem. Phys. Lipids* **2005**, *135*, 213–221.
- (26) Sykora, J.; Mudogo, V.; Hutterer, R.; Nepras, M.; Vanerka, J.; Kapusta, P.; Fidler, V.; Hof, M. ABA-C15: A New Dye for Probing Solvent Relaxation in Phospholipid Bilayers. *Langmuir* **2002**, *18*, 9276–9282.
- (27) Jurkiewicz, P.; Olzynska, A.; Langner, M.; Hof, M. Headgroup Hydration and Mobility of DOTAP/DOPC Bilayers: A Fluorescence Solvent Relaxation Study. *Langmuir* **2006**, *22*, 8741–8749.
- (28) Sengupta, A.; Hazra, P. Solvation Dynamics of Coumarin 153 in SDS Dispersed Single Walled Carbon Nanotubes (SWNTs). *Chem. Phys. Lett.* **2010**, *501*, 33–38.
- (29) Sengupta, A.; Khade, R. V.; Hazra, P. How Does the Urea Dynamics Differ from Water Dynamics inside the Reverse Micelle? *J. Phys. Chem. A* **2011**, *115*, 10398–10407.
- (30) Tamoto, Y.; Segawa, H.; Shirota, H. Solvation Dynamics in Aqueous Anionic and Cationic Micelle Solutions: Sodium Alkyl Sulfate and Alkyltrimethylammonium Bromide. *Langmuir* **2005**, *21*, 3757–3764.
- (31) Holland, P. M.; Rubingh, D. N. *Mixed Surfactant Systems*. American Chemical Society: Washington, DC, 1992.
- (32) Rosen, M. J.; Tracy, D. J. Gemini Surfactants. *J. Surfactants Deterg.* **1998**, *1*, 547–554.
- (33) Menger, F. M.; Keiper, J. S.; Azov, V. Gemini Surfactants with Acetylenic Spacers. *Langmuir* **2000**, *16*, 2062–2067.
- (34) Menger, F. M.; Keiper, J. S. Gemini Surfactants. *Angew. Chem., Int. Ed.* **2000**, *39*, 1906–1920.
- (35) Zana, R. Dimeric and Oligomeric Surfactants. Behavior at Interfaces and in Aqueous Aolution: A Review. *Adv. Colloid Interface Sci.* **2002**, *97*, 205–253.
- (36) Tiwari, A. K. Sonu; Sowmiya M.; Saha, S. K. Micellization Behavior of Gemini Surfactants with Hydroxyl Substituted Spacers in Water and Water-Organic Solvent Mixed Media: The Spacer Effect. *J. Mol. Liq.* **2012**, *167*, 18–27.
- (37) Danino, D.; Talmon, Y.; Zana, R. Alkanediyl- $\alpha$ - $\omega$ -Bis (Dimethylalkylammonium Bromide) Surfactants (Dimeric Surfactants). 5. Aggregation and Microstructure in Aqueous Solutions. *Langmuir* **1995**, *11*, 1448–1456.
- (38) Oda, R.; Panizza, P.; Schumutz, M.; Lequeux, F. Direct Evidence of the Shear-induced Structure of Wormlike Micelles: Gemini Surfactant 12–2-12. *Langmuir* **1997**, *13*, 6407–6412.
- (39) Shukla, D.; Tyagi, V. K. Cationic Gemini Surfactants: A Review. *J. Oleo Sci.* **2006**, *55*, 381–390.
- (40) Nagarajan, R.; Wang, C. C. Solution Behavior of Surfactants in Ethylene Glycol: Probing the Existence of a CMC and of Micellar Aggregates. *J. Colloid Interface Sci.* **1996**, *178*, 471–482.
- (41) Kabir-ud-din; Koya, P. A. Effects of Solvent Media and Temperature on the Self-aggregation of Cationic Dimeric Surfactant 14–6-14, 2Br– Studied by Conductometric and Fluorescence Techniques. *Langmuir* **2010**, *26*, 7905–7914.
- (42) Yip, R. W.; Wen, Y. X.; Szabo, A. G. Decay Associated Fluorescence Spectra of Coumarin 1 and Coumarin 102: Evidence for a Two-state Solvation Kinetics in Organic Solvents. *J. Phys. Chem.* **1993**, *97*, 10458–10462.
- (43) Jones, G.; Jackson, W. R.; Choi, C. Y.; Bergmerk, W. R. Solvent Effects on Emission Yield and Lifetime for Coumarin Laser Dyes. Requirements for a Rotatory Decay Mechanism. *J. Phys. Chem.* **1985**, *89*, 294–300.
- (44) Chudoba, C.; Nibbering, E. T. J.; Elsaesser, T. Site-Specific Excited-State Solute-Solvent Interactions Probed by Femtosecond Vibrational Spectroscopy. *Phys. Rev. Lett.* **1998**, *81*, 3010–3013.
- (45) Liu, Y.; Ding, J.; Shi, D.; Sun, J. Time-Dependent Density Functional Theory Study on Electronically Excited States of Coumarin 102 Chromophore in Aniline Solvent: Reconsideration of the Electronic Excited-State Hydrogen-Bonding Dynamics. *J. Phys. Chem. A* **2008**, *112*, 6244–6248.
- (46) Palit, D. K.; Zhang, T.; Kumazaki, S.; Yoshihara, K. Hydrogen-Bond Dynamics in the Excited State of Coumarin 102–Aniline Hydrogen-Bonded Complex. *J. Phys. Chem. A* **2003**, *107*, 10798–10804.
- (47) Zhao, G. J.; Han, K. L. Early Time Hydrogen-Bonding Dynamics of Photoexcited Coumarin 102 in Hydrogen-Donating Solvents: Theoretical Study. *J. Phys. Chem. A* **2007**, *111*, 2469–2474.
- (48) Maiti, N. C.; Krishna, M. M. G.; Britto, P. J.; Periasamy, N. Fluorescence Dynamics of Dye Probes in Micelles. *J. Phys. Chem. B* **1997**, *101*, 11051–11060.
- (49) Kinoshita, Jr.; Kawato, S.; Ikegami, A. A Theory of Fluorescence Polarization Decay in Membranes. *J. Biophys.* **1977**, *20*, 289–305.
- (50) Rosen, M.; Liu, L. Surface Activity and Premicellar Aggregation of Some Novel Diquaternary Gemini Surfactants. *J. Am. Oil Chem. Soc.* **1996**, *73*, 885–890.
- (51) Muthusubramanian, S.; Tiwari, A. K. Sonu; Saha, S. K. A Cationic Surfactant-Concentration Dependent Binding of a Guest

Molecule with the Nanotubes of  $\beta$ -Cyclodextrin and its Release from the Nanotubular Cavities. *Soft Matter* **2012**, *8*, 11072–11084.

(52) Tiwari, A. K.; Sonu, S.; Saha, S. K. Aggregation Behaviour and Thermodynamics of Mixed Micellization of Gemini Surfactants with a Room Temperature Ionic Liquid in Water and Water-Organic Solvent Mixed Media. *J. Chem. Thermodyn.* **2013**, *60*, 29–40.

(53) Williams, R. J.; Phillips, J. N.; Mysels, K. J. The Critical Micelle Concentration of Sodium Lauryl Sulphate at 25 °C. *Trans. Faraday Soc.* **1955**, *51*, 728–737.

(54) Tiwari, A. K.; Sonu, S.; Sowmiya, M.; Saha, S. K. Study on Premicellar and Micellar Aggregates of Gemini Surfactants with Hydroxyl Substituted Spacers in Aqueous Solution using a Probe Showing TICT Fluorescence Properties. *J. Photochem. Photobiol. A* **2011**, *223*, 6–13.

(55) Wettig, S. D.; Nowak, P.; Verrall, R. E. Thermodynamic and Aggregation Properties of Gemini Surfactants with Hydroxyl Substituted Spacers in Aqueous Solution. *Langmuir* **2002**, *18*, 5354–5359.

(56) Reichardt, C.; Ratajczak, H.; Thomas, W. J. O. *Molecular Interaction*; Wiley: New York, 1982.

(57) Kosower, E. M.; Dodiuk, H.; Tanizawa, K.; Ottolenghi, M.; Orbach, N. Intramolecular Donor-Acceptor Systems. Radiative and Nonradiative Processes for the Excited States of 2-*n*-arylamino-6-naphthalenesulfonates. *J. Am. Chem. Soc.* **1975**, *97*, 2167–2178.

(58) Sowmiya, M.; Purkayastha, P.; Tiwari, A. K.; Jaffer, S. S.; Saha, S. K. Characterization of Guest Molecule Concentration Dependent Nanotubes of  $\beta$ -Cyclodextrin and their Secondary assembly: Study with trans-2-[4 (dimethylamino) styryl] benzothiazole, a TICT-Fluorescence Probe. *J. Photochem. Photobiol. A* **2009**, *205*, 186–196.

(59) Dutta, R.; Chowdhury, M.; Winnik, M. A. Solvent Dependence of Magnetic-Field Effect in a Polymer-linked Exciplex System. *Polymer* **1995**, *36*, 4445–4448.

(60) Balasubramanian, S.; Bagchi, B. Slow Solvation Dynamics Near an Aqueous Micellar Surface. *J. Phys. Chem B* **2001**, *105*, 12529–12533.

(61) Balasubramanian, S.; Pal, S.; Bagchi, B. Hydrogen-bond Dynamics Near a Micellar Surface: Origin of the Universal Slow Relaxation at Complex Aqueous Interfaces. *Phys. Rev. Lett.* **2002**, *89*, 115505–1–4.

(62) Rosen, M. J.; Song, L. D. Dynamic Surface Tension of Aqueous Surfactant Solutions 8. Effect of Spacer on Dynamic Properties of Gemini Surfactant Solutions. *J. Colloid Interface Sci.* **1996**, *179*, 261–268.

(63) Wang, X.; Wang, J.; Wang, Y.; Yan, H.; Li, P.; Thomas, R. K. Effect of the Nature of the Spacer on the Aggregation Properties of Gemini Surfactants in an Aqueous Solution. *Langmuir* **2004**, *20*, 53–56.

(64) Ruiz, C. C. Rotational Dynamics of Coumarin 153 in Non-ionic Mixed Micelles of n-Octyl- $\beta$ -D-thioglucoiside and Triton X-100. *Photochem. Photobiol. Sci.* **2012**, *11*, 1331–1338.

(65) Seth, D.; Sarkar, S.; Sarkar, N. Dynamics of Solvent and Rotational Relaxation of Coumarin 153 in a Room Temperature Ionic Liquid, 1-Butyl-3-methylimidazolium Octyl Sulfate, Forming Micellar Structure. *Langmuir* **2008**, *24*, 7085–7091.

(66) Saha, S. K.; Purkayastha, P.; Das, A. B.; Dhara, S. Excited state Isomerization and Effect of Viscosity- and Temperature-dependent Torsional Relaxation on TICT Fluorescence of trans-2-[4-(dimethylamino)styryl]benzothiazole. *J. Photochem. Photobiol. A* **2008**, *199*, 179–187.

(67) Pisarchevik, L., II.; Trachoniotoskp, P., II Physical Properties of Glycerine and its Solutions. *J. Russ. Phys. Chem. Soc.* **1910**, *42*, 249–295.

(68) Fayed, T. A. Probing of Micellar and Biological Systems using 2-(p-dimethylaminostyryl)benzoxazole: An Intramolecular Charge Transfer Fluorescent Probe. *Colloids Surf. A: Physicochem. Eng. Aspects* **2004**, *236*, 171–177.

(69) Mallick, A.; Haldar, B.; Chattopadhyay, N. Spectroscopic Investigation on the Interaction of ICT Probe 3-Acetyl-4-oxo-6,7-

dihydro-12H indolo-[2,3-a] quinolizine with Serum Albumins. *J. Phys. Chem. B* **2005**, *109*, 14683–14690.

(70) Quitevis, E. L.; Marcus, A. H.; Fayer, M. D. Dynamics of Ionic Lipophilic Probes in Micelles: Picosecond Fluorescence Depolarization Measurements. *J. Phys. Chem.* **1993**, *97*, 5762–5769.

(71) Horng, M. L.; Gardecki, J. A.; Maroncelli, M. Rotational Dynamics of Coumarin 153: Time-Dependent Friction, Dielectric Friction, and Other Nonhydrodynamic Effects *J. Phys. Chem. A* **1997**, *101*, 1030–1047.

(72) Johansson, L. B. A.; Niemi, A. Electronic Energy Transfer in Anisotropic Systems. 1. Octadecylrhodamine B in Vesicles. *J. Phys. Chem.* **1987**, *91*, 3020–3023.