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Effect of amide bonds on the self-assembly of gemini surfactants†

Cite this: DOI: 10.1039/c3cp55244f

Jialu Hoque,^a Spandhana Gonuguntla,^a Venkateswarlu Yarlagadda,^a Vinod K. Aswal^b and Jayanta Halder^{*a}

This study provides an insight into the micellar aggregation properties in aqueous solutions of various gemini surfactants bearing one or more amide groups at the side chains and/or in the spacer by conductivity and small angle neutron scattering (SANS) studies. The amide functionality was found to enhance the surfactant aggregation properties as compared to the surfactants having no amide bond. Furthermore, the aggregation properties of the gemini surfactants bearing amide groups were found to strongly depend on the position and number of amide bonds. With the increase in the number of amide bonds, the aggregation number (*N*) and the size of the micelles increased. Additionally, the size and shape of the micelles were also found to depend both on the hydrocarbon chain length and the spacer chain length. It was also found that the aggregation number and the size of the micelles increased with an increase in concentration and decreased with an increase in temperature. The critical micellar concentration (CMC) values of the gemini surfactants obtained by a conductometric method were found to vary greatly with variation in the hydrocarbon chain.

Received 12th December 2013,
Accepted 6th April 2014

DOI: 10.1039/c3cp55244f

www.rsc.org/pccp

Introduction

Over the past few decades, gemini (dimeric) surfactants have drawn attention due to their superior physicochemical properties over the conventional surfactants made up of a polar head group and a hydrophobic tail.^{1–10} Structurally, gemini surfactants are a pair of conventional surfactants held together by a covalent linkage referred to as a spacer, either between the head or tail groups. Because of such unique structure, gemini surfactants have proved to be very efficient in lowering the surface or interfacial tension and critical micelle concentration (CMC).^{1–4} Furthermore, by varying the spacer chain length, the physicochemical properties of the gemini surfactants can be fine-tuned without changing the properties greatly.¹¹ Due to these unique properties, gemini surfactants are being used

extensively in various fields such as agriculture, medicine, biotechnology, food industry *etc.*^{12–17}

However, most of the surfactants used are non-degradable in nature. The usage of the non-degradable surfactants have raised serious issues about the aquatic toxicity and environmental safety.^{18–21} To make surfactants degradable, various cleavable groups such as ester,²² amide,²³ carbonate,²⁴ *etc.* have been introduced, which are susceptible to chemical/enzymatic hydrolysis.^{24–26} Previously, we have reported the development of cleavable surfactants by introducing amide bonds into the hydrophobic tail.²⁷ However, in order to make surfactants even more degradable, it is desirable to introduce higher number of amide functionalities into the molecules while maintaining their chemical stability. Herein, we have developed cationic gemini surfactants bearing cleavable amide linkages both in the hydrocarbon chain as well as in the spacer unit (Fig. 1).

Further, aggregation plays a major role in determining the physicochemical properties of surfactants. The aggregation properties of the gemini surfactants in aqueous solution have been found to depend on various factors such as concentration, temperature, presence of additives, spacer chain length, *etc.*^{1–9} The presence of functional groups such as amides in the structure has also been found to influence the aggregation properties. In our previous report, we have shown that the amide functionality in the hydrophobic tail enhanced the aggregation properties of the gemini surfactants possibly by intermolecular hydrogen bonding.²⁷ However, there are no systematic reports on the aggregation properties of the gemini surfactants bearing multiple amide groups *i.e.*, how the aggregation properties change

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† Electronic supplementary information (ESI) available: Structure of various monomeric surfactants without or with amide bonds. ¹HNMR and high resolution mass spectrometry (HRMS) data for various non-cleavable and cleavable surfactants. Figures showing determination of CMC values by a conductometric method, SANS distribution profile, changes in the aggregation number, and the ratio of semimajor axis to semiminor axis of various monomeric surfactants, and ¹HNMR spectra of enzymatic hydrolysis. Table showing the degree of ionization, scattering length density, and molecular volumes of various surfactants used in this study. See DOI: 10.1039/c3cp55244f

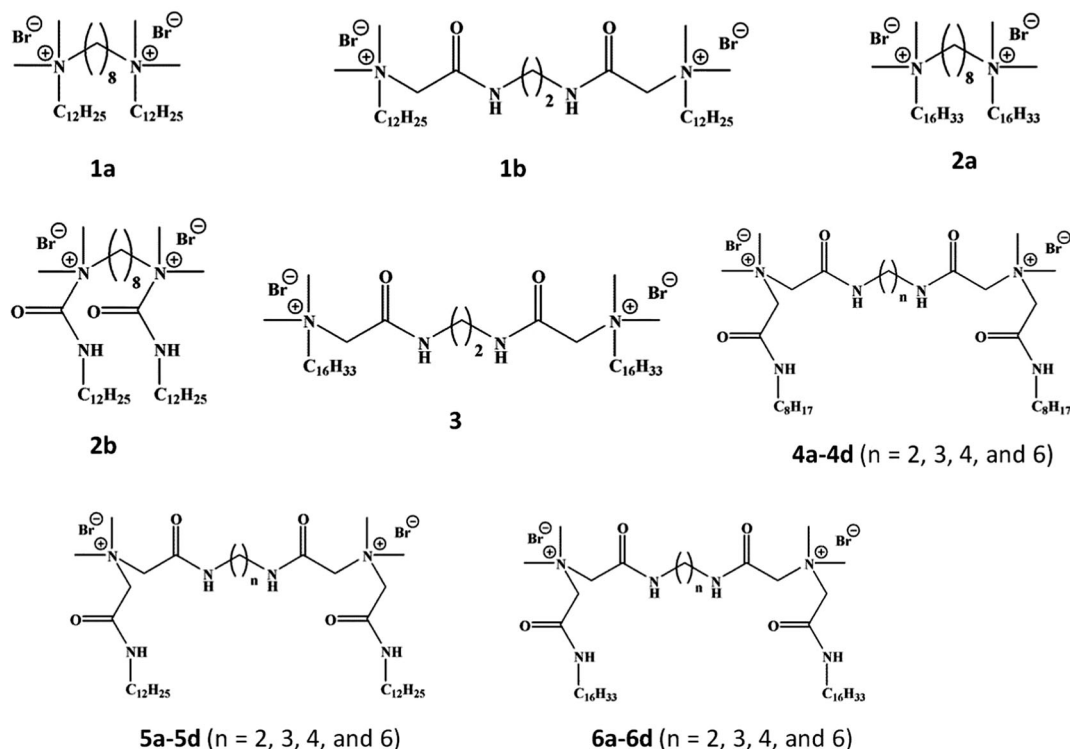


Fig. 1 Structures of cationic gemini surfactants used in the study.

with the increase in the number of amide groups as compared to the surfactants having no or lesser number of amide groups. Furthermore, the position of the amide groups on the aggregation properties of the gemini surfactants is yet to be understood.

Herein, we attempt to decipher the role of number and position of the amide groups on the micellar aggregation properties of the gemini surfactants bearing amide linkages in aqueous solution. We report three sets of cationic cleavable gemini surfactants (**4a–4d**, **5a–5d** and **6a–6d**) with different methylene spacers ($n = 2, 3, 4$, and 6) and varying hydrocarbon chain length ($-C_8H_{17}$, $-C_{12}H_{25}$, and $-C_{16}H_{33}$) bearing amide linkages both in the hydrocarbon chain as well as in the spacer chain along with the surfactants having no amide bonds (**1a** and **2a**), bearing amide bonds only at the spacer (**1b** and **3**), bearing amide bonds only at the alkyl chain (**2b**) (Fig. 1) and their aggregation behaviour by small angle neutron scattering (SANS) and conductivity methods. The amide group was found to have an enhanced effect on the micellar aggregation as compared to the surfactants having no amide bond (**1a** and **2a**) and amide groups present either in the hydrocarbon chain (**2b**) or in the spacer (**1b** and **3**). The micellar aggregation properties of the gemini surfactants containing amide groups were also found to depend on the position and number of amide bonds in the molecular structure.

Experimental section

Materials

All the amide bearing surfactants were synthesized following the protocol of our previous report.²⁷ Surfactants **1a** and **2a** were

synthesized by a well-known method as reported earlier.^{37,38} In order to synthesize **1b** and **3**, an activated intermediate was made by reacting 1,2-diaminoethane with bromoacetyl bromide and then subsequently quaternized with *N,N*-dimethyldodecylamine and *N,N*-dimethylhexadecylamine. Surfactant **2b** and amide-containing monomeric surfactants were synthesized following our previous report.²⁷ All the surfactants were characterised by ¹H NMR and mass spectrometry (ESI⁺). D₂O (99.5 atom% D), obtained from the Heavy Water Division of BARC, India, was used for the SANS studies. All the reagents and solvents used in this study were of analytical grade. Double distilled Millipore water was used for conductivity measurements.

Conductivity measurements

The electrical conductivity method was employed to determine the critical micellar concentration (CMC) of the surfactants at 30 ± 0.3 °C using a EUTECH CON 501 cyberscan conductivity meter with a cell constant of 1.0 cm^{-1} . Millipore water (specific conductivity of $0.066 \mu\text{S cm}^{-1}$ at 25 °C) was used to prepare the solutions for all the surfactants. Concentrated solutions of individual surfactants of known concentrations were prepared. Solutions were then progressively diluted and the specific conductivity values were measured. The CMC values of each surfactant were determined as the cross point of the two straight lines by plotting the values of the specific electrical conductivity, κ , against the surfactant concentration, C (Fig. S2, ESI⁺). The degree of ionization (α) of the micelles was calculated from the ratio of the slopes of the two straight lines above and below the CMC (Table S1, ESI⁺). The variation in CMC and

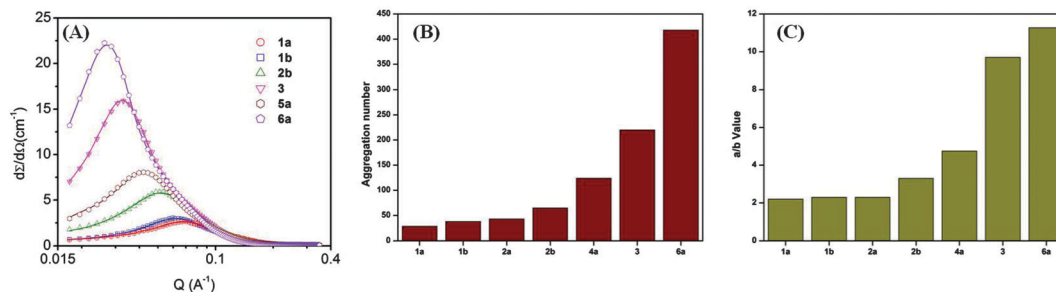


Fig. 2 (A) SANS distributions of aqueous solution of the gemini surfactants (**1a**, **1b**, **2b**, **3**, **5a**, and **6a**) at 50 mM concentration at 30 °C. The lines shown are theoretical fits and the solid marks are experimentally determined data points. SANS experimental data for surfactant **2a** were taken from the earlier report.³⁷ The effect of the multiple amide bonds on the aggregation properties of the gemini surfactants without or with amide bonds at various positions; (B) the effect on the aggregation number; and (C) the effect on the ratio of semimajor axis (*a*) to semiminor axis (*b*).

α values of micelles was established using surfactants with different spacers.

Small angle neutron scattering (SANS) measurements

Data collection. All the small angle neutron scattering (SANS) experiments were performed in the aqueous solution (D_2O) of gemini surfactants bearing amide groups both in the hydrocarbon side chains and in the spacers **4a–4d**, **5a–5d**, and **6a–6d** ($n = 2, 3, 4$, and 6) along with the corresponding monomeric surfactants **7**, **8**, and **9** and other gemini surfactants such as **1a** (no amide group), **1b** and **3** (amide groups in the spacer), and **2b** (amide groups in the hydrocarbon chain). In a SANS experiment, D_2O instead of H_2O provides an enhanced contrast between the micelles and the solvent in order to study the micellar aggregation. A SANS spectrometer at the Dhruva Reactor, Trombay, India was used to perform all the neutron-scattering measurements. The sample-to-detector distance was 1.8 m for all the runs. The spectrometer makes use of a Beryllium oxide (BeO) filtered beam to provide a mean wavelength (λ) of 0.52 nm and a wavelength resolution ($\Delta\lambda/\lambda$) of about 15%. A one-dimensional position-sensitive detector (PSD) has been used to record the angular distribution of the scattered neutrons. The range of accessible wave vector transfer, $Q (= 4\pi \sin^{1/2}\theta/\lambda$, where θ is the scattering angle), for this instrument is between 0.015 and 0.4 \AA^{-1} . The PSD allowed a simultaneous recording of the data over the full Q range.

The aqueous solutions of the surfactants were held in a UV grade quartz sample holder (path length 0.2 cm) with tight-fitting teflon stoppers, sealed by parafilm. In most of the measurements, the concentration of the gemini surfactants was fixed at 50 mM and the temperature of the sample was kept at $30 \pm 0.1 \text{ }^\circ\text{C}$. The effect of the concentration on the SANS distribution was investigated for the gemini surfactants **4c**, **5c**, and **6c** ($n = 4$) in the concentration range of 12–50 mM at $30 \text{ }^\circ\text{C}$. Similarly, the effect of temperature was also studied for the **4c**, **5c**, and **6c** ($n = 4$) micellar systems at 50 mM in the temperature range of $30\text{--}60 \text{ }^\circ\text{C}$. SANS experiments were done for the monomeric surfactants **7**, **8**, and **9** using 100 mM of the surfactant concentration at $30 \text{ }^\circ\text{C}$.

Data treatment. Neutron scattering intensities from the surfactant solutions were corrected for detector background and sensitivity, empty cell scattering, and sample transmission.

The solvent intensity was subtracted from that of the sample. The resulting corrected intensities were normalized to absolute cross section units and thus $d\Sigma/d\Omega$ vs. Q was obtained. The absolute calibration has an estimated uncertainty of 10%. The experimental points are fitted using a nonlinear least-square routine as shown in the subsequent section. Comparisons between the experimental and the calculated cross sections are shown in Fig. 2–5 and Fig. S3 (ESI†) and the fitted parameters are shown in Tables 1–3.

Analysis of SANS data. The coherent differential scattering cross section, $d\Sigma/d\Omega$, can be reduced for an assembly of monodispersed micelles as given by^{28–35}

$$d\Sigma/d\Omega = nV_m^2(\rho_m - \rho_s)^2P(Q)S(Q) \quad (1)$$

where n denotes the number density of the micelles, ρ_m and ρ_s are, respectively, the scattering length densities of the micelles and the solvent and V_m is the volume of the micelles. $P(Q)$ is the single (orientationally averaged) intraparticle structure factor and $S(Q)$ is the interparticle structure factor. The detailed analysis of the SANS data has been given in the ESI.†

The data in Fig. 2–5 corresponding to different surfactants **1a–1b**, **2b**, **3**, **4a–4d**, **5a–5d**, and **6a–6d** were analyzed using the aggregation number N , micellar dimensions (semimajor axis a and semiminor axis b of the ellipsoidal shape) and the fractional charge on the micelles α as the parameters for the fit. The solid marks in Fig. 2–5 are experimentally determined data points and the lines shown are theoretical fits. The semimajor axis a ($3N\nu/4\pi b^2$) was obtained from the knowledge of the above parameters, where ν is the volume of the individual surfactant molecule. The values of N , α , a , and b are given in Tables 1–3. The effects of concentration and temperature on size parameters for **4c**, **5c**, and **6c** ($n = 4$) were also obtained by similar methods.

Results and discussion

Critical micelle concentration (CMC)

The CMC for each surfactant was determined by plotting the specific conductivities (κ) of surfactant solutions as a function of concentration (Fig. S2, ESI†). For the aqueous solution of each surfactant, reproducible breaks were observed in κ vs.

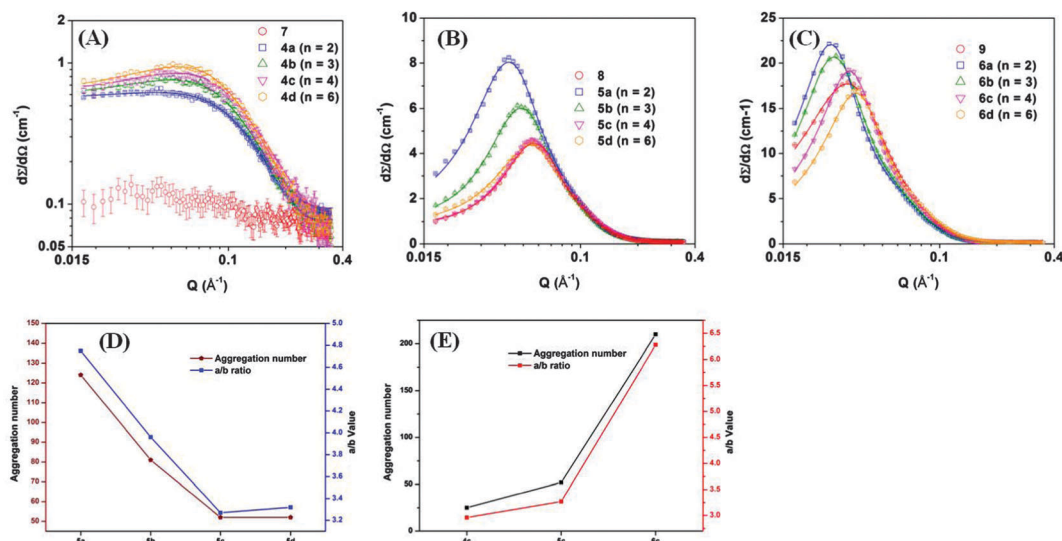


Fig. 3 SANS distributions of the aqueous solution of gemini surfactants (A) for **4a–4d**, (B) for **5a–5d**, and (C) for **6a–6d** at 50 mM concentration at 30 °C and the corresponding monomeric surfactants **7**, **8**, and **9** at 100 mM concentration at 30 °C. The lines shown are theoretical fits and the solid marks are experimentally determined data points. (D) The effect of the spacer on the micellar aggregation properties of the gemini surfactants having same hydrocarbon chain lengths **5a–5d** ($n = 2, 3, 4$, and 6). (E) The effect of the hydrocarbon chain length on the aggregation properties of the gemini surfactants having same spacers **4c** (octyl), **5c** (dodecyl), and **6c** (hexadecyl).

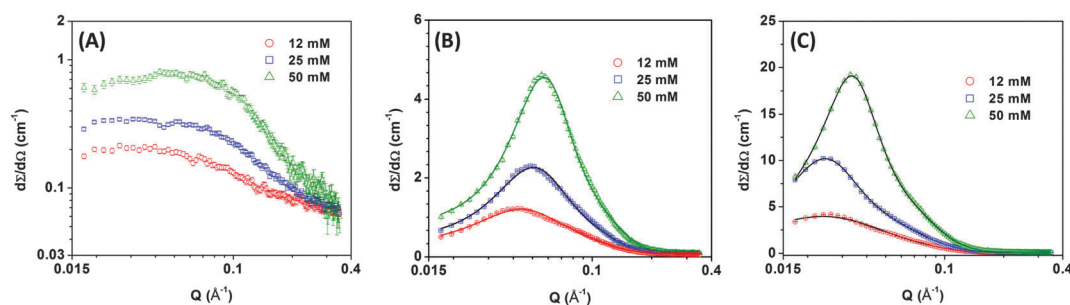


Fig. 4 SANS distributions of micellar solution of gemini surfactants bearing multiple amide groups at different concentrations (12–50 mM) at 30 °C (A) for **4c**, (B) for **5c**, and (C) for **6c**. The lines shown are theoretical fits and the solid marks are experimentally determined data points.

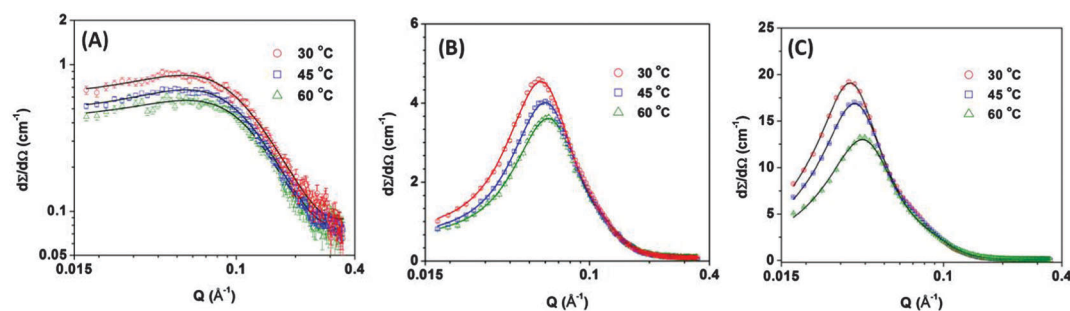


Fig. 5 SANS distributions of micellar solution of gemini surfactants bearing multiple amide groups at different temperatures (30–60 °C) at 50 mM (A) for **4c**, (B) for **5c**, and (C) for **6c**. The lines shown are theoretical fits and the solid marks are experimentally determined data points.

concentration plots indicating the micellar aggregation. The CMC values of gemini surfactants having $-C_8H_{17}$ long chain (**4a–4d**) were 8.50–10.05 mM (Table 1) whereas the corresponding monomeric surfactant **7** did not form micelles even up to 60 mM concentration (Fig. S2A and B, ESI†). This might be due to the $-C_8H_{17}$ long chain which probably does

not introduce sufficient hydrophobicity in order to form stable aggregates for the surfactant **7**. The CMC values of gemini surfactants **4a–4d** were found to decrease with the increase in the spacer chain length from 10.05 mM for $n = 2$ to 8.50 mM for $n = 6$ and **4d** having the lowest CMC value in the group. This is because with the increase in the spacer chain

Table 1 Effect of the spacer length (n) in micellar systems of amide bearing cationic gemini surfactants on the Q value^a

Micellar system	CMC ^b (mM)	Aggregation number (N)	Fractional charge (α)	Semimajor axis (a) (Å)	Semiminor axis ($b = c$) (Å)	a/b
4a ($n = 2$)	10.05	28	0.20	37.6	14.2	2.65
4b ($n = 3$)	9.50	27	0.25	38.3	14.1	2.72
4c ($n = 4$)	9.06	25	0.28	39.4	13.3	2.96
4d ($n = 6$)	8.50	26	0.28	42.7	13.5	3.16
5a ($n = 2$)	0.34	124	0.15	96.0	20.2	4.75
5b ($n = 3$)	0.29	81	0.22	74.8	18.9	3.96
5c ($n = 4$)	0.25	52	0.30	57.2	17.5	3.27
5d ($n = 6$)	0.21	52	0.23	58.7	17.7	3.32
6a ($n = 2$)	0.052	418	0.12	270.5	24.0	11.27
6b ($n = 3$)	0.030	360	0.15	254.5	23.2	10.97
6c ($n = 4$)	0.028	210	0.22	156.4	22.8	6.86
6d ($n = 6$)	0.026	158	0.26	135.7	21.6	6.28
7	— ^c	— ^c	— ^c	— ^c	— ^c	— ^c
8	4.4	113	0.17	45.7	18.0	2.54
9	0.33	377	0.08	113.8	22.7	5.01

^a All of the SANS spectra were recorded at 30 °C using 50 mM for all the dimeric surfactants (**4a–4d**, **5a–5d**, and **6a–6d**) and 100 mM for monomeric surfactants **7**, **8**, and **9**. ^b CMC values were determined by a conductivity method. ^c Could not be determined.

Table 2 Effect of concentration in micellar systems of cationic gemini surfactants bearing multiple amide groups on the Q value^a

Micellar system	Concentration (mM)	Aggregation number (N)	Fractional charge (α)	Semimajor axis (a) (Å)	Semiminor axis ($b = c$) (Å)	a/b
4c	12	15	0.51	23.6	13.3	1.77
4c	25	19	0.35	30.0	13.3	2.26
4c	50	25	0.28	39.4	13.3	2.96
5c	12	38	0.32	41.8	17.5	2.39
5c	25	46	0.31	50.7	17.5	2.89
5c	50	52	0.30	57.2	17.5	2.98
6c	12	96	0.30	71.5	22.8	3.14
6c	25	130	0.25	96.8	22.8	4.25
6c	50	210	0.22	156.4	22.8	6.86

^a All of the SANS spectra were recorded at 30 °C using 12–50 mM concentration of all the gemini surfactants (**4c**, **5c**, and **6c**).

Table 3 Effect of temperature in micellar systems of cationic gemini surfactants bearing multiple amide groups on the Q value^a

Micellar system	Temperature (°C)	Aggregation number (N)	Fractional charge (α)	Semimajor axis (a) (Å)	Semiminor axis ($b = c$) (Å)	a/b
4c	30	25	0.28	39.4	13.3	2.96
4c	45	23	0.34	37.4	13.2	2.83
4c	60	21	0.37	34.0	13.3	2.56
5c	30	52	0.30	57.2	17.5	3.27
5c	45	46	0.34	51.0	17.3	2.95
5c	60	41	0.37	47.3	17.0	2.78
6c	30	210	0.22	156.4	22.8	6.86
6c	45	185	0.24	149.3	21.9	6.82
6c	60	143	0.28	119.8	21.5	5.57

^a All of the SANS spectra were recorded at 50 mM from 30 to 60 °C for all the gemini surfactants (**4c**, **5c**, and **6c**).

length, hydrophobicity increases and so the aggregation tendency.

The CMC values of gemini surfactants having $-C_{12}H_{25}$ long chain (**5a–5d**) were found to be 0.21–0.34 mM and are 13–21 times lesser than the corresponding monomeric analogue **8** (CMC = 4.4 mM) (Table 1). This is due to the presence of two hydrophilic head groups and two hydrophobic tails connected by a hydrophobic methylene spacer in the gemini surfactants as compared to only one hydrophilic head group and one hydrophobic tail in the monomeric surfactant which cause the former to have higher aggregation tendency in water, a common and expected property of the gemini surfactants. It is important to note that the CMC values of gemini surfactants

having amide groups only at the hydrophobic long chain as reported earlier²⁷ (CMC = 0.11 and 0.08 mM for $n = 8$ and 12 having $-C_{12}H_{25}$ long chain) are in the same order to that of the surfactants having amide groups both in the spacer and in the long chain with the same chain length, **5a** and **5d** (CMC = 0.34 and 0.21 mM).

The CMC values of gemini surfactants having $-C_{16}H_{33}$ long chain (**6a–6d**) were found to be very low (CMC = 0.026–0.052 mM) and are 6–13 times lesser than the corresponding monomeric analogue **9** (CMC = 0.33 mM). It is interesting to note that the micellar aggregation is highly pronounced for this set of surfactants as compared to **4a–4d** or **5a–5d** (having $-C_8H_{17}$ and $-C_{12}H_{25}$ long chains) (Table 1). For example, the

CMC value of the surfactant **6c** is 0.028 mM whereas the CMC values of **4c** or **5c** are 9.06 and 0.23 mM respectively. A similar observation was seen for the monomeric surfactant **9** having $-C_{16}H_{33}$ long chain as compared to **8** (having $-C_{12}H_{25}$ long chain) (Table 1). This proves that the aggregation tendency increases rapidly with the increase in the hydrocarbon chain length.

While conductivity measurements are carried out in H_2O , SANS studies require D_2O as medium. The influence of a solvent isotope may be negligible in routine surfactants but may be profound in systems having multiple exchangeable protons of the amide bearing surfactants. In order to establish whether the solvent isotope has any influence on the aggregation of the amide bearing surfactants, the conductivity measurement was also performed in D_2O with one of the gemini surfactants (**5c**, $n = 4$). The CMC of **5c** was found to be 0.249 mM in H_2O whereas the CMC value of **5c** is 0.245 mM in D_2O . This showed that the CMC values are quite similar and therefore the influence of the solvent isotope is negligible for the amide bearing surfactants. To further confirm the negligible influence of the solvent isotope on aggregation, the CMC values of **5c** were also determined by steady state fluorescence measurements using pyrene as a fluorescent probe both in H_2O and D_2O . It was found that the CMC values of **5c** were similar both in H_2O and D_2O (0.239 mM and 0.241 mM respectively) and are in good agreement with the values obtained by the conductivity method.

For practical reasons, the degree of ionization is very important in many applications such as morphological switchover such as spherical to cylindrical,³⁹ viscoelastic behaviour,⁴⁰ the rate of a chemical reaction involving micelles,⁴¹ gene delivery,⁴² *etc.* that demand the micelles as a charged interface. We measured the degree of ionization (α) from the ratio of the slopes of the two straight lines above and below the CMC for all the newly synthesized surfactants. It was found that the degree of ionization is higher for the gemini surfactants as compared to the monomeric surfactant. For example, the degree of ionization of the gemini surfactants **5a–5d** is 0.5 to 0.66 whereas for the monomeric surfactant **8** it is 0.27. This is probably due to the presence of two cationic headgroups and two bromide counterions in the gemini surfactants as compared to only one cationic headgroup and one counterion in the monomeric surfactant and are in agreement to our previous report.²⁷ A similar phenomenon was observed for the surfactants having $-C_{16}H_{33}$ long chain with degree of ionization 0.4–0.6.

Enzymatic and chemical hydrolysis of amide bearing gemini surfactants

As the gemini surfactants presented in this work bear amide bonds both in the spacer as well as in the hydrocarbon chain, the stability of these surfactants in the presence of proteolytic enzymes and base was studied. When subjected to enzymatic hydrolysis, gemini surfactants with amide bonds were found to be degraded in the presence of a proteolytic enzyme trypsin thereby indicating that these surfactants were susceptible towards enzymatic hydrolysis (Fig. S8, ESI†). The gemini surfactant bearing

amide groups also hydrolyzed in the presence of base implying that these surfactants were susceptible towards alkaline hydrolysis (Fig. S9, ESI†). The above results thus indicated that the amide containing surfactants are cleavable in nature (in the presence of enzymes and base).

Small angle neutron scattering (SANS) studies

In a neutron scattering experiment, a beam of neutron is directed towards the sample under examination and the intensities of the neutron scattering in various directions are measured. Since neutrons are scattered by the nuclei of atoms in the sample, even isotopes of the same elements differ in their scattering power. Thus, by taking micellar aggregates in D_2O rather than in H_2O , the scattering densities of various regions can be obtained, as deuterons and protons differ widely in their respective scattering capacities. SANS measurements have been found to provide useful information regarding the shapes of various self-organizing micellar systems in a non-invasive manner.^{27,36,37,43,44} Previously we have examined how cleavable gemini surfactants with amide groups in the hydrocarbon chain adopt different morphologies in aqueous media depending on their spacer chain length (n) using SANS.²⁷ Herein, we have taken an initiative to investigate the role of the number and position of the amide groups in the micellar aggregation properties of amide containing gemini surfactants by SANS. We also studied the effect of the variation in the spacer chain and hydrocarbon chain length on the aggregation properties of these cleavable surfactants. The effects of the variation in concentration and temperature on the micellar aggregation were also investigated.

Effect of incorporation of multiple amide groups in gemini surfactants on aggregation properties

We compared the aggregation properties of the gemini surfactants having no amide bond (**1a** and **2a**), bearing amide bonds only at the spacer (**1b** and **3**), amide bonds only at the hydrocarbon chain (**2b**) and amide bonds both in the spacer as well as in the hydrocarbon chains with a comparable chain length (**5a** and **6a**). SANS distribution profile of these surfactants is shown in Fig. 2A at 50 mM and 30 °C where measurements have covered Q ranges from 0.015 to 0.4 \AA^{-1} . As can be seen from Fig. 2B and C the aggregation number and the a/b ratio of the surfactants increase with the introduction of the amide bonds in the molecule. For example, the aggregation number N and a/b values of the surfactants **1a** and **2a** devoid of any amide groups are 29 and 2.2, and 43 and 2.3 respectively; whereas the N and a/b values of the surfactants **1b** and **3** having amide bonds only in the spacer, and **2b** having amide bonds only in the hydrocarbon chain are 38 and 2.9, and 65 and 3.3, and 220 and 9.7 respectively. However, with the further introduction of the amide bonds, *i.e.*, amide bonds both in the spacer and the hydrophobic chains, the aggregation number N and a/b values increased rapidly. For example, the N and a/b values of **5a** and **6a** having amide bonds both in the spacer and the hydrophobic chains are 124 and 4.75, and 418 and 11.27 respectively. This confirms the fact that the multiple amide groups in the

surfactant molecules enhance the aggregation tendencies of the surfactant probably by an intermolecular association (Fig. 2B and C). The presence of an amide linkage probably facilitates an intermolecular association between surfactants through hydrogen bonding interactions in organized assemblies. Also, as these amide linkages are located near the *Stern-layer* region of the micelles, hydrogen-bonding interactions between the surfactant molecules may also operate *via* interfacially adhering to water molecules which are in agreement to our previous report.²⁷

Another point that should be noted here is that the amide bonds placed in the hydrocarbon chain have a greater effect on the aggregation properties of the gemini surfactants bearing equal number of amide bonds in the spacer. For example, the aggregation number and the a/b value of surfactant **2b** having amide bonds between the head group and the long hydrophobic chain ($-C_{12}H_{25}$) are 65 and 3.3, respectively, whereas that of surfactant **1b** having amide bonds in the spacer connecting the head group are 43 and 2.3, respectively, at the same concentration and temperature (at 50 mM and 30 °C). This proved that the amide groups placed in the hydrocarbon chain have a better impact on the aggregation of the surfactants which might result from a stronger H-bonding between amide units of the hydrocarbon region than the spacer region probably due to lower polarity at the hydrocarbon region compared to the spacer region.

It is interesting to note that compared to DTAB and CTAB devoid of amide bond, monomeric surfactants **8** and **9** bearing amide bonds between the head group and the hydrocarbon chain have a considerably higher aggregation number (for DTAB, $N = 70$ and CTAB, $N = 160$ whereas for surfactant **8**, $N = 113$ and surfactant **9**, $N = 377$) at the same concentration and temperature (at 100 mM and 30 °C). Furthermore, the a/b value of surfactants **8** and **9** is more than double to that of DTAB or CTAB (a/b value of surfactants **8** and **9** is 2.54 and 5.01 whereas the a/b value of DTAB and CTAB is 1.22 and 2.05, respectively) (Fig. S3, ESI†). Consequently, these results indicated that the micellar growth of surfactants **8** and **9** is much more pronounced than the micellar growth of DTAB and CTAB in aqueous solution under identical conditions. Although DTAB also possesses only one Me_3N^+ headgroup and a single hydrocarbon chain, in a micellar aggregate surfactants **8** and **9** are expected to be more “tightly” associated because of the presence of an amide unit $[-NH-C(O)-]$ that links the Me_3N^+ headgroup with the hydrocarbon chain in a similar fashion as explained before.

Effect of molecular structure of the surfactants on aggregation properties

First, we report the results of the measurements of neutron cross sections from the micellar solutions of the gemini surfactants **4a–4d**, **5a–5d**, and **6a–6d** at 50 mM along with monomeric surfactants **7**, **8**, and **9** at 100 mM in D_2O at 30 °C (Fig. 3A–C). SANS distributions for all the gemini surfactants (**4a–4d**, **5a–5d**, and **6a–6d**) as well as for the monomeric surfactants **8**, and **9** showed well-defined peaks except the monomeric surfactant **7**

having $-C_8H_{17}$ long chain. The origin of this peak is because of a corresponding peak in the interparticle structure factor $S(Q)$. Usually this peak occurs at $Q_m \sim 2\pi/d$, where d is the average distance between the micelles. As Q_m was found to vary with the spacer length (n) for each set of gemini surfactants, it can be concluded that the number density (n_d) of micelles was not the same in each set of samples at identical concentrations (50 mM). The above observations further indicated that the aggregation number of the micelle, N , depends on the spacer chain length n and the length of the hydrocarbon tail. However, it was not apparent that the micelles were spherical. In the following analysis, we, therefore, assumed them to be prolate ellipsoids ($a \neq b = c$), sphere being a special case of that. The reason behind for not getting a definite peak in the SANS distribution for monomeric surfactant **7** could be the inability of this surfactant to form micelles at the concentration under examination. In fact it was found to be true as it did not show aggregation even up to 60 mM concentration in a conductivity study.

For the gemini surfactants with $-C_8H_{17}$ hydrocarbon chain, **4a–4d**, in D_2O at 50 mM, the aggregation number N and the effective fractional charge (α) appeared to vary to a very small extent from 25 to 28 and 0.20 to 0.28 (Table 1). Thus it is obvious that the variation in aggregation properties of the gemini surfactants with $-C_8H_{17}$ hydrocarbon chain are less pronounced with variation of the spacer chain length which is also evident from the changes in a/b values (2.65–3.16). This might be due to the lesser hydrophobic interaction of $-C_8H_{17}$ hydrocarbon chains where the increase in the spacer chain length causes a small increase in hydrophobicity within this set of gemini surfactants (**4a–4d**).

For the gemini surfactants with $-C_{12}H_{25}$ hydrocarbon chain, **5a–5d**, in D_2O at 50 mM, the aggregation number, N , appeared to decrease from 124 to 52 with the increase in the spacer chain length from $n = 2$ to $n = 4$ and remain unchanged with further increase in the spacer length (for $n = 6$, **5d**) (Table 1). The effective fractional charge (α) on micelles, on the other hand, increased from 0.15 to 0.30 upon increasing the spacer chain length from **5a** ($n = 2$) to **5c** ($n = 4$) and again decreased to 0.23 upon increasing the spacer length (for $n = 6$) for **5d**. Since spheroids and ellipsoids differ in terms of curvature, a larger effective charge would be expected for a spheroidal micelle and a smaller effective charge would be associated with an ellipsoidal structure. Thus, it appeared that for the gemini surfactants with $-C_{12}H_{25}$ hydrocarbon chain, the shape of the micelles progressively became less elliptical (*i.e.*, more spherical) with the increase in the spacer length at 50 mM concentration. In contrast, higher aggregation number N and substantially lower values of fractional charge α for micelles with $n = 2$ (for **5a**) and $n = 3$ (for **5b**) indicated more ellipsoidal morphology. This is further supported by the changes in a/b values as a function of spacer chain length. Within the gemini surfactants with $-C_{12}H_{25}$ hydrocarbon chain, a/b values decreased from 4.75 to 3.27 as n values increased from $n = 2$ to $n = 4$ and then again increased to 3.32 for $n = 6$ (Fig. 3D). These findings are in good agreement with the earlier reports of SANS study of dimeric surfactants with $-C_{12}H_{25}$ long chain.^{27,38}

The aggregation number (N), and the fractional charge (α) of micellar solution of monomeric surfactant **8** ($n = 0$) at 30 °C and 100 mM was found to be 113 and 0.17 respectively. The ratio of semimajor axis to semiminor axis (a/b value) was 2.54 for the monomeric surfactant **8**. It is evident from Table 1 that the a/b value of surfactant **8** (at a concentration twice that of the gemini surfactants) is much lower than that of gemini surfactants thus indicating that the micellar aggregates of the monomeric surfactant is more spheroidal compared to gemini surfactants under the experimental conditions. For the gemini surfactants with $-C_{16}H_{33}$ hydrocarbon chain, **6a–6d** in D_2O at 50 mM, the aggregation number, N , appeared to decrease from 418 to 158 with the gradual increase in the spacer chain length from $n = 2$ to $n = 6$ (Table 1) and found to follow the same trend like the surfactants having $-C_8H_{17}$ or $-C_{12}H_{25}$ hydrocarbon chain.

In order to have better insight into the role of the hydrocarbon chain length on aggregation properties of the gemini surfactants with an identical molecular structure, we plotted the aggregation number and a/b values of the surfactants **4c**, **5c**, and **6c** bearing $-C_8H_{17}$, $-C_{12}H_{25}$, and $-C_{16}H_{33}$ chains. For the same spacer chain length and at the same concentration, the increase in the aggregation number is much more pronounced for the surfactant with the highest hydrocarbon chain ($-C_{16}H_{33}$). For example, at 30 °C, the aggregation number of **4c** (surfactant with $-C_8H_{17}$ hydrocarbon chain) and **5c** (surfactant with $-C_{12}H_{25}$ hydrocarbon chain) are 25 and 52, respectively, whereas the aggregation number of **6c** (surfactant with $-C_{16}H_{33}$ hydrocarbon chain) is 210 at the same concentration (50 mM) (Fig. 3E). This indicated that the surfactants with higher chain length have higher aggregation tendency and form a bigger micelle due to higher hydrophobic interaction. This is further evident from their a/b values: the a/b value of **4c** is 2.96, **5c** is 3.27 whereas that of **6c** is 6.86 at 50 mM which indicated that the surfactant with $-C_{16}H_{33}$ hydrocarbon chain (**6c**) is more ellipsoidal whereas the surfactant with the $-C_8H_{17}$ hydrocarbon chain (**4c**) is structurally less ellipsoidal (more spheroidal) (Fig. 3E). The effective fractional charge (α) on the gemini units of **4c** is 0.28 whereas the α value of **6c** is 0.22 at 50 mM and 30 °C. The decrease in α with the increase in the hydrocarbon chain length again proves that the micellar system progressively becomes more elliptical with the same spacer length under identical conditions.

Effect of surfactant concentration

The effect of variation in concentration on SANS distributions was studied using **4c**, **5c**, and **6c** ($n = 4$) surfactant systems at 30 °C and are shown in Fig. 4. As previously mentioned, the peak in $d\Sigma/d\Omega$ arises from the intermicellar interference effects and occurs at $Q_m = 2\pi/d$, where d is the average distance between the micellar particles. With an increase in concentration, the interparticle distance decreases and hence the peak shifts to higher Q values for all the surfactants with different alkyl chain lengths. However, as it can be seen from Fig. 4 that this effect is very less pronounced for **4c** compared to **5c** or **6c**. This might be due to the fact that surfactant **4c** with $-C_8H_{17}$ hydrocarbon chain does not form stable micellar aggregates as

mentioned before. The range of concentration examined was from 12 to 50 mM and it was observed that the calculated distributions gave the peak positions in $d\Sigma/d\Omega$ with good concordance with experimentally determined points. Furthermore, it was found that the peak in the measured distribution broadens with significant shifts in the position with the decrease in the surfactant concentration for all the surfactants. However, this effect was again less pronounced for a surfactant with $-C_8H_{17}$ hydrocarbon chain.

As can be seen from Fig. 4A, the shifting in the peak position for the surfactant with $-C_8H_{17}$ hydrocarbon chain is very less with the increase in concentration. These results indicated that the number-density of **4c** surfactant micelles increased to a very lesser extent as the concentration increased. This explains why the aggregation number N and the a/b value increased only from 15 to 25 and 1.77 to 2.96, respectively, (Table 2). The effective fractional charge (α) of **4c** changes from 0.51 to 0.28 as the concentration increases from 12 mM to 50 mM. A small change in α with the increase in concentration of **4c** further proved the poor aggregation nature due to lesser hydrophobic interaction.

The peak position for surfactants with $-C_{12}H_{25}$ and $-C_{16}H_{33}$ hydrocarbon chains and $n = 4$ spacer (**5c** and **6c**) also found to shift towards the higher Q region like the surfactant with $-C_8H_{17}$ long chain but in a much more pronounced way (Fig. 4B and C). The aggregation number of **5c** and **6c** increased gradually (from 38 to 52 and 96 to 210) with the increase in concentration from 12 to 50 mM. With the increase in surfactant concentration, the axial ratio (a/b) was found to increase from 2.39 to 2.98 and 3.14 to 6.86 (Table 2) which indicated that the micellar shape tends to become more ellipsoidal as the concentration of this surfactant increases. The effective fractional charge (α) on the gemini surfactants **5c** and **6c** changed from 0.32 to 0.30 and 0.30 to 0.22 as the concentration increases from 12 mM to 50 mM. The decrease in α with the increase in concentration also proved that the micellar system became more elliptical with the gradual increase in concentration as explained before.

It is evident from Table 2 that for the same spacer chain length and at the same concentration, the increase in the aggregation number is much more pronounced for the surfactant with the highest hydrocarbon chain ($-C_{16}H_{33}$) with the increase in concentration. For example, at 30 °C, the aggregation number of **4c** (surfactant with $-C_8H_{17}$ hydrocarbon chain) and **5c** (surfactant with $-C_{12}H_{25}$ hydrocarbon chain) increased from 19 to 25 and 46 to 52, respectively, whereas the aggregation number of **6c** (surfactant with $-C_{16}H_{33}$ hydrocarbon chain) increased from 130 to 210 from 25 to 50 mM. This indicated that the surfactants with higher chain length have higher aggregation tendency and form more stable micelles due to higher hydrophobic interaction. This is further evident from their a/b values: the a/b value of **4c** is 2.26, of **5c** is 2.89 whereas for **6c** it is 4.25 at 25 mM which indicated that the surfactant with $-C_{16}H_{33}$ hydrocarbon chain (**6c**) is more ellipsoidal whereas the surfactant with the $-C_8H_{17}$ hydrocarbon chain (**4c**) is less ellipsoidal.

Effect of temperature

In order to find out the effect of the temperature on the micellar aggregates, we also performed SANS experiments at various temperatures (from 30 °C to 60 °C) for surfactants with different hydrocarbon chain lengths (**4c**, **5c**, and **6c**). Fig. 5 shows the variation in neutron cross sections for **4c**, **5c**, and **6c** ($n = 4$) micellar systems with the increase in temperature. The neutron cross sections were found to shift at higher Q values and the peak in the measured distribution broadens as the temperature is increased for all the surfactants with $-C_{12}H_{25}$ and $-C_{16}H_{33}$ hydrocarbon chains (**5c** and **6c**) whereas for the surfactant with $-C_8H_{17}$ hydrocarbon chain, the shifting in the peak position is almost negligible. This might be due to the fact that surfactant **4c** with $-C_8H_{17}$ hydrocarbon chain does not form stable micellar aggregates and are highly dynamic in nature as mentioned before. The aggregation number N and the fractional charge for **4c** ($n = 4$) at 50 mM varies from 21 to 25 and from 0.28 to 0.37, respectively, with an increase in temperature from 30 to 60 °C (Table 3).

The aggregation number for **5c** (surfactant with $-C_{12}H_{25}$ hydrocarbon chain) ($n = 4$) at 50 mM decreased from 52 to 41 and the fractional charge was found to increase from 0.30 to 0.37, with an increase in temperature from 30 to 60 °C (Table 3). The aggregation number for **6c** ($n = 4$) (surfactant with $-C_{16}H_{33}$ hydrocarbon chain) at 50 mM decreased from 210 to 143 and the fractional charge was found to increase from 0.22 to 0.28, with an increase in temperature from 30 to 60 °C (Table 3). With the increase in temperature, the degree of ionization and hence the magnitude of electrostatic repulsion among the positively charged surfactant molecules increases leading to a reduction in the aggregation number. Since ellipsoidal morphology relates to a smaller effective charge, an increase in temperature appears to induce towards less ellipsoidal structures (more spheroidal) for **5c** and **6c**. This observation is also supported by the gradual decrease in a/b values from 3.27 to 2.78 and 6.86 to 5.57 for **5c** and **6c**, respectively, as the temperature increases.

Conclusion

From the detailed measurements of SANS cross sections, it was found that the amide functionality increases the surfactant aggregation tendencies as compared to the surfactants having no amide bond. It was also found that the aggregation properties of the gemini surfactants bearing amide groups depend strongly on the position and number of amide bonds. Amide bonds placed between the hydrocarbon chain and the polar head group were found to have a greater effect on the aggregation properties of the gemini surfactants as compared to the same number of amide bonds positioned in the spacer connecting the polar head groups. Furthermore, the extent of growth and variation in shapes of the micellar aggregates of these gemini micelles were found to depend strongly both on the hydrocarbon chain length and on the spacer length and are more pronounced with a short spacer length ($n \leq 4$) and higher

hydrocarbon chain length ($-C_{12}H_{25}$ and $-C_{16}H_{33}$ long chains). With the increase in concentration, the aggregation number (N) and the size of the micelles increased for all sets of surfactants. With the increase in temperature, the aggregation number (N) decreased and the shape of the micellar aggregates were found to be less ellipsoidal (more towards spheroidal morphology) for all the compounds. With an increase in the spacer chain length, CMC was found to decrease in each set of surfactants.

Acknowledgements

We thank Prof. C. N. R. Rao, FRS (JNCASR) for his constant support and encouragement. J. Hoque thanks JNCASR for a junior research fellowship (JRF). S. Gonuguntla is thankful to JNCASR for a summer research fellowship. J. Haldar would like to acknowledge the Department of Science and Technology, Government of India for the Ramanujan Fellowship (SR/S2/RJN-43/2009).

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