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Formation and Growth of Gemini Surfactant (12-*s*-12) Micelles as a Modulate by Spacers: A Thermodynamic and Small-Angle Neutron Scattering (SANS) Study

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ABSTRACT: A series of symmetrical cationic gemini surfactants of the type *N*,*N*′-didodecyl-*N*,*N*,*N*′,*N*′-tetramethylalkane-α,ω-diammonium dibromide "12-*s*-12" (*s* = 2, 4, 6, 8, 10, and 12) are synthesized, and their micellization study in aqueous solution is systematically reported. Specific conductivity as a function of surfactant concentration was measured, and critical micelle concentration (CMC), degree of counterion dissociation (α) of the micelle, and thermodynamic parameters, namely, Gibbs energy (ΔG_m), enthalpy (ΔH_m), and entropy (ΔS_m), of micellization were evaluated using this data at various temperatures. Surface tension studies at 298.15 K provided similar CMCs as given by conductometry along with information on the efficiency/effectiveness and the area occupied per molecule. Small-angle neutron scattering (SANS) inferred the presence of few morphological geometries ranging from spherical to rodlike micelles. Results are explained in terms of the hydrophobicity of spacer chain length along with the electrostatic repulsion between the cationic centers of gemini surfactant molecules.

1. INTRODUCTION

Conventional surfactants hold wide applications in the field of cleaning, pharmaceutical, cosmetics, paints, and so forth. Over the last few decades, a new class of surfactant known as gemini (dimeric) surfactants has received keen attention due to their superior physicochemical properties over the conventional surfactants. Structurally they are a pair of conventional surfactants held together by a covalent linkage either between the head or the tail units referred as spacers.[1−3] Because of such a unique structure, gemini surfactants have proved to be very efficient and versatile in lowering surface or interfacial tension and critical micelle concentration (CMC) and thereby exhibit better foaming, wetting, and solubilizing capabilities.[4−6]

Gemini surfactants, *N*,*N*′-didodecyl-*N*,*N*,*N*′,*N*′-tetramethylalkane-α,ω-diammonium dibromide, are generally referred as "*n*-*s*-*n*", where *n* and *s* represent the carbon numbers present in the alkyl chain of surfactant tail and in the polymethylene group in spacer, respectively. Literature has revealed significantly the importance of spacer stereochemistry and the alkyl chain in understanding the micellization phenomenon and thermodynamic properties.[7−15] These dimeric surfactants have been found to be far more superior to the corresponding monomeric ones,[16,17] thus motivating us to pursue their synthesis and study their CMC, degree of counterion dissociation (α), and aggregation behavior in aqueous solution.

To study the influence of spacers on the micellar properties of gemini surfactants, we examine a comprehensive temperature dependence of the 12-*s*-12 series (*s* = 2, 4, 6, 10, and 12) in aqueous solution using electrical conductivity measurements. Thermodynamic parameters of micellization, namely, Gibbs energy (ΔG_m), enthalpy (ΔH_m) of micellization, and $T\Delta S_m$ (where ΔS_m is entropy of micellization) were also evaluated. The results along with those reported in the literature were compared and discussed in terms of spacer chain length. Surface tension measurements were done to investigate the minimum area occupied per molecule at the air−solution interface (A_{min}), surface tension at CMC (γ_{CMC}), and efficiency (C_{20}) of these surfactants. Although an in-depth study on micellar and thermodynamics properties of geminis has appeared in the literature,[1,2,5,10,12,18,19] there is no systematic small-angle neutron scattering (SANS) study showing the influence of the spacer on micellar properties in the 12-*s*-12 series. Based on these findings, we have systematically investigated the influence of the spacer conformation and length on the aggregation features. Micellar shape and size are also investigated as a function of the spacer.

2. MATERIALS

A laboratory synthesis of gemini surfactants of the 12-*s*-12 series, namely, *N*,*N*′-didodecyl-*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diammonium dibromide (12-2-12), *N*,*N*′-didodecyl-*N*,*N*,*N*′,*N*′-tetramethylbutane-1,4-diammonium dibromide (12-4-12), *N*,*N*′-didodecyl-*N*,*N*,*N*′,*N*′-tetramethylhexane-1,6-diammonium dibromide (12-6-12), *N*,*N*′-didodecyl-*N*,*N*,*N*′,*N*′-tetramethyloctane-1,8-diammonium dibromide (12-8-12), *N*,*N*′-didodecyl-*N*,*N*,*N*′,*N*′-tetramethyldecane-1,10-diammonium dibromide (12-10-12), and *N*,*N*′-didodecyl-*N*,*N*,*N*′,*N*′-tetramethyldodecane-1,12-diammonium dibromide (12-12-12) were done by refluxing *N*,*N*,*N*′,*N*′-tetramethylalkane-α,ω-diamine (viz., *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine, *N*,*N*,*N*′,*N*′-tetramethylbutane-1,4-diamine, *N*,*N*,*N*′,*N*′-tetramethylhexhane-1,6-diamine, *N*,*N*,*N*′,*N*′-tetramethyloctane-1,8-diamine, *N*,*N*,*N*′,*N*′-tetramethyldecane-1,10-diamine, *N*,*N*,*N*′,*N*′-tetramethyldodecane-1,12-diamine) (all

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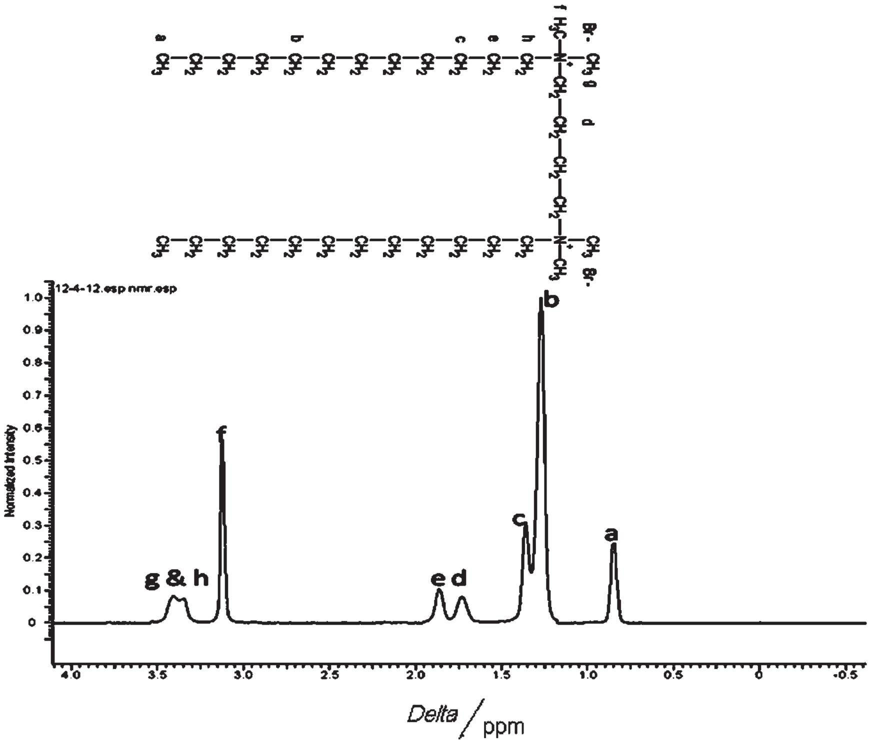

Figure 1. ^{1}H NMR spectra and structural formula of 12-4-12.

0.98 mass fraction pure from Merck and Fisher scientific) in dry acetone with 1-bromododecane (0.98 mass fraction pure from Sigma Chemical Co.) according to the method reported by Zana et al.[1] The solvent was then removed from the reaction mixture under vacuum. The purity of the synthesized gemini surfactant was confirmed by ^{1}H NMR.

Figure 1 shows the representative ^{1}H NMR spectra of 10 mM 12-4-12 with its structural formula. For ^{1}H NMR chemical shift values (δ/ppm) are generally higher for headgroup region protons and decrease further as we go toward alkyl chain protons.[20] Protons attached with a highly hydrophobic section of surfactant molecule reside in the core portion of micelle (a, b, and c protons) which are highly shielded hence show an ^{1}H NMR peak at lower ppm-(downfield). However as we move near to nitrogen atom (i.e., close to headgroup) the proton becomes less shielded and absorbed at quite upfield (d and e protons). Protons g, h, and f are more near to nitrogen hence, highly deshielded, and show upfield absorption peak.

All products were recrystallized at least three times using hexane−ethyl acetate mixtures. Deuterium oxide, D_2O (0.99 mass fraction of D), from Sigma Chemical Co. (USA) and triply distilled water were used throughout the experimental work for preparing solutions for SANS and specific conductivity study.

3. EXPERIMENTAL METHODS

3.1. Conductometry. The specific conductance of aqueous solution gemini surfactants were measured using an ESICO microprocessor based conductivity bridge, model 1601 with a dip-type cell made of platinum black having a unit cell-constant. The instrument was calibrated using KCl solutions of known concentration. Temperature equilibrium was maintained throughout the experiment. For all of the experiments performed, a temperature range of (298.15 to 323.15) K was set with an error of ± 0.2 K. CMC and α values were determined from the change in the specific conductance versus surfactant concentration plot. In each experimental set, 50 to 60 data were registered, and the break point appears in the plot as two straight lines intersecting at a particular point, which corresponds to the CMC. Data above and below the break point were linearly fitted with correlation coefficients greater than 0.998; α was calculated from the ratio of slopes of linear line above and below the CMC values. The α is measure of dissociation of the counterion Br^- from the headgroup of surfactant monomers in micelle. A decrease in α attributes the level of neutralization of the charges on the micelle surface.

3.2. Surface Tension. Surface tension measurements were performed using a Kruss (model K10T) tensiometer using a sand-blasted platinum plate of ca. 0.05 m perimeter. The plate was cleaned with distilled water and flamed before each measurement. The desirable composition of gemini surfactant was made by dissolving the weighed amount of the respective surfactant in triply distilled water which had a surface tension of $0.072\ \mathrm{N \cdot m^{-1}}$. All dilutions were allowed to rest for one day before measurements for proper equilibration. Surface tension (γ) was measured as a function of log C (where C is surfactant concentration in $\mathrm{mol \cdot kg^{-1}}$), where the CMC value corresponds to the break point in the plot. The error in the surface tension measurements was approximately $\pm\ 0.0002\ \mathrm{N \cdot m^{-1}}$.

3.3. Small-Angle Neutron Scattering (SANS). SANS measurements were performed at the Dhruva reactor, BARC, India to investigate micellar size, shape, and aggregation number of 12-*s*-12 in aqueous solution.[21] An incident neutron beam of $5.2 \cdot 10^{-10}$ m

Table 1. Critical Micelle Concentration (CMC), Degree of Counterion Dissociation (α), Thermodynamic Parameters of Micellization (ΔG_m, ΔH_m, $T\Delta S_m$) at Different Temperature (T), Melting Point (T_M), and Krafft Temperature (T_K) of 12-*s*-12 (*s* = 2, 4, 6, 8, 10, and 12) Gemini Surfactant

	T	10^3 CMC		ΔG_m	ΔH_m	$T\Delta S_m$	T_M	T_K
surfactant	K	$\mathrm{mol \cdot kg^{-1}}$	α	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	K	K
12-2-12	298.15	0.88 ± 0.05	0.20 ± 0.03	-71.4	-25.1	46.2		
		$(0.89 \pm 0.04)^{a}$	$(0.18 \pm 0.02)^{a}$	$(-72.1)^{b}$				
	303.15	0.97 ± 0.05	0.21 ± 0.03	-71.3	-25.7	45.6	423^{c}	287.4^{c}
	308.15	1.06 ± 0.05	0.23 ± 0.03	-70.5	-26.1	44.4		
	313.15	1.11 ± 0.05	0.25 ± 0.03	-70.6	-26.6	44.0		
	318.15	1.17 ± 0.05	0.28 ± 0.03	-69.4	-26.8	42.7		
	323.15	1.23 ± 0.05	0.30 ± 0.03	-69.2	-27.2	42.0		
12-4-12	298.15	1.14 ± 0.05	0.27 ± 0.03	-65.8	-18.6	47.2		
		$(1.17 \pm 0.04)^{a}$	$(0.26 \pm 0.02)^{a}$					
	303.15	1.20 ± 0.05	0.29 ± 0.03	-65.5	-19.0	46.6	481^{c}	283.6^{c}
	308.15	1.26 ± 0.05	0.31 ± 0.03	-65.2	-19.3	45.9		
	313.15	1.34 ± 0.05	0.36 ± 0.03	-63.1	-19.1	44.0		
	318.15	1.40 ± 0.05	0.39 ± 0.03	-62.2	-19.2	43.0		
	323.15	1.47 ± 0.05	0.45 ± 0.03	-59.5	-18.7	40.8		
12-6-12	298.15	1.05 ± 0.05	0.39 ± 0.03	-59.8	-14.7	45.2		
		$(1.09 \pm 0.04)^{a}$	$(0.34 \pm 0.02)^{a}$	$(-63.1)^{b}$				
	303.15	1.08 ± 0.05	0.43 ± 0.03	-58.5	-14.6	43.9	488^{c}	$<273^{c}$
	308.15	1.12 ± 0.05	0.46 ± 0.03	-57.6	-14.7	42.9		
	313.15	1.19 ± 0.05	0.49 ± 0.03	-56.5	-14.7	41.8		
	318.15	1.25 ± 0.05	0.52 ± 0.03	-55.5	-14.8	40.7		
	323.15	1.30 ± 0.05	0.55 ± 0.03	-54.4	-14.8	39.7		
12-8-12	298.15	0.81 ± 0.07	0.44 ± 0.06	-58.5	-12.2	46.3		
		$(0.84 \pm 0.03)^{a}$	$(0.46 \pm 0.04)^{a}$					
	303.15	0.83 ± 0.07	0.49 ± 0.06	-56.6	-12.0	44.5	466^{c}	$<273^{c}$
	308.15	0.86 ± 0.07	0.52 ± 0.06	-55.6	-12.1	43.5		
	313.15	0.88 ± 0.07	0.54 ± 0.06	-55.2	-12.2	43.0		
	318.15	0.93 ± 0.07	0.56 ± 0.06	-54.7	-12.4	42.3		
	323.15	0.99 ± 0.07	0.59 ± 0.06	-53.5	-12.3	41.1		
12-10-12	298.15	0.60 ± 0.07	0.48 ± 0.05	-57.8	-8.1	49.8		
		$(0.62 \pm 0.03)^{a}$	$(0.51 \pm 0.06)^{a}$					
	303.15	0.61 ± 0.07	0.55 ± 0.05	-54.7	-7.8	46.9	415^{c}	$<273^{c}$
	308.15	0.63 ± 0.07	0.58 ± 0.05	-53.7	-7.8	45.9		
	313.15	0.65 ± 0.07	0.62 ± 0.05	-52.0	-7.7	44.3		
	318.15	0.67 ± 0.07	0.65 ± 0.05	-50.9	-7.7	43.3		
	323.15	0.68 ± 0.07	0.69 ± 0.05	-49.2	-7.5	41.7		
12-12-12	298.15	0.35 ± 0.07	0.55 ± 0.07	-56.4	-23.3	33.1		
		$(0.36 \pm 0.03)^{a}$	$(0.56 \pm 0.08)^{a}$					
	303.15	0.39 ± 0.07	0.60 ± 0.07	-53.8	-22.8	31.1	397^{c}	286.6^{c}
	308.15	0.43 ± 0.07	0.67 ± 0.07	-50.0	-21.7	28.3		
	313.15	0.45 ± 0.07	0.73 ± 0.07	-47.0	-20.8	26.2		
	318.15	0.49 ± 0.07	0.78 ± 0.07	-44.3	-20.1	24.3		
	323.15	0.54 ± 0.07	0.81 ± 0.07	-42.8	-19.8	22.9		

[a] Ref 13. [b] Ref 26. [c] Data (not measured) directly taken from ref 25.

wavelength was obtained by polycrystalline BeO diffractomator which works as monochromator. The solutions of surfactant were prepared in D_2O to eliminate the poor contrast of H_2O for neutron scattering experiments. They were placed in a 0.005 m thick quartz cell with Teflon stoppers. All measurements were carried out at 313.15 ± 0.1 K. The angular distribution of the scattered neutron was recorded by a linear 1 m long He^{3+} position sensitive detector (PSD) in the Q range ($0.017 \cdot 10^{10}$ to $0.35 \cdot 10^{10}$) $\mathrm{m^{-1}}$. The data were corrected for the background and solvent contributions and were normalized to the cross-sectional unit using standard procedures. The measured scattering data gives all of the necessary micellar parameters for the surfactant systems. The concentration taken was 0.1 $\mathrm{mol \cdot kg^{-1}}$ (fixed) for the entire gemini series.

For a SANS experiment, the differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of scattering vector Q for a micellar system can be calculated using:

$$\frac{d\Sigma}{d\Omega} = n_m {V_m}^2 (\rho_m - \rho_s)^2 \{<F^2(Q)> + <F(Q)>^2 [S(Q) - 1]\} + B \qquad (1)$$

Here n_m denotes the number density of the micelles having a volume V_m; ρ_m and ρ_s are scattering length densities of the micelle and solvent, respectively. B is a constant that represents the incoherent scattering background, which is mainly due to hydrogen in the sample. $F(Q)$ is the single particle (intraparticle) form factor, whereas $S(Q)$ is an interparticle structure factor which shows a peak at $Q_m = 2\pi/d$, where d is the average distance between micelles and Q_m is the value of Q at the peak position. The calculation of $S(Q)$ depends on the spatial arrangement of micelle and on the inter micellar interactions.[22]

4. RESULTS AND DISCUSSION

4.1. Physicochemical and Thermodynamic Study of 12-*s*-12 in Aqueous Solution. CMC, α, and thermodynamic parameters for the 12-*s*-12 series (*s* = 2, 4, 6, 8, 10, and 12) were determined by means of conductometry method for temperatures ranging from (298.15 to 223.15) K and are reported in Table 1. CMC and α at 298.15 K agree well with the literature values.[13]

The specific conductance study of gemini surfactants revealed a similar trend like other surfactants. An increase in temperature influences these surfactants in two different ways: (i) As the temperature increases, the degree of hydration of hydrophilic group decreases thereby favoring micellization, and (ii) the structure of water around the hydrophobic group in micelles gets disrupted leading to increase the solubility of surfactant molecules and thereby increasing the CMC.[23] Our findings reported in Table 1 suggest that the second effect predominates in the temperature range studied. Similarly, an increase in the temperature causes a decrease in the charge density at micellar surface by lowering the aggregation number of micelle which leads to increase in α.[23,24]

For the gemini surfactant studied here, it is found that the melting point (T_M) values are higher for 12-4-12 and 12-6-12 which is in accordance with their respective higher CMC values. T_M values indicated a minimum stability of surfactant in the melt/liquid state. Since the surfactant in a micellar state can be considered to be in liquid state, a higher CMC show minimum stability for 12-4-12 and 12-6-12. Further, for conventional ionic surfactants, T_M and Krafft point (T_K) values follow a similar trend with number of carbons in tail, while an opposite trend was observed for gemini surfactants with number of carbon in spacer group which manifest the effect of spacer length on physical properties of gemini surfactants.[25]

CMC, α, ΔG_m, and ΔH_m values for 12-*s*-12 series at 298.15 K are plotted against the number of spacer carbon atoms (Figure 2). The trend in these values is similar as reported by Zana et al.[2] It is observed from Figure 2a that the CMC values go through a maximum as the spacer carbon atom of increases in the range of *s* = 4 to 6. For *s* = 2 due to the short distance between two alkyl tails, the hydrophobic interaction facilitates this which restricts hydrophobic hydration and minimizes electrostatic repulsion between the two alkyl tails of the surfactant molecule, resulting in the lower values of CMC. For *s* = 4 to 8, the shorter spacer chain tends to remain in an as much extended conformation as possible at the expense of undesirable contact of the hydrocarbon spacer with bulk water, which increases hydrophobic hydration and restricts micellization, thereby increasing the CMC.[10,27] However, after *s* > 8 a linear decrease is found in CMC and α as a function of spacer carbon atom (Figure 2b) because the spacer becomes hydrophobic and flexible in nature that it takes a loop like conformation and becomes part of the micelle core, thereby weakening the binding strength of the counterion (i.e., increase in α) with the surfactant head.[10,24]

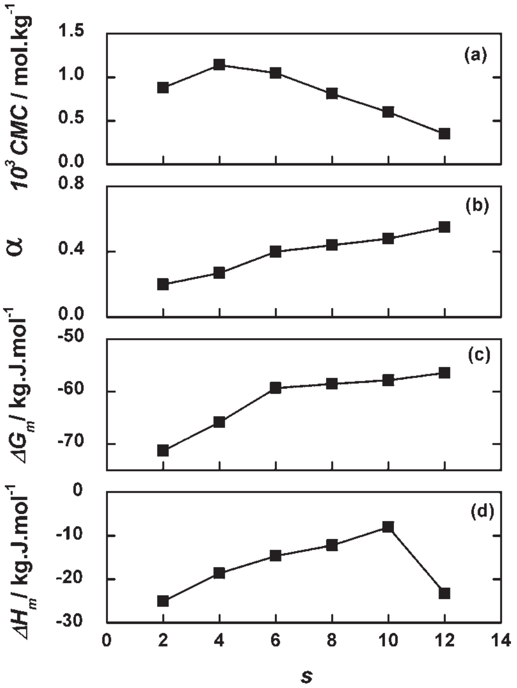

Figure 2. Variation of the (a) critical micelle concentration (CMC), (b) degree of counterion dissociation (α), (c) Gibbs energy of micellization (ΔG_m), and (d) enthalpy of micellization (ΔH_m) with respect to the number of carbon atoms in spacer (*s*) at 298.15 K.

For all of the surfactants studied, the Gibbs energy of micellization was calculated using eq 2.[26]

$$\Delta G_m = 2(1.5 - \alpha)RT \ln X_{CMC} \qquad (2)$$

where R is the gas constant, T the temperature in Kelvin, and X_{CMC} stands for the CMC in the mole fraction unit.

The plot of ΔG_m versus the spacer carbon number at 298.15 K in Figure 2c shows two straight lines. The first straight line corresponds to *s* = 2 to 6 and second to *s* = 6 to 12. The slope of these lines gives the Gibbs energy of transfer for $-CH_2-$ unit of spacer from the bulk to the micellar region.[28] For *s* = 2 to 6 and *s* = 6 to 12, the values for Gibbs energy of transfer were found to be 3.0 kJ·mol^{-1} and 0.5 kJ·mol^{-1}, respectively. This manifests that with the spacer of $s \leq 6$ micellization is less favorable as transfer of the $-CH_2-$ unit of spacer from the bulk to the micellar phase becomes less spontaneous. When *s* > 6 transfer of the $-CH_2-$ unit becomes easier, that is, micellization is more favored with the increase in spacer length, these findings go well in agreement with the CMC values. For ionic surfactants an increase in temperature leads to more dissociation of counterions that promotes repulsion between head groups and suppresses the micellization;

hence ΔG_m increases with temperature. This explanation is in accordance with our results.

Knowledge of temperature dependence of CMC and α value enables the calculation of the enthalpy of micellization (ΔH_m) for surfactants using the Gibbs−Helmholtz equation:

$$\Delta H_m = -2RT^2(1.5 - \alpha)\frac{d \ln X_{CMC}}{dT} \qquad (3)$$

The values of $\ln X_{CMC}$ for each gemini surfactant were plotted against the temperature, T. The slope value determined from the linear plot gives the value of $d \ln X_{CMC}/dT$.

Accordingly, the entropy change for micellization (ΔS_m) is calculated by eq 4.[29]

$$\Delta S_m = \frac{(\Delta H_m - \Delta G_m)}{T} \qquad (4)$$

The determination of ΔH_m has been done using eq 3 which does not consider the change in size and shape of micelles with temperature. Hence, values of ΔH_m and $T\Delta S_m$ reported here are different than that measured by calorimetric means.[28] For the gemini surfactant system studied, it was found that ΔH_m values are negative, confirming the phenomenon of micellization to be an exothermic one. Further, ΔH_m increases with the spacer (i.e., it become less negative), and there is a small maximum found around s = 4 to 6 (Figure 1d), corresponding to the maxima in the CMC values.

As described by Zana and co-workers,[19] for any ionic surfactant, the enthalpy of micellization is contributed by several factors. The fundamental contribution is due to the release of water molecules surrounded by a hydrophobic tail (have a different structure than bulk water) during their transformation from bulk phase to micelle (i.e., during micellization process). This factor increases ΔH_m negatively. Other important factors are electrostatic interactions between head groups (repulsive), between bounded counterions (repulsive), and between head groups and bounded counterions (attractive) at the micelle surface. It is well-known that attractive and repulsive interactions are endothermic and exothermic respectively. Since, in the case of surfactants, attractive interactions are less pronounced,[19] thus the remaining interactions contribute negatively to ΔH_m (make more negative). Several other factors that contribute to ΔH_m are (i) steric interaction between head groups due to their anchoring at micelle surface, although low contribution by this factor is reported,[30] and (ii) conformation change of surfactant alkyl tail during transformation from bulk phase to micellar phase. However, this factor is not considered here since all gemini surfactants studied have an identical tail, but the conformation changes of spacers are important and discussed later.

From Figure 2d it was observed that for s = 4 to 8, ΔH_m increases (become less negative) as compared to shortest (s = 2) and longest (s = 12) spacer. The former resides at the micelle surface and precludes residual contacts between alkyl chains and water; that is, the hydration of surfactant alkyl chain (hydrophobic hydration) is reduced to a greater extent. Whereas the later (flexible) spacer partly incorporates in the micelle core. this is attributed to a more easy transfer of surfactant tail from aqueous bulk phase to the pseudo micellar phase (facilitate release of hydrated water molecule surrounded to alkyl tail) giving evidence of micellization to be more exothermic for 12-2-12 and 12-12-12. Thus, for these geminis the hydrophobic hydration of alkyl tail is less, and hydrophobic interaction between alkyl tails is more which promotes micellization and leads to the formation of a more compact micelle.[2,18,19] Our findings are well-supported by relatively higher values reported for N_{agg} (obtained from SANS measurements for 12-2-12 and 12-12-12 (Table 3)). Further, for 12-s-12, the diameter of a cylinder embedding an alkyl chain is ca. $0.52 \cdot 10^{-9}$ m where as the length of extended spacer of 12-2-12 and 12-4-12 is ca. $0.38 \cdot 10^{-9}$ m and > $0.52 \cdot 10^{-9}$ m, respectively.[19] Thus, in the case of 12-2-12, it is not possible that two alkyl chains remain in a *cis* conformation (i.e., molecule remain in *trans* position) when molecule remains in a dispersed state (before CMC) which restricts their rotation around the C−C bond (steric hindrance). However, in an aggregate state, the 12-2-12 molecule must adopt a *cis* conformation, and this transformation from *trans* to *cis* contributes negatively to ΔH_m. This contribution decreases with the increase in spacer length because for s = 4 to 12 (length < $0.52 \cdot 10^{-9}$ m), the *cis* conformation is possible even in a dispersed state. Thus the value of ΔH_m become less negative with an increase in spacer length. For 12-12-12, its value is more negative than s = 4 to 10 which is due to the loop conformation of spacer in micelle core or other way; for a longer spacer the secondary alkyl chain is long enough to penetrate into the micelle core, and the hydrophobic interaction is enhanced (restrict hydration). Hence, the values of ΔH_m become much more negative.[31]

Another factor influencing ΔH_m is the electrostatic interaction at the micelle surface, which depends upon counterion dissociation and on the distance between charge centers of gemini surfactant. A negative contribution to ΔH_m due to this factor increases with increasing in α and s. From above explanation it is also evident that ΔH_m values give an approximate idea about the structure of the micelle,[18] which was further inferred by SANS results.

For ionic surfactants, temperature can affect the ΔH_m in two ways: First, by breaking water structure surrounding the alkyl chain (negative increase ΔH_m), and the second is negative associated with the condensation of alkyl chain into micelle (negatively decrease). An increase in the temperature causes a decrease in the first factor and prevents breaking of water structure, whereas the second contribution remains almost unaffected.[19] Therefore, for each gemini surfactant studied, ΔH_m decreases and becomes more negative with increase in temperature.

From the values of ΔH_m and $T\Delta S_m$ for surfactant studied here, it is apparent that $T\Delta S_m > -\Delta H_m$; that is, micellization is entropy-driven as in the case of a conventional ionic surfactant.[19]

4.2. Surface Tension Measurements. For all gemini surfactants, γ was measured as function of log C for surfactant concentrations ranging from above and below their CMC as shown in Figure 3.

It was observed that there is a linear decrease in γ with an increase in the log C up to CMC after which γ becomes almost constant. CMC values obtained from the break point in γ vs log C plot are in reasonable agreement with the reported values.[2,10] This plot provides additional information to evaluate C_{20} (surfactant concentration required to reduce the surface tension of the solvent by $20 \cdot 10^{-3}$ N·m^{-1}), γ_{CMC} and A_{min} . These data are listed in Table 2.

Γ_{max} (surface excess concentration) for gemini surfactant is calculated using the Gibbs equation,

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{\partial \gamma}{\partial \log c}\right)_{T,P} \qquad (5)$$

where R = 8.32 J·mol^{-1}·K^{-1} is the gas constant, T = 298.15 K, n = 3 for bis(quaternary ammonium) gemini surfactant[10,27] and

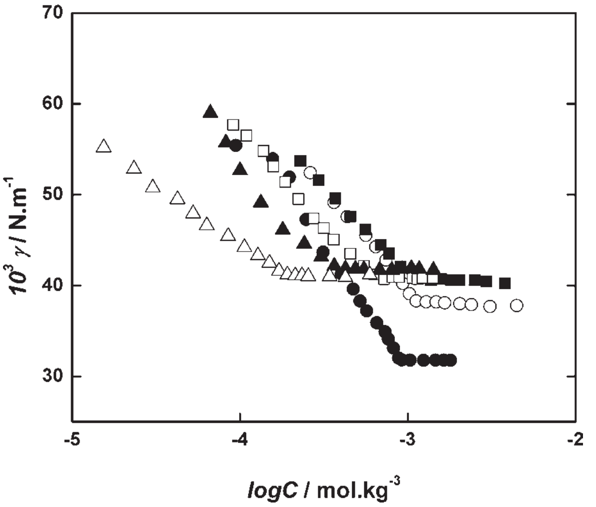

Figure 3. Variation of surface tension (γ) with the log of surfactant concentration (C) at 298.15 K: ●, 12-2-12; ○, 12-4-12; ■, 12-6-12; □, 12-8-12; ▲, 12-10-12, and △, 12-12-12.

Table 2. Values of Critical Micelle Concentration (CMC), Surface Tension at CMC (γ_{CMC}), Surfactant Concentration Required to Reduce the Surface Tension of the Solvent by $20 \cdot 10^{-3}$ N·m^{-1} (C_{20}) and Minimum Area Occupied Per Molecule at Air Water Interface (A_{min}) for Surfactants at 298.15 K

	10^3 CMC	$10^3\ \gamma_{\text{CMC}}$	$10^3\ C_{20}$	$10^{10}\ A_{\text{min}}$
surfactant	mol·kg^{-1}	N·m^{-1}	mol·kg^{-1}	m^2
12-2-12	0.91 ± 0.02	31.79 ± 0.4	0.20 ± 0.02	79.4 ± 0.5
12-4-12	1.10 ± 0.02	38.19 ± 0.4	0.27 ± 0.02	110.4 ± 0.5
12-6-12	1.00 ± 0.02	40.73 ± 0.4	0.29 ± 0.02	146.1 ± 0.5
12-8-12	0.66 ± 0.02	40.61 ± 0.4	0.18 ± 0.02	177.8 ± 0.5
12-10-12	0.38 ± 0.02	41.82 ± 0.4	0.14 ± 0.02	217.8 ± 0.5
12-12-12	0.21 ± 0.02	41.11 ± 0.4	0.03 ± 0.02	193.4 ± 0.5

($d\gamma/d \log C$) is the slope of linear portion of the graph before CMC where γ is expressed in 10^{-3} N·m^{-1} and C in mol·kg^{-1}. A_{min} was calculated using eq 6

$$A_{\text{min}} = 10^{16}/N\Gamma_{\text{max}} \tag{6}$$

where N is Avogadro's number and Γ_{max} in 10^2 mol·m^{-2}.[32]

From Table 2, it is observed that A_{min} increases with spacer carbon number up to $s \leq 10$. A possible explanation to it is that spacer remains in an extended fashion between two headgroups at the air—water interface in contact with water. On the other hand, when $s > 10$, the spacer is too hydrophobic to remain in contact with water and by adopting looped (wicket-like) conformation moves to air side of the interface. The variation in the values of the headgroup area with spacer chain length (s) is consistent with the variation in the CMC values as a function of s. The linear decrease in CMC with increasing s (beyond $s = 8$), corresponding to the incorporation of the spacer into the core of the micelle.[2,10,33]

The γ_{CMC} values describes the effectiveness of surfactant to reduce surface tension of solvent. It is observed from Table 2 that the γ_{CMC} value increases up to $s = 10$ and then for $s = 12$ it decreases little. The gemini surfactant 12-2-12 has the shortest spacer and also possesses the lowest α value (0.20) manifest the small net charge on the headgroup leading to reduced intermolecular repulsion and tight packing of surfactant molecule at the air—water interface which accounts for lowest γ_{CMC} for 12-2-12.[34] With $s \leq 10$, spacer remains extended at the air—water interface, and with increasing s values, the distance between the head groups increases along with an increase in the α value.

According to Rosen[32] the effectiveness of surfactant is described by the maximum surfactant concentration (saturation) that it can attain at interface. This maximum surfactant concentration depends on the minimum area of interface occupied by a surfactant monomer. It is obvious that smaller the area of interface occupied by surfactant monomer higher is the concentration of that surfactant at the interface. Depending on this explanation and from the value of A_{mim}, it is apparent that the effectiveness of surfactant decreases with the spacer. However, for $s > 10$ the spacer is flexible enough that it takes a loop-like conformation and remains outward from interface which facilitates closer packing than $s = 10$ (lower A_{min} for 12-12-12 as compared to 12-10-12). Thus due to long and flexible spacer for 12-12-12 their concentration is higher at the interface. Further, more hydrophobicity generated by long spacer (for $s > 6$) facilitates micellization at a lower concentration which leads the saturation of surfactant at the interface with a lower reduction in surface tension at CMC (i.e, higher γ_{cmc} value). Thus, the A_{min} and γ_{CMC} values of gemini surfactant manifest that 12-2-12 is most effective among the surfactant studied to reduce surface tension of water.

In contrast to the situation with effectiveness, the efficiency (C_{20} values) appears to increase with the length of the hydrophobic spacer. The larger the value of pC20 (smaller the value of C_{20}), the more efficiently the surfactant is adsorbed at the air—water interface, and the more efficiently it reduces surface or interfacial tension. Thus, smaller bulk phase concentrations required to reduce the surface tension by $20 \cdot 10^3$ N·m^{-1}.[32] Further, as discussed above with increasing spacer length (hydrophobicity) concentration of surfactant required to attain saturation at interface is reduced. From these explanations, it is apparent that for gemini surfactant efficiency increase with spacer length.

4.3. Effect of Spacer Length on Micellar Shape, Size, and Aggregation Number. The SANS distribution of micellar solution for ionic surfactant generally shows a correlation peak which corresponds to a peak in inter particle structure factor $S(Q)$ and indicates the presence of repulsive interaction between micelles. Here we have assumed the micellar system to be monodispersed for the simplicity of the calculation and to limit the number of unknown parameters in the analysis. The semimajor axis (a), semiminor axis (b) and the fractional charge (β) are the parameters obtained after analyzing the SANS data and are listed in Table 3. The aggregation number (N_{agg}) is calculated using relation $N_{\text{agg}} = 4\pi ab2/3v$, where v is the volume of the surfactant monomer. Throughout the data analysis, corrections were made for instrumental smearing. The parameters in the analysis were optimized by means of nonlinear least-squares fitting program, and the errors of the parameters were calculated by the standard methods used.[35−37]

Figure 4 shows the SANS distribution curve obtained for 0.1 mol·kg^{-1} surfactant solution after analysis. It is observed that with an increase in s (for $s = 2$ to 6), the peak position (Q_{m}) shifts toward a higher Q region which manifests that the distance between micelle decreases (because $Q_{\text{m}} = 2\pi/d$), that is, with an

Table 3. Semi Major Axis (a), Semi Minor Axis (b), Fractional Charge (β), and Aggregation Number (N_{agg}) for 0.1 mol·kg^{-1} Gemini Surfactants Obtained from SANS at 303.15 K

Surfactant	10^{-10} a/m	10^{-10} b/m	β	N_{agg}	a/b
12-2-12	169.8 ± 1.8	19.8 ± 0.5	0.12 ± 0.01	318 ± 10	8.58
12-4-12	69.4 ± 1.6	15.8 ± 0.5	0.20 ± 0.01	78 ± 7	4.39
12-6-12	34.7 ± 1.2	15.7 ± 0.5	0.30 ± 0.02	36 ± 3	2.21
12-8-12	35.9 ± 1.2	15.5 ± 0.5	0.27 ± 0.02	34 ± 3	2.32
12-10-12	41.3 ± 1.2	15.0 ± 0.5	0.26 ± 0.02	35 ± 3	2.75
12-12-12	69.7 ± 1.6	15.0 ± 0.5	0.19 ± 0.01	56 ± 5	4.64

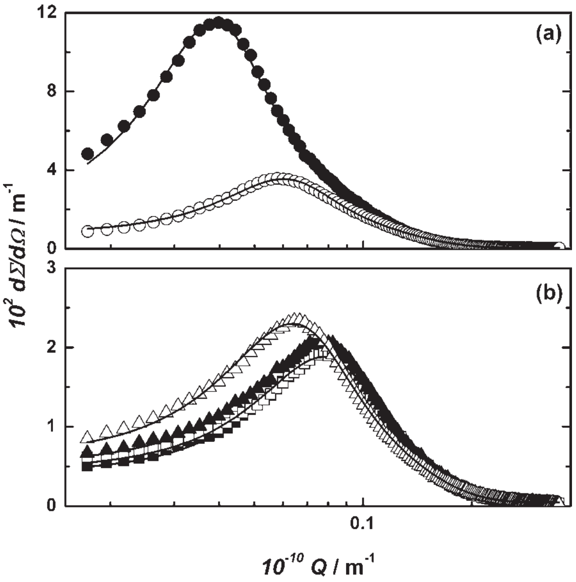

Figure 4. Plot showing a normalized neutron scattering cross-section ($d\Sigma/d\Omega$) versus the scattering vector (Q) for the 12-s-12 gemini surfactant at 303.15 K: (a) ●, 12-2-12; ○, 12-4-12 and (b) ■, 12-6-12; □, 12-8-12; ▲, 12-10-12 and △, 12-12-12. Solid line represents fitted data.

increase in spacer length distance between micelle decreases or number density of micelle increases; hence one can conclude that micelle size and shape also change. However, for s = 6, 8, and 10, Q_m remain almost constant, evidence that these surfactant micelled are almost the same in shape and size. For 12-12-12, the Q_m shift toward the lower Q region, suggesting a decrease in micelle size (as compared to s = 6 to 10).

Values of β are attributed to the headgroup polarity.[39] For 12-2-12, a minimum β (0.12) is found among the surfactant studied which gives evidence for lower headgroup polarity,that is, less electrostatic/Coulombic repulsion between headgroups that facilitates a larger number of surfactant molecules to aggregate, leading to the formation of large micelles with relatively higher aggregation numbers (N_{agg} = 318). This explanation is also supported by the most negative value of ΔH_m, relative low CMC, and least α value for 12-2-12. On the other hand for 4 < s > 12 as appears in Table 3, β remains more or less constant and relatively higher as compared to 12-2-12. Further, a lower β (0.19) for 12-12-12 as compared to s = 6, 8, 10 implies that in case of 12-12-12 there is less electrostatic repulsion (due to the looplike conformation of spacer). This facilitates a larger number of monomers to aggregate. The trend observed in aggregation number is similar to the one reported by Danino et al.[12] With an increase in spacer length, N_{agg} decreases. However, they remain mostly unaltered for s = 6, 8, and 10. These results suggest the formation of comparatively small (as compare to 12-2-12) and almost constant sized micelle for s = 6, 8, and 10 as apparent from Table 3.

A decrease in N_{agg} with spacers is more abrupt for $s \leq 4$, indicating conformation changes of the spacer. Moreover, the positive charges present on gemini are close enough that it can compete with electrostatic repulsion. As a result, micelles formed are of low curvature and with high aggregation number (wormlike or rod like), whereas for s = 6 to 10 it is almost constant showing that the conformation of the spacer is almost the same as the distance between positive charges which is equivalent to the electrostatic equilibrium. Hence, an oblate spherical micelle is formed with relatively lower N_{agg}. Further for s = 12, N_{agg} slightly increases as spacer is long and hydrophobic enough to incorporate in the hydrophobic core of micelle thus preventing the hydration of micelle and increasing hydrophobic interaction which leads to increase in N_{agg} and micellar size.[2,12,13,38] A similar trend was found for the a/b ratio.

5. CONCLUSION

This study investigates the effect of spacer length on the micellization of a synthesized cationic gemini surfactant of the type 12-s-12 (s = 2, 4, 6, 8, 10, and 10). A systematic comparison between their micellar parameters, namely, critical micelle concentration (CMC), degree of counterion dissociation (α), free energy (ΔG_m), enthalpy ΔH_m, entropy of micellization in terms of $T\Delta S_m$, minimum area occupied by surfactant monomer at the air—water interface (A_{min}), surface tension at CMC (γ_{CMC}), aggregation number (N_{agg}), and size as a function of spacer carbon number is performed. It is observed that the CMC increase up to s = 4 and then it decreases; this trend is due to the conformational effect of a spacer. An increase in the α value with an increase in spacer length indicates weak binding of counterion with the surfactant head as the s value increases. ΔG_m versus the spacer carbon number at 298.15 K shows two straight lines; the first corresponds to s = 2 to 6 and the second to s = 6 to 12. This proved that micellization is less favorable for s = 2 to 6 as compared to s > 6. ΔH_m values are negative for all gemini surfactants studied. An increase in ΔH_m is relatively more for s = 2 compared to s = 4 to 6 and can be understood by the change in hydrophobic interaction and hydration of surfactant molecule which depends on the spacer carbon number. The aggregation number for studied surfactants decreases with the increase in spacer length abruptly from s = 2 to 6, whereas for s = 6 to 10 it is almost constant and for s = 12 slightly increases again. The variation in the values of the A_{min} with spacer s is somewhat consistent with the variation in the CMC. γ_{CMC} values increase up to s = 10; then for s = 12 it decreases slightly as compares to s = 10 due to the loop-like conformation of a spacer at the air—water interface.

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