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Study on premicellar and micellar aggregates of gemini surfactants with hydroxyl substituted spacers in aqueous solution using a probe showing TICT fluorescence properties

Amit K. Tiwari, Sonu, M. Sowmiya, Subit K. Saha*

Department of Chemistry, Birla Institute of Technology and Science, Pilani 333031, Rajasthan, India

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ABSTRACT

The aggregation properties of two gemini surfactants, 12-3(OH)-12,2Br$^-$ and 12-4(OH)$_2$-12,2Br$^-$ with hydroxyl substituted spacer group have been studied. The changes in photophysical properties of a single probe, trans-2-[4-(dimethylamino)styryl]benzothiazole (DMASBT) showing dipolar nature in its twisted intramolecular charge transfer (TICT) excited state have been exploited rather than using multiple probes to describe various properties of micellar aggregates. Formation of a number of premicellar aggregates has been demonstrated in addition to the description of the micropolarity and the microviscosity of environment using steady-state fluorescence spectroscopy and fluorescence anisotropy of DMASBT. Conductometric measurements have been carried out to determine degree of micellar ionization (α) and to verify critical micelle concentration (CMC) values estimated by fluorescence method. Hydroxyl substituted spacer group induces the formation of premicellar aggregates. The micropolarity of environment around probe molecules increases on going from premicellar to micellar aggregates. The growth of micellar aggregates has been demonstrated by a continuous increase in the microviscosity of environment. The micropolarity of micellar environment of 12-4(OH)$_2$-12 is found to be less than that of 12-3(OH)-12. The microviscosity of premicellar and micellar aggregates of 12-4(OH)$_2$-12 are higher than that of 12-3(OH)-12. CMC increases, whereas α decreases with increasing spacer chain length as well as number of hydroxyl substitution of a spacer group.

1. Introduction

A class of surfactants called 'Gemini' containing two hydrophobic tails and two hydrophilic headgroups connected by a spacer group has attracted special research interests for their enhanced surface properties [1–3]. There are reports on aggregation behavior of gemini surfactants depending on the chemical nature of hydrocarbon chains and spacer groups [4–7]. A recent article [4] describes the effect of spacer group on the association behavior of gemini surfactants in aqueous medium.

In the present work, two bis(quaternary ammonium bromide) surfactants having *n*-alkyl tails of 12 carbon atoms in length and a spacer group of 3 methylene units in length with one hydroxy (12-3(OH)-12)- and a spacer group of 4 methylene units in length with two hydroxy (12-4(OH)$_2$-12)-substituted methylene groups are chosen. Their structures are represented by Scheme 1 (denoted as Gemini-1 and Gemini-2, respectively hereafter). Mathias et al. [6] reported the premicellar aggregation of 14-3(OH)-14 and 16-3(OH)-16 with chloride ions as counter ions in 0.1 M NaCl at 50 °C and of 16-4(OH)$_2$-16 with bromide ions as counter ions in aqueous medium at 25 °C using steady-state and time-resolved fluorescence quenching of pyrene. However, they did not notice the formation of premicellar aggregates in cases of 12-3(OH)-12 and 12-4(OH)$_2$-12.

It has been observed in many cases of surfactants that the occurrence of the micellar phase is preceded by the formation of different comparatively smaller aggregates known as premicellar aggregates [6,8–11]. Hadgiivanova et al. [12,13] have developed a thermodynamic model to study the mechanism of aggregation. There are reports in the literature [5,6,14–18] for some gemini surfactants without hydroxyl substituted spacer group in aqueous solution that they start to self-aggregate at concentrations below the critical micelle concentration (CMC) only when the surfactant alkyl chains are long enough. However, Pei et al. [19] in their recent work have indicated the formation of premicellar aggregates of Gemini-1. In view of these reports, present work is based on aggregation behavior of both Gemini-1 and Gemini-2 in their submicellar concentration regions. The highly sensitive fluorescence properties of a probe, trans-2-[4-(dimethylamino)styryl]benzothiazole (DMASBT) (Scheme 2) to the polarity [20–22] and to the viscosity [23,24]

* Corresponding author. Tel.: +91 1596 515238; fax: +91 1596 244183.
E-mail addresses: subitksaha@gmail.com, sksaha@bits-pilani.ac.in (S.K. Saha).

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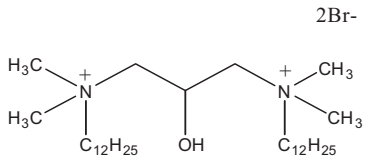
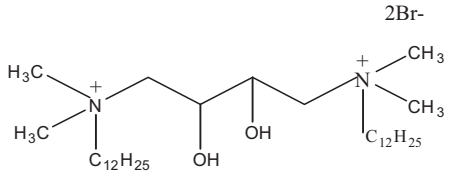


1,3-bis(dodecyl-N,N-dimethylammonium bromide)-2-propanol (Gemini-1)



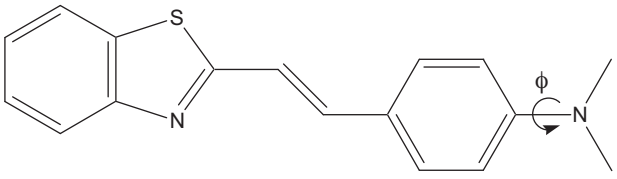
1,4-bis(dodecyl-N,N-dimethylammonium bromide)-2,3-butanediol (Gemini-2)

Scheme 1. Chemical structure of gemini surfactants.

of environment have been explored earlier to study the aggregation behavior of conventional surfactants [20,21]. In the present work, we have used steady-state fluorescence and fluorescence anisotropic properties of DMASBT showing twisted intramolecular charge transfer (TICT) fluorescence [22] to characterize the self-aggregation behavior of gemini surfactants. Studies have shown that the dipolar nature of DMASBT in its TICT excited state, makes it useful as a surface probe for phenomena such as premicellar and micellar aggregation of surfactants.

DMASBT gives normal fluorescence from the locally excited (LE) state in a nonpolar medium, whereas a highly Stokes-shifted fluorescence from the TICT state is observed in a polar medium [22]. The TICT state (S_3 state) is originated as a result of transfer of electron from the twisted donor group, $-N(CH_3)_2$ (torsion angle, $\phi = 90^\circ$, Scheme 2) to the acceptor group, styrylbenzothiazole [22]. The nonradiative processes become faster in a highly polar medium because of closer proximity of the TICT state towards triplet as well as S_0^{TICT} states as a result of greater stabilization of the TICT state. With decreasing the polarity of the medium, the TICT fluorescence quantum yield increases with the blue shift of fluorescence due to the concomitant increase in the energy gap between S_3^{TICT} and S_0^{TICT} states as well as triplet state.

In addition to fluorescence, conductometric measurements have also been performed to support the CMC values obtained from the fluorescence method and also to determine the degree of micellar ionization (α). Gemini-1 and Gemini-2 are chemically different only in terms of length of spacer groups and number of hydroxyl substitution in it. This work aims to examine the combined effect of increase of spacer chain length and the number of hydroxyl substitution in it on the properties of aggregates viz. premicellar aggregation concentration, CMC, degree of micellar ionization, micropolarity and microviscosity of environment around probe molecule. Generally, pyrene is used to determine the micropolarity [25,26], whereas diphenylhexatriene (DPH) is used to determine the microviscosity [26]. However, in the present study, the changes in fluorescence properties of a single probe molecule enabled us to do multiple things like demonstration of an important event in the colloid science, i.e. premicellar aggregation and determination of micropolarity and microviscosity of environment around probes in various aggregates.



Scheme 2. Molecular structure of DMASBT.

2. Experimental

2.1. Materials

The procedures for synthesis of surfactants used in this study were reported in the literature [27]. Synthesis of Gemini-1 and Gemini-2 were carried out by reacting required amounts of 1,3-dibromo-2-propanol and 1,4-dibromo-2,3-butanediol, respectively with 2 molar equivalent (plus a 10% excess) of N,N-dimethyldodecylamine. The mixture was refluxed in dry ethanol for 72 h and then cooled at the end of the reaction. The solid material obtained from the reaction was recovered by filtration and recrystallized several times from a mixture of ethylacetate/methanol (10:1 v/v). The structures of synthesized compounds were confirmed by FT-IR and ^{1}H NMR data.

DMASBT was procured from Aldrich Chemical Company, WI, USA. The methods of recrystallization and purity check of DMASBT are mentioned elsewhere [22]. Triple distilled water was used for the preparation of aqueous solutions. All other solvents used were of spectroscopic grades and procured from Spectrochem Chemical Company, India. KH_2PO_4 and Na_2HPO_4 used for the adjustment of pH of the solutions were procured from Qualigens, India. To record UV–visible absorption and fluorescence spectra, the aqueous solutions of different concentrations of a gemini surfactant were prepared with constant concentration of DMASBT. 0.05 mL of a stock solution of DMASBT (1 mM) in methanol was added to required amount of an aqueous solution of gemini with an extra 0.05 mL of methanol and the final volume of it was adjusted to 10 mL using water. The concentration of DMASBT in final solution was 5 μM. Methanol was added due to low solubility of DMASBT in water. However, only one percent of methanol was present in each experimental solution. The fluorescence quantum yields were determined with respect to that of quinine sulfate in 0.1 N H_2SO_4 (0.55). All aqueous solutions were adjusted to a pH value of 7.4 by the use of a dilute solution of phosphate buffer.

2.2. Methods

The absorption spectra were recorded using a Hitachi U-2900 UV–visible spectrophotometer. Fluorescence measurements were performed using a Horiba Jobin Yvon Fluoromax-4 scanning spectrofluorimeter. The steady state fluorescence anisotropy measurements were performed with the same steady state spectrofluorimeter fitted with a polarizer attachment. The excitation and emission bandwidths used for the anisotropy measurements were 5 nm each. The details of estimation of steady-state anisotropy (r) values are given elsewhere [23,28]. All spectroscopic measurements were done at room temperature, $25 \pm 1\,^\circ$C. The conductivity and pH measurements were performed using direct reading Eutech Instruments combined pH and conductometer, model PC 510. The conductivity dip cell (cell constant = 1.0 cm^{-1}) was calibrated with a standard KCl solution of specific conductivity 1413 μS cm^{-1} procured from Merck. Concentrated stock solutions of gemini surfactants were prepared by dissolving required amounts of surfactants in triple distilled water of specific conductivity 2–4 μS cm^{-1}. Stock solution was then added progressively using a micropipette to a container containing 20 mL of water kept in a thermostat with a temperature accuracy of $\pm 0.01\,^\circ$C. Before the measurement of specific conductance, κ, proper mixing and equilibration of solutions were ensured. Molar conductivity value was estimated as $(\kappa - \kappa_o)/C$ (where κ_o is specific conductance of water) from the experimental value of κ [5,19]. All pH and con-

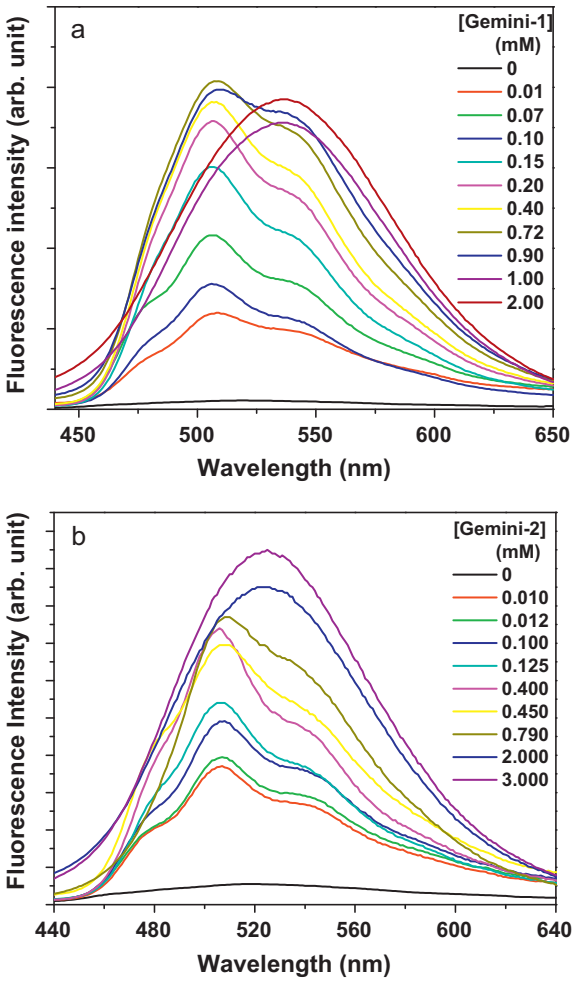


Fig. 1. Fluorescence emission spectra of DMASBT in various concentrations of aqueous solutions of (a) Gemini-1 and (b) Gemini-2. λ_{ex} = 370 nm, [DMASBT] = 5 μM.

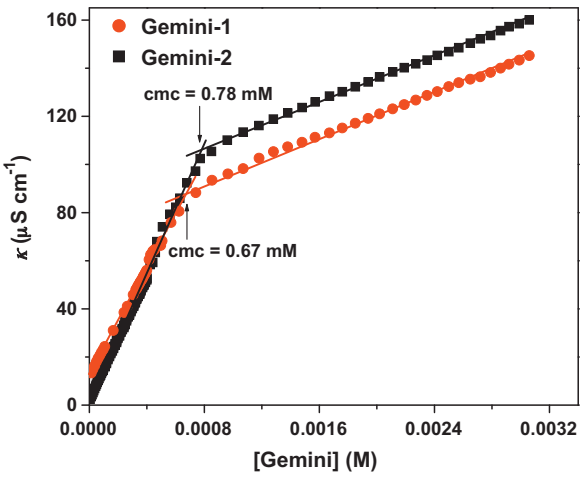


Fig. 2. Plots of specific conductivity (κ) versus concentration of aqueous solutions of gemini surfactants at 25 °C.

ductometric measurements were carried out at a temperature of 25 ± 0.01 °C.

3. Results and discussion

3.1. Fluorescence spectral properties of DMASBT in aqueous solutions of Gemini-1 and Gemini-2

The absorption spectra of DMASBT in aqueous solutions of Gemini-1 and Gemini-2 of various concentrations did not show much variation indicating the low sensitivity of absorbance by the change in concentration of surfactant. The fluorescence spectra of DMASBT in some solutions of Gemini-1 are shown by Fig. 1a. A fluorescence band appears at ~520 nm in water, which continued to be blue shifted up to ~506 nm at a concentration of ~0.07 mM of Gemini-1 with the development of a structured band. It is noteworthy that the peak maxima almost remain constant after this concentration, however, intensities of structured fluorescence bands increase with increasing concentration of surfactant with some irregularity at a few concentrations (discussed later). The fluorescence bands are structured up to 0.9 mM concentration of Gemini-1. However, a structureless broad single band starts appearing above this concentration. In case of Gemini-2 (Fig. 1b), similar broad band appears at a little higher concentration of it as compared to that of Gemini-1. Our previous work [22] has shown that DMASBT exhibits LE fluorescence in a nonpolar medium giving a structured fluorescence band with a peak maximum at ~450 nm and a highly Stokes-shifted TICT fluorescence in a polar medium with a broad structureless fluorescence band of peak maximum at ~520 nm (in aqueous medium). Therefore, the structured fluorescence bands observed in the present study at a low concentration range of both the surfactants are because of the presence of DMASBT molecules in a microenvironment of low polarity giving LE fluorescence to some extent. Evolution of structured fluorescence bands at ~506 nm at low concentration of solutions of both Gemini-1 and Gemini-2 surfactants suggests that the probe molecules are residing neither in a very hydrophobic region nor in a highly polar region but in a region with an intermediate polarity favoring some extent of LE fluorescence. The decrease in the polarity of the environment around the probe molecules due to the penetration of more and more molecules inside the surfactant aggregates is responsible for the blue shift and the accompanying increase in the fluorescence intensity of the fluorophore. The initial blue shift of the fluorescence band of DMASBT indicates its interaction with the surfactant aggregates and its possible location somewhere in the upper part of the hydrophobic region [20,21] near the headgroups of the premicellar aggregates (discussed later). It is important to note that when the concentration of Gemini-1 reaches 0.72 mM, the fluorescence band is red-shifted by 3 nm (Fig. 1a) giving peak maximum at 509 nm. Similar change in a fluorescence band occurs at 0.79 mM concentration of Gemini-2 (Fig. 1b) with a band of same peak maximum at 509 nm. In fact, at this concentration of Gemini-2, there is a prominent change in the structured nature of the band. The shoulder of the band at lower wavelength side is completely diminished. Based on the changes in the nature of fluorescence bands and intensity (discussed in Section 3.2), the CMCs of Gemini-1 and Gemini-2 are found to be 0.72 mM and 0.79 mM, respectively. The CMC values are also determined by the conductivity measurements. Fig. 2 represents the plots of specific conductivities (κ) of aqueous solutions of Gemini-1 and Gemini-2 against their concentrations. The CMC values at 25 °C have been measured from the inflection point of the plot of κ versus surfactant concentration [29]. Although, the conductivity measurements give CMC of Gemini-1 as 0.67 mM, the same is 0.78 mM for Gemini-2. The CMC values determined by two methods are well corroborated. The structured characteristics of a fluorescence band starts disappearing with a red-shift of the band after the formation of micelles indicating the fact that the microenvironment around the probe is more polar in micelles than that in the premicellar aggregates [20,21]. It is pertinent to note that the fluorescence bands become completely structureless and broad at 1 mM of Gemini-1 and 2 mM of Gemini-2, and undergo a

significant red shift (Fig. 1a and b). This suggests that the microenvironment around DMASBT molecules in the aggregates of Gemini-1 and Gemini-2 favors only TICT fluorescence at this concentration range. It can be mentioned here that the DMASBT in its TICT form has a positive charge on the nitrogen atom of $-N(CH_3)_2$ group and a dispersed negative charge on the styrylbenzothiazole moiety [22]. Thus after the formation of micelles, DMASBT molecules are somewhat pushed out to the surface from the hydrophobic region due to the interaction between its dipole and the surface charges of micelles. Hence, DMASBT molecules experience a more polar environment, which results in the less structured fluorescence band at micellar region followed by completely structureless bands at postmicellar concentrations. The probe molecules are located at a more polar environment of aggregates in postmicellar solutions giving completely structureless, broad TICT fluorescence bands. Location of probe molecules at a more polar environment of micellar aggregates compared to that of premicellar aggregates has also been observed in our previous work with the micelles of conventional surfactants [20,21].

The peak maxima of broad, structureless TICT fluorescence bands of DMASBT in solutions of high concentrations (1.5–2.5 times of CMC) of Gemini-1 and Gemini-2 appear at ~537 nm and at ~525 nm, respectively. The intensity of such fluorescence further increases with increasing surfactant concentration (Fig. 1a and b) without any change in peak position. It has been discussed later that in this concentration range, at some concentrations of Gemini-1 and Gemini-2, some rearrangements of surfactant molecules or changes in sizes/shapes of aggregates occur before micellization process approaches saturation. It is noteworthy that the fluorescence bands are red shifted with respect to the TICT band in pure water at this concentration range of surfactant solutions. Moreover, the fluorescence intensities of respective fluorescence bands are also much higher than that in water. Greater stabilization of TICT state (red shift of the band) in these micellar aggregates compared to that in water is in accordance with the stronger interactions between the dipole of a DMASBT molecule and the surface charges of the micelles. The higher fluorescence intensity in this phase as compared to that in water and also the increase in intensity with increasing concentration of surfactant can be explained by the fact that the probe molecules are staying more and more in the polar region with increasing size of aggregates and at the same time the negative end of dipole of a DMASBT molecule is possibly getting increasingly attached to the positive surface charges of the aggregates electrostatically [20,21]. As a result, the molecular motions are getting restricted thus increasing the fluorescence intensity as has been observed at a concentration of surfactant much higher than CMC. This increase is supported by the increase in fluorescence anisotropy (discussed later), which reflects the rigidity of the surrounding environment of DMASBT [20,21]. Unlike other TICT probe, such as dimethylaminobenzonitrile (DMABN) which shows a continuous increase in intensity with hypsochromic shift with the increase in the surfactant concentration [30,31], DMASBT does not penetrate to the hydrophobic core of the micelles. This is probably because of its cylindrical nature, with some degree of flexibility in the middle. That is why DMASBT acts as a surface probe and becomes efficient and sensitive to the changing environment in every phase of the premicellar aggregation.

The same peak maxima of structured fluorescence bands noted at the low concentration range of solutions of both Gemini-1 and Gemini-2 depict that the microenvironment around the probe in the premicellar aggregates and that in the micellar aggregates at their CMCs are same for both the cases. However, the environment around the probe molecules in Gemini-2 postmicellar aggregates is less polar than that in Gemini-1. The peak position of a TICT band in Gemini-2 (~525 nm) is blue shifted by ~12 nm as compared to that in Gemini-1 (~537 nm) indicating the decrease in the polarity of microenvironment of micellar aggregates with increasing number of hydroxyl substitution and carbon atoms of the spacer group of surfactant. Two conclusions can be drawn from this observation: (i) highly Stokes-shifted charge-transfer bands suggest that the probe molecules reside near to the wet Stern layer [22,32], as a result of electrostatic interactions between the dipole of a DMASBT molecule and the surface charges, and (ii) the environment surrounding probe molecules in Gemini-2 micelles is comparatively less polar than that in Gemini-1. The second factor could be due to the protection of the probe molecules to be in contact with the water molecules as a result of greater extent of hydrogen bonding interactions between the hydroxyl groups on a spacer group in Gemini-2 and the water molecules [33]. It attributes that the screening of water molecules through hydrogen bonding interactions inhibits probe molecules to be in contact with water molecules which results in giving less polar microenvironment of probe in Gemini-2. Thus, probe molecules in case of Gemini-2 are located in such a region which is comparatively less wet than that of Gemini-1. Of course, it is becoming possible because of short chain spacer group being located at the interface of aggregate and water compared to longer spacer group being folded into the core of an aggregate [4,16,33,34].

3.2. Determination of premicellar and critical micellar concentrations by correlating steady-state fluorescence with fluorescence anisotropy

Fluorescence intensity and fluorescence anisotropy of DMASBT at various concentrations of Gemini-1 and Gemini-2 are plotted in Fig. 3a and b, respectively with the intention of characterization of their aggregates [20,21]. Depending on the polarity of aggregates, DMASBT molecules get attached to different parts of them. The rearrangements of surfactant molecules during the process of formations of different premicellar and micellar aggregates are demonstrated and indicated by thin arrows in Fig. 3a and b for Gemini-1 and Gemini-2, respectively. The concentrations of surfactant solutions at which all these aggregates formed are also mentioned in the same figures. The change in the fluorescence intensity reflecting one such process has been correlated with the fluorescence anisotropy [35]. As mentioned above, in the premicellar aggregates and the micellar aggregates at CMC, DMASBT presumably gives LE fluorescence. However, fluorescence emissions of DMASBT in the postmicellar aggregates mostly occur from its TICT state. Therefore, during the course of micellization through the formation of smaller premicellar aggregates, there is a progressive change in the nature of the probe molecule and its location in the aggregates reflecting the changes in its photophysical properties [20,21]. In general, whenever there is a new rearrangement of the surfactant molecules especially during the formation of a new premicellar aggregate, DMASBT molecules experience more polar environment as a result of greater exposure to the aqueous environment showing decrease in the fluorescence intensity (Fig. 3) [22]. This is also supported by the reduction in fluorescence anisotropy because of greater extent of molecular motion (Fig. 3) [26,35]. Increase in intensity happens right after this event, mostly resembling the restricted rotational motion of DMASBT molecules, which is supported by the increase in fluorescence anisotropy (Fig. 3). The values of premicellar concentrations, CMC and the postmicellar concentrations (CMC′ and/or CMC″) corresponding to the rearrangements or changes in sizes/shapes of micelles are determined by monitoring simultaneous increase in the fluorescence intensity and the fluorescence anisotropy and are given in Table 1 along with the CMC values reported in the literature [33,36]. Observed CMCs are well corroborated with the literature CMC values. Four to six distinct kinds of aggregations including rearrangements or changes in sizes/shapes of micelles

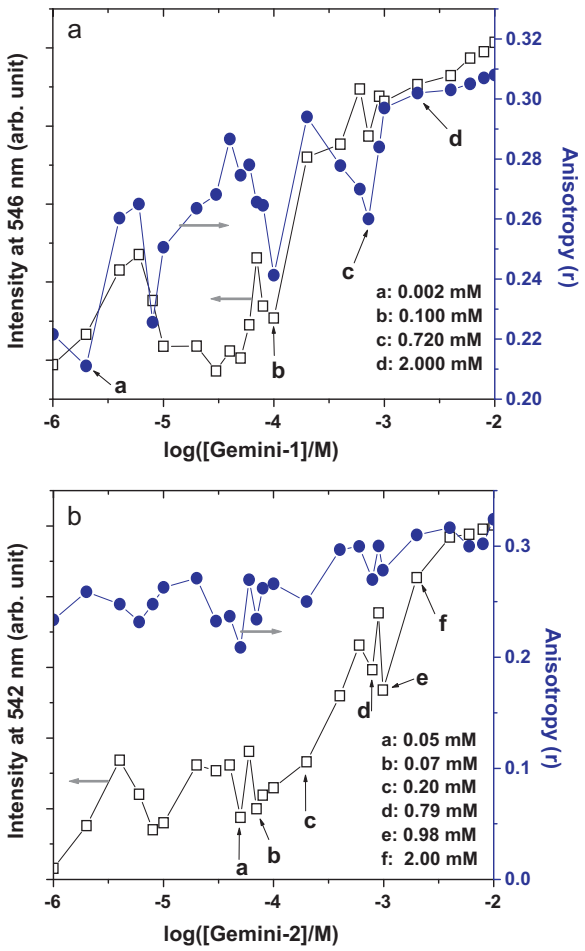


Fig. 3. Variation of fluorescence intensity and fluorescence anisotropy (r) of DMASBT as a function of (a) Gemini-1 (anisotropy at λ_{em} = 535 nm) and (b) Gemini-2 (anisotropy at λ_{em} = 520 nm) concentrations. The thin arrows indicate the premicellar, critical micellar and concentrations of surfactants where micellar aggregates change their arrangements or sizes/shapes and the thick grey arrows indicate the corresponding y-axes.

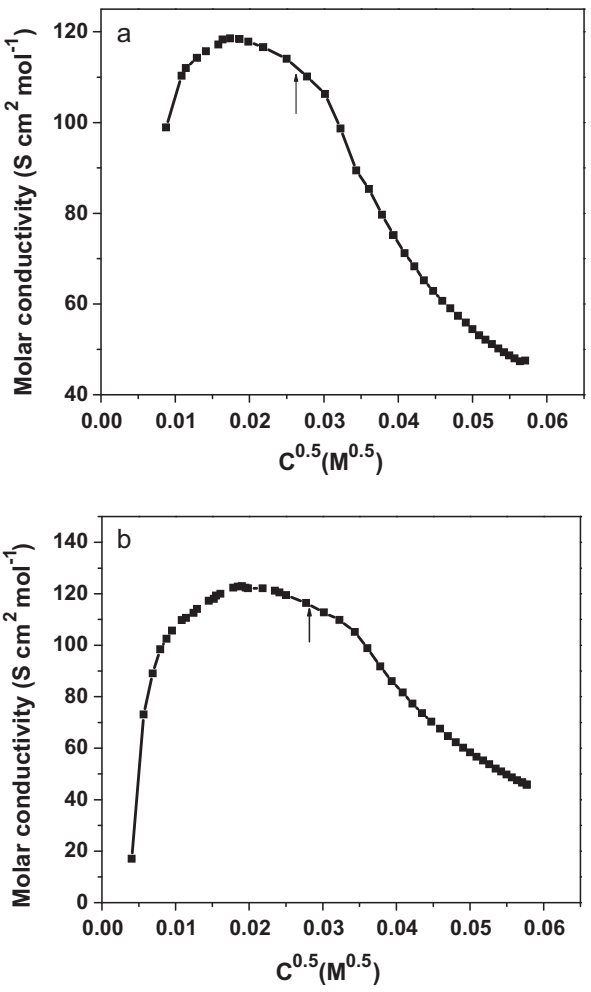


Fig. 4. Plots of variation of molar conductivity (Λ) with $C^{0.5}$ (where C = concentration of surfactant) of (a) Gemini-1 and (b) Gemini-2 at 25 °C. The arrow in each plot indicates the CMC as obtained from the corresponding κ versus C plot in Fig. 2.

have been observed for the concentration range studied in the present work (Table 1). A rearrangement process occurring even after the start of micellization at CMC is probably representing a phase where there is a readjustment of the shapes or sizes of micelles before approaching complete micellization [20]. The irregular behavior of fluorescence intensity with concentration of surfactant (Fig. 3) is because of surface-probing nature of DMASBT with its dual emission properties (LE and TICT fluorescence) controlled by the changing microenvironment of the probe in the aggregates during micellization through the formation of premicellar aggregates.

Table 1
Premicellar and micellar concentrations of Gemini-1 and Gemini-2 at 25 °C.

Gemini-1		Gemini-2	
Phase[a]	[Gemini-1] (mM)	Phase	[Gemini-2] (mM)
Ag1	0.002	Ag1	0.05
Ag2	0.100	Ag2	0.07
CMC[b]	0.720	Ag3	0.20
CMC′	2.000	CMC[c]	0.79
		CMC′	0.98
		CMC″	2.00

[a] Ag stands for a premicellar aggregation.
[b] Literature value: 0.78 mM for Gemini-1 with Cl^- ion as counter ion, Ref. [36].
[c] Literature value: 0.87 mM, Ref. [33].

The occurrence of premicellar aggregation was noticed by many groups [5,6,14–18]. Zana [5] reported self-aggregation at submicellar concentration of solutions of gemini surfactants, m-s-m (where m = number of carbon atoms in alkyl chain and s = number of carbon atoms of an alkanediyl spacer group) with only $m \geq 14$. However, in the present study, the formations of premicellar aggregates have been observed even if m = 12 with short chain hydroxyl substituted spacer groups. Therefore, it seems that hydroxyl groups present in the spacer groups are inducing the formation of premicellar aggregates may be through intermolecular hydrogen bonding interactions [19]. More number of premicellar aggregates for Gemini-2 surfactant molecules as compared to that for Gemini-1 is in accordance with the greater extent of hydrogen bonding interactions as the number of substituted hydroxyl groups in the spacer group of the former is higher than that of the later. Recently, premicellar aggregation of Gemini-1 has been indicated by Pei et al. [19]. However, in the present work, formations of multiple premicellar aggregates have been demonstrated. The occurrences of premicellar aggregation have been confirmed by conductivity measurements [4,5,37]. The variation of molar conductivity (Λ) with $C^{0.5}$ (where C = concentration of surfactant) of Gemini-1 and Gemini-2 are represented by Fig. 4a and b, respectively. The Λ versus $C^{0.5}$ plot for both the geminis show a maximum. This maximum is the signature of premicellar aggregation in a solution of surfactant. It arises because the equivalent conductance of a small

aggregate formed by surfactant ions is larger than the sum of the equivalent conductances of the ions constituting it [4,5,37].

It can be seen from Table 1 that the CMC values of Gemini-1 and Gemini-2 are 0.72 mM and 0.79 mM, respectively at 25 °C. There is a very small difference between the CMC values. These values obtained from the conductivity measurements at 25 °C are 0.67 and 0.78 mM, respectively (Fig. 2). Fluorescence as well as conductivity measurements show higher CMC value of Gemini-2 than that of Gemini-1. Wettig et al. [33] have reported the decrease in CMC of gemini surfactants with increasing number of substituted hydroxyl groups on a spacer group containing 4 methylene units ($s = 4$) in length. They have explained the decrease in CMC on hydroxyl substitution on the basis of the fact that the substituted spacer can form hydrogen bonds with water more readily, thereby reducing the unfavorable interactions between the hydrocarbon tails and water molecules. However, in the present case CMC value is increased where both s and the number of hydroxyl groups on a spacer group are increased for Gemini-2 with respect to Gemini-1. The increase in CMC with increasing s giving a maximum at a value of s apparently equal to 5 has been reported [29] for a series of gemini surfactants, 10-s-10,2Br$^-$ with $s = 2$, 3, 4 and 6. Also, Rodriguez et al. [38] have noticed a continuous increase in CMC with increasing s for a series of gemini surfactants, 12-s-12,2Br$^-$ with spacer groups of $s = 3$, 4 and 5. Based on these reports, our suggestion is that two opposing effects work for the change in CMC from Gemini-1 to Gemini-2. With increasing the number of carbon atoms of a spacer group CMC can increase, but on the other hand with increasing the number of hydroxyl groups CMC decreases. As a result of these opposing effects, there is only a slight increase in CMC of Gemini-2 in comparison to Gemini-1. One can also conclude that the effect of increased number of spacer carbon atoms on CMC is more pronounced than that of increase in the number of substituted hydroxyl groups in a spacer group.

The mean micellar aggregation number (N_{agg}) of two geminis at 5 mM concentration in aqueous medium have been estimated by the usual method of steady-state fluorescence quenching of pyrene (3 μM) by cetylpyridinium chloride (0–0.09 mM) [39–41]. The values of N_{agg} of Gemini-1 and Gemini-2 are found to be 27 and 23, respectively. The lower N_{agg} of Gemini-2 as compared to that of Gemini-1 is in accordance with the higher CMC of the former than that of the later.

3.3. Micropolarity and microviscosity of environment around DMASBT in various aggregates

The micropolarity is expressed in equivalent scale of $E_T(30)$ which is an empirical solvent polarity parameter comparing the fluorescence behavior of the probe molecule in microheterogeneous systems to that in a mixture of homogeneous solvents (dioxane–water) of varying compositions [20,21,24,35,42–44]. Details of the method of determination of micropolarity have been given elsewhere [20,21,24]. The micropolarity of environment around DMASBT in micellar aggregates of gemini surfactants at their CMCs expressed in equivalent scale of $E_T(30)$ have been calculated. But, the micropolarity of micellar aggregates in postmicellar solutions could not be calculated by this method as electrostatic interactions between the dipole of DMASBT and surface charges contribute to the stabilization of TICT states in these aggregates. The Stokes-shift values of DMASBT at 0.72 mM of Gemini-1 and 0.79 mM of Gemini-2 are found to be 4863 cm^{-1} ($\lambda^{ab}_{max} = 408$ nm and $\lambda^{fl}_{max} = 509$ nm) and 4744 cm^{-1} ($\lambda^{ab}_{max} = 410$ nm and $\lambda^{fl}_{max} = 509$ nm), respectively. The micropolarity values calculated comparing the Stokes-shift of DMASBT in micellar systems to that in dioxane–water mixtures of varying compositions [20,21,24,35,42–44] are found to be 45.8 ± 0.5 and 44.3 ± 0.5 for Gemini-1 and Gemini-2, respectively. The plot of Stokes-shift against the $E_T(30)$ values corresponding to various dioxane–water mixtures is given elsewhere [22] and also provided as supplementary material (see Supplementary material, Fig. S1). The lower micropolarity value in case of Gemini-2 as compared to that of Gemini-1 micelles is in accordance with the fact that the probe molecules are more protected from the exposure to the water molecules in the former micelles because of greater extent of hydrogen bonding interactions between substituted hydroxyl groups on a spacer group and water molecules. Although, the difference between the micropolarities of Gemini-1 and Gemini-2 at their micellar aggregates at CMCs is small, but it is expected to be very high at their postmicellar aggregates as the difference between the TICT peak maxima is significantly large (~12 nm).

Since fluorescence anisotropy of a fluorophore is intimately connected with the viscosity of the microenvironment around it, microviscosity is often estimated from a comparison of the fluorescence anisotropy of a fluorescent probe in an environment with those of the probe in different environments of known viscosities [24,35,45–47]. With a similar intention, we have attempted the fluorescence anisotropy measurements of DMASBT in different percentages (w/w) of glycerol in glycerol–water mixtures and compared the values with the anisotropy values of DMASBT in various concentrations of Gemini-1 and Gemini-2. Details of the method of determination of microviscosity are explained elsewhere [23,24]. The steady-state fluorescence anisotropy values (r) of DMASBT in solutions of various concentrations of Gemini-1 and Gemini-2 are given in Table 2. The chosen concentrations are their premicellar concentrations and various CMCs (CMC, CMC′ and CMC″) obtained from fluorescence measurements (Table 1). Correlating these anisotropy values (Table 2) with the anisotropy values of DMASBT in various glycerol–water mixtures [24] (see Supplementary material, Fig. S2) followed by correlating with the viscosity of the mixtures [48] (see Supplementary material, Fig. S3), the found microviscosity values (η) are also tabulated in Table 2. The average microviscosity of premicellar aggregates of Gemini-1 and Gemini-2 are 10.1 ± 0.3 and 12.1 ± 0.3, respectively. For micellar aggregates, average values are found to be 33.7 ± 0.3 and 43.5 ± 0.3, respectively. Therefore, one can correlate the growth of micellar aggregates through the formation of premicellar aggregates with a continuous increase in the microviscosity of environment around probe. It is to be noted that the microviscosity of environment of Gemini-2 where DMASBT molecules reside is greater than that of Gemini-1.

3.4. Degree of micellar ionization (α)

The degree of micellar ionization, α value has been calculated from the ratio of the slopes of the two straight lines above and below the CMC in the plot of κ versus surfactant concentration shown by Fig. 2 [29]. The α along with the CMC (already mentioned above) values thus obtained are presented in Table 3. The α value of Gemini-2 is lower than that of Gemini-1. It is reported that a polar protic solvent can act as a good hydrating agent for an anion through the formation of hydrogen bonds [49]. Therefore, a spacer group of a Gemini-2 surfactant molecule having two hydroxyl groups is expected to be a better hydrating agent for the counter ion, Br$^-$ compared to that of a Gemini-1 surfactant molecule with only one substituted hydroxyl group in it. This could be the possible reason that Gemini-2 micellar surface will bind more number of Br$^-$ ions as compared to the micellar surface of Gemini-1, which leads to the lower value of α of the former than the later. This explanation has also been supported by the fluorescence quantum yield values of DMASBT in the micellar aggregates of geminis at their CMCs. The quantum yield of DMASBT in 0.72 mM of Gemini-1 is found to be 0.31, whereas the same in 0.79 mM of Gemini-2 is only 0.04. These two concentrations (0.72 mM and 0.79 mM) as mentioned

Table 2
Steady-state fluorescence anisotropy (r) and microviscosity (η) of environment around the DMASBT molecule in premicellar and micellar aggregates of Gemini-1 and Gemini-2 at 25 °C.

[Gemini-1] (mM)	r	η (cP)	[Gemini-2] (mM)	r	η (cP)
0.002 (Ag1)	0.21 ± 0.01	8.1 ± 0.3	0.05 (Ag1)	0.21 ± 0.01	8.1 ± 0.3
0.100 (Ag2)	0.24 ± 0.01	12.1 ± 0.3	0.07 (Ag2)	0.23 ± 0.01	12.1 ± 0.3
0.720 (CMC)	0.26 ± 0.01	19.9 ± 0.3	0.20 (Ag3)	0.25 ± 0.01	16.0 ± 0.3
2.000 (CMC′)	0.30 ± 0.01	47.5 ± 0.3	0.79 (CMC)	0.27 ± 0.01	27.8 ± 0.3
			0.98 (CMC′)	0.28 ± 0.01	35.7 ± 0.3
			2.00 (CMC″)	0.31 ± 0.01	67.0 ± 0.3

Table 3
CMC, degree of micellar ionization (α) and ΔG°_{m} of Gemini-1 and Gemini-2 at 25 °C.

Surfactant	CMC (mM)	α	ΔG°_{m} (kJ mol^{-1})
Gemini-1	0.67 ± 0.02	0.21 ± 0.01	−72.7
Gemini-2	0.78 ± 0.02	0.18 ± 0.01	−73.1

above are CMCs of Gemini-1 and Gemini-2, respectively found from fluorescence measurements. The significantly lower value of quantum yield in case of Gemini-2 as compared to that in Gemini-1 is because of greater extent of fluorescence quenching of DMASBT by Br^- ions in the former. Since the concentration of Br^- ions is higher on the surface of Gemini-2 micellar aggregates as compared to that on Gemini-1, DMASBT molecules being present on the surface experience more fluorescence quenching in the former than that in the later. Quenching of fluorescent probes by Br^- ions present on the micellar surface containing positively charged headgroups have been reported in the literature [50,51]. Reports on increase in α value with increasing number of *s* in a series of gemini surfactants of type 12-*s*-12,2Br^- are available in the literature [38]. Therefore, in the present study observed concomitant decrease in α of Gemini-2 could be because of predominant effect of greater extent of hydration of Br^- ions over the effect of increasing number of s in the spacer. It has also been reported [38] for the gemini surfactants of type, 12-*s*-12,2Br^- that the average distance between two cationic centers of headgroups becomes larger with increasing the spacer chain length at least in case of short chain spacer groups. Therefore, the average electrostatic repulsion between the positively charged headgroups is lowered with increasing the spacer chain length which results in an increase in α value. Thus, in our case the decrease in the α value of Gemini-2 in comparison to that of Gemini-1 further supporting the dominating effect of number of substituted hydroxyl groups on a spacer group.

The standard Gibbs free energy of micellization per monomer molecule, ΔG°_{m} has been calculated [52], at a given temperature using Eq. (1):

$$\Delta G^{\circ}_{m} = RT(3 - 2\alpha) \ln X_{CMC} \quad (1)$$

where the parameters R and T have their usual meaning, X_{CMC} is the mole fraction of surfactant at CMC, α is the degree of micellar ionization and the partial dissociation of counter ions from the micelles is accounted by the factor (3-2α). Data in Table 3 indicate that ΔG°_{m} value of Gemini-1 is almost same as Gemini-2 could be because of same reason (two opposing effect) for which the difference between the CMCs of two geminis is very small.

4. Conclusions

The present work demonstrates the use of photophysical changes of a single charge-transfer fluorescent probe rather than using multiple probes to describe various properties of micellar aggregates. The TICT fluorescence properties of a probe, DMASBT being very much sensitive to the polarity as well as to the viscosity of the medium, enabled us to demonstrate an important event in the field of colloid science namely premicellar aggregation in addition to the determination of micropolarity and microviscosity of environment. A progressive change in the location of probe molecule and its nature during the process of aggregation is reflected by the change in its fluorescence properties, which have been explored for the characterization of aggregates especially multiple premicellar aggregates. It has been shown that the effect of increase in spacer chain length on CMC is more pronounced than that of increased number of hydroxyl substitution of a spacer group. The occurrence of premicellar aggregation even in the case of gemini surfactants with C_{12} hydrocarbon tails could be induced by intermolecular hydrogen bonding interactions. Micropolarity of environment around probe molecules increases on going from premicellar to micellar aggregates. The microenvironment of Gemini-2 micellar aggregates is less polar than that of Gemini-1 due to the protection of probe molecules to be in contact with water molecules as a result of greater extent of hydrogen bonding interactions between the hydroxyl groups on spacer group in Gemini-2 and water molecules. Because of greater extent of hydration of counter ions, Br^- by hydroxyl groups of a spacer group in Gemini-2 compared to that in Gemini-1, the α value of the former is less than that of the later. The growth of micellar aggregates has been demonstrated by a continuous increase in microviscosity of aggregates on going from premicellar to micellar aggregates. The microviscosity of environment around DMASBT in Gemini-2 is higher than that of Gemini-1. A rearrangement process of postmicellar aggregates represents a phase where there are readjustments of the sizes/shapes of micelles itself before approaching complete micellization.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.07.009.

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