Chapter 4

Effect of Spacer Chain Length on Aggregation Properties of Alkanediyl-α,ω-bis(hexadecyl hydroxylethyl methyl ammonium bromide) Bis-cationic surfactants

Contents

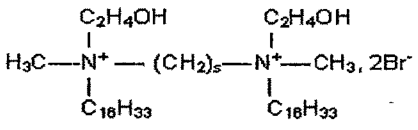
4.1 Introduction

Physicochemical properties of surfactant molecules are primarily decided by the structure of the molecule under consideration [1]. For example, the CMC of a conventional cationic surfactant hexadecyltrimethylammonium bromide (CTAB) decreases from 0.9 mM to 27 μM, when two CTAB molecules are covalently joined by a four methylene unit spacer at the head group level. This type of surfactant is known as a 'gemini' or 'dimeric' surfactant [2-4]. Reports are available on the synthesis of anionic, cationic, non-ionic and zwitterionic gemini surfactants [2,5-7]. Studies on the solution behavior of these surfactants show that they have extremely low CMC, surface tension and also potential germicidal properties [4,8-10]. Structure of the gemini surfactants can be tailored either by introducing different types of spacers such as polymethylene, polyoxyethylene and aromatic rings in the molecule or by changing nature of the spacer [11,12]. Studies have also been carried out on the effect of variation of the spacer polarity and chain length on the physicochemical properties of gemini surfactants [9-14].

Micellar solutions of surfactants form exotic structures and mesophases, which are examined through electron microscopy at Cryogenic Temperature [3]. Though this technique provides absolute information regarding the shape and size of the aggregates formed, no information regarding the aggregation number and immediate micelle environment can be obtained. Small angle neutron scattering (SANS) is a well-established technique for the study of micellar solutions of surfactants [11,14-17]. SANS can probe information about the micelle size, shape, charge and aggregation number through use of proper model [18].

Alkanediyl-α,ω-bis(hexadecyl dimethyl ammonium bromide) type of gemini surfactants, referred to as 16-s-16 DMA, contain $-N(CH_3)_2$ head groups and have been studied in detail [3,4,19]. The aggregate structures of these surfactants in solutions are studied by SANS [11,13,14].

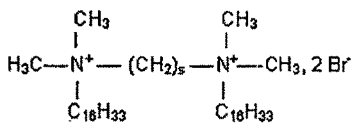
In this chapter, we report the synthesis, characterization and effect of variation of spacer chain length on aggregation behavior of alkanediyl-α,ω-bis(hexadecyl hydroxyethyl methyl ammonium bromide) gemini surfactants referred as 16-s-16 MEA. The general structure of these surfactants is:



$$H_3C-\underset{C_{16}H_{33}}{\overset{C_2H_4OH}{N^+}}-(CH_2)_s-\underset{C_{16}H_{33}}{\overset{C_2H_4OH}{N^+}}-CH_3,\ 2Br^-$$

16-s-16 MEA

MEA = monoethanol amine



$$H_3C-\underset{C_{16}H_{33}}{\overset{CH_3}{N^+}}-(CH_2)_s-\underset{C_{16}H_{33}}{\overset{CH_3}{N^+}}-CH_3,\ 2\,Br^-$$

16-s-16 DMA

DMA = dimethyl amine

where s = 4, 6, 8 and 10

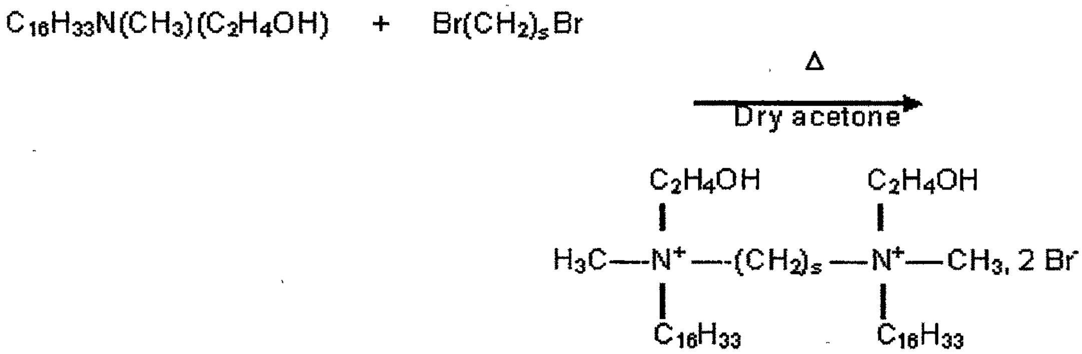
4.2 Experimental

4.2.1 Materials

n-Hexadecyl bromide, α,ω- dibromoalkane and 2(methylamino)ethanol were purchased from Lancaster Chemical Company, England. All the reagents and solvents used were of AR grade. Solutions for SANS studies were prepared in D_2O (at least 99 atom % D) obtained from Heavy Water Division, Bhabha Atomic Research Centre, Mumbai, India. Double-distilled and deionized water was used for all physicochemical studies.

4.2.2 Synthesis of Dimeric Surfactants and Characterization

The gemini surfactants were synthesized by refluxing 2.2 moles of hydroxyethylmethylhexadecyl amine in dry acetone with 1.0 mole of α,ω-dibromoalkane for 70 - 96 h at 58 - 60°C. The overall yield of the surfactant was observed to be 60 - 75 %. The crude white solid thus obtained was washed with hexane/ethyl acetate mixture and recrystallized from acetone/methanol mixture for at least three to four times till the purity of the compound was confirmed through TLC. Products were further characterized through FTIR, ^1H NMR and elemental analysis.



$$C_{16}H_{33}N(CH_3)(C_2H_4OH) + Br(CH_2)_sBr \xrightarrow[\text{Dry acetone}]{\Delta} H_3C-\overset{C_2H_4OH}{\underset{C_{16}H_{33}}{N^+}}-(CH_2)_s-\overset{C_2H_4OH}{\underset{C_{16}H_{33}}{N^+}}-CH_3,\ 2\,Br^-$$

(where s = 4, 6, 8 and 10)

FTIR spectra of all the gemini surfactants showed absorption bands at 3400–3654 cm^{-1} (OH stretching), 2917 cm^{-1} (CH stretching), 1109 cm^{-1}(CN stretching),1085 cm^{-1} (CO stretching) and 722 cm^{-1} (CH rocking).

Butanediyl-1,4-bis(hexadecyl hydroxyethyl methyl ammonium bromide), is represented as **16-4-16 MEA**. ^1H NMR spectrum of it in $CDCl_3$, showed signals at δ 0.84 ppm (t, 6H, $2CH_3$), 1.11–1.40 ppm (br, m, 52H, 2 x13CH_2), 1.71–2.03 ppm (d, 8H, 2 x 2CH_2), 3.25 ppm (s, 6H, 2 NCH_3), 3.35–3.74 ppm (t, 12H, 2 x $N(CH_2)_3$), 4.06 ppm (t, 4H, $2CH_2$–O), 4.27ppm (br, s, 2H, 2OH).

Percentage of C, H, N calculated for $C_{42}H_{90}N_2O_2Br_2$ (16-4-16 MEA) was C: 61.90, H: 11.13, N: 3.44% and experimentally found was C: 62.02, H: 11.36, N: 3.54 %.

Melting point of the surfactant was observed to be 226 ± 2°C.

Hexanediyl-1,6-bis(hexadecyl hydroxyethyl methyl ammonium bromide), is represented as **16-6-16 MEA**. ^1H NMR spectrum of it in $CDCl_3$, showed signals at δ 0.84 ppm (t, 6H, 2 x CH_3),1.1-1.4 ppm (br, m, 52H, 2 x 13CH_2),1.4 -1.8 ppm (d, 8H, 2 x 2 CH_2 alkyl chain and spacer chain),1.92 ppm (s,4H, 2 CH_2 of spacer), 3.26 ppm (s, 6H, N^+ $2CH_3$), 3.35-3.75 ppm (br, m, 12H, $2N^+(CH_2)_3$ alkyl chain and spacer chain), 4.03 ppm (s,4H, $2CH_2$-O), 5.03 ppm (s,2H,2OH).

Percentage of C, H, N calculated for $C_{44}H_{94}N_2O_2Br_2$ (16-6-16 MEA) was C: 62.69, H: 11.24, N: 3.32 % and experimentally found was C: 62.47, H: 11.54, N: 3.44%.

Melting point of the surfactant was observed to be 235± 2°C.

Octanediyl-1,8-bis(hexadecyl hydroxyethyl methyl ammonium bromide), is represented as **16-8-16 MEA.** ^1H NMR spectrum of it in $CDCl_3$, showed signals at δ 0.85 ppm (t, 6H, $2CH_3$), 0.95-1.5 ppm (br, m, 60H, 26 CH_2, alkyl chain, 4 CH_2, spacer chain), 1.5-2.09 ppm (br, m, 8H, $2N^+C$-CH_2, spacer chain and alkyl chain), 3.25 ppm (s, 6H, $2N^+$ CH_3), 3.3-3.8 ppm (br, m, 12H, $2N^+$-$(CH_2)_3$ alkyl chain and spacer chain), 4.06 ppm (t, 4H, $2CH_2$ -O), 5.06 ppm (s, 2H, 2OH).

Percentage of C, H, N calculated for $C_{46}H_{98}N_2O_2Br_2$ (16-8-16 MEA) was C: 63.42, H: 11.34, N: 3.22% and experimentally found was C: 63.12, H: 11.78, N: 3.32 %.

Melting point of the surfactant was observed to be 224± 2°C.

Decanediyl-1,10-bis(hexadecyl hydroxyethyl methyl ammonium bromide), is represented as **16-10-16 MEA**. ^1H NMR spectrum of it in $CDCl_3$, showed signals at δ 0.83 ppm (6H, $2CH_3$), 1.1-1.5 ppm (br, m, 64H, 26 CH_2 alkyl chain, 6 CH_2 spacer chain), 1.71 ppm (br, s, 8H, 2 N^+C-CH_2 spacer chain and alkyl chain), 3.24 ppm (s, 6H, $2N^+$ CH_3), 3.3-3.8 ppm (br, t, 12H, N^+ $2(CH_2)_3$ alkyl chain and spacer chain), 4.05 ppm (s, 4H,$2CH_2$-O), 5.10 ppm (t, 2H, 2OH).

Percentage of C, H, N calculated for $C_{48}H_{102}N_2O_2Br_2$, (16-10-16 MEA) C: 64.12, H: 11.43, N: 3.11% and experimentally found was C: 63.73, H: 11.76, N: 3.44%. Melting point of the surfactant was observed to be 232± 2°C.

4.2.3 Procedure

The measurements of conductance, surface tension and SANS were done following the procedures described in section 2.2.

4.3 Results and Discussion

4.3.1 Kraft Temperature

The kraft temperatures (k_T) of 16-s-16 MEA series of gemini surfactants were determined through conductance measurement. The details of the measurements are described in section 2.2.2. The k_T values for the series of gemini surfactants are given in Table 4.1. The k_T was observed to decrease with increase in spacer length except at spacer s = 6. Davey et al [20] and Gregory and Tartar [21] have reported that increase in k_T is due to increase in solubility or stability of surfactant monomers in the presence of hydrated crystals. Zhao et al [22] have also observed similar trend for a homologue series of cationic surfactant with variable spacer length.

Table 4.1 Kraft temperature of 16-s-16 MEA surfactants

16-s-16 MEA surfactant with s as	Kraft temperature k_T (°C)
4	38
6	43
8	30
10	24

4.3.2 Critical Micelle Concentration (CMC)

The CMC values determined by the surface tension and conductance measurements for a series of synthesized surfactants were observed to be in good agreement (Table 4.2). The CMC of the surfactants was observed to be one order of magnitude lower than those of conventional gemini surfactants as shown in Table 4.2. This unusual behavior of low CMC and its variation with polymethylene spacer chain length (Fig. 4.1) is due to a combination of surfactant conformational variations and larger magnitude of the transfer free energy coming from both the tails [23]. In the gemini surfactants free energy contributions in addition to those considered for monomeric surfactants [24] arise because of the spacer and increased polarity of the head group due to the presence of two ethanolic groups per molecule. The CMC of a gemini surfactant depends upon the free energy per molecule and not upon the free energy per chain. Therefore, even if the free energy per chain of a gemini surfactant is comparable to that of its monomeric analog, the free energy per molecule is significantly lower for the gemini, implying a much lower CMC.

The spacer shields the hydrophobic core of the aggregate from contact with water and constrains the distance between the head groups, thus opposing the intramolecular hydrogen bonding and imposing nonuniformity of charge distribution at the aggregate surface. The spacer also prevents the two linked tails from having a packing conformation inside the micelle identical to that of analogous unlinked single chain surfactants. The spacer can be partially buried inside the micelle core provided its length and the molecular interactions including hydrogen bonding of head groups allow it. A combination of the above mentioned factors explain the observed maximum CMC value for 16-6-16 MEA gemini surfactants. Similar trend in CMC with spacer length for 12-s-12 DMA surfactant was also reported by Zana et al [9]. The CMC values of 16-s-16 MEA surfactants are given in Table 4.2.

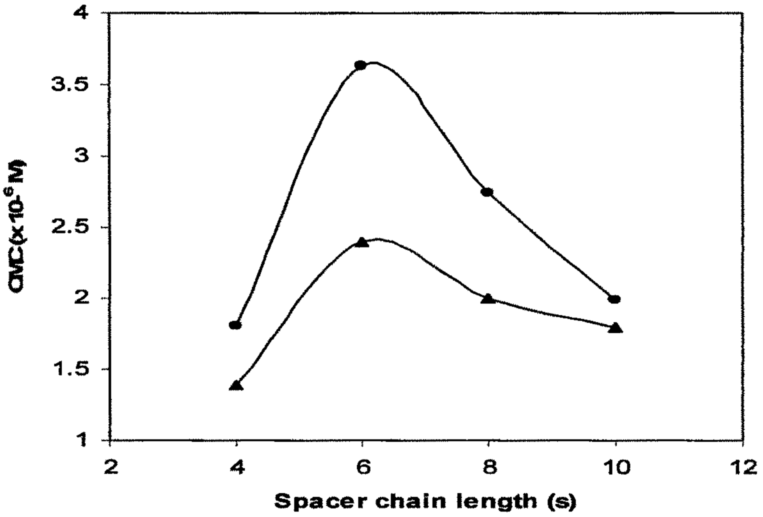


Figure 4.1 Effect of spacer chain length on critical micellar concentration of 16-s-16 MEA series of bis-cationic surfactants at 30°C, variation in CMC values with spacer chain length, **by conductometry (•) and tensiometry (▲)**

Table 4.2 Critical micellar concentration of 16–s–16 MEA gemini surfactants at 30 °C.

Spacer length (s)	CMC by surface tension (μM)	CMC by conductance (μM)
4	1.39±0.10 (27±1.0)	1.81±0.10
6	2.40±0.10 (43±1.0)	3.63±0.10
8	2.0±0.15 (33±1.5)	2.75±0.10
10	1.80±0.10 (27±1.5)	1.99±0.10

Note. The numbers given in brackets are the CMC values for conventional 16-s-16 DMA gemini surfactants as taken from Ref. [13].

4.3.3 Thermodynamic Parameters of Micellization

Thermodynamic parameters of micellization such as ΔG^{o}_{m} , ΔH^{o}_{m} and ΔS^{o}_{m} were determined from conductance data (Fig. 4.2) by using equations 1, 2 and 3 from section 2.3.4 and values are given in Table 4.3. The observed more negative ΔG^{o}_{m} value for the surfactant with shorter spacer s = 4 indicates more favored micellization. Negative values of enthalpy (ΔH^{o}_{m}) of micellization indicate exothermic nature of micellization process. The observed exothermicity can be attributed to possible surfactant-solvent interactions. The enthalpy values do not vary significantly with temperature, indicating no significant change in the environment surrounding the hydrocarbon chain of surfactant molecule. The entropy of micellization (ΔS^{o}_{m}) being more positive, in the system under study, micellization is entropy (ΔS^{o}_{m}) driven. The more positive values of entropy may be due to the breaking of bulk water structure around the surfactant molecules. This leads to more disorder in the structure of water and favors the micellization at lower concentration. More positive entropy values indicate micellization process to be more spontaneous. The observed sharp increase in the entropy values, indicates that shorter spacer (s = 4) favors micellization process more than that of larger spacer s = 6, 8 and 10.

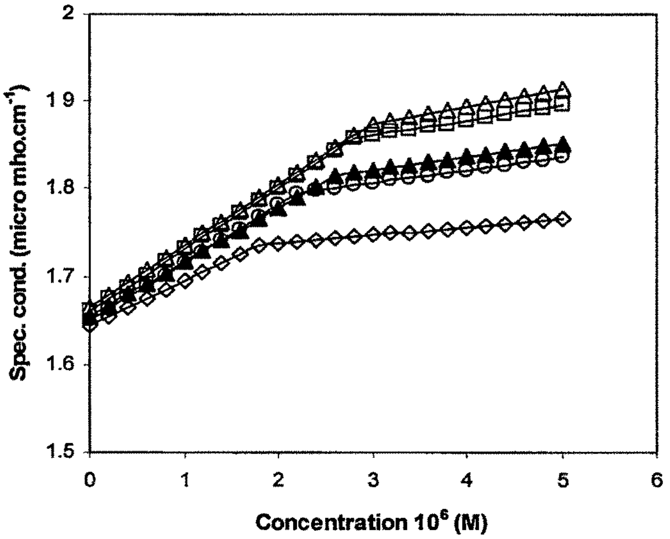


Figure 4.2(a) Effect of temperature on CMC of 16-4-16 MEA bis-cationic surfactant,

at 30 (◇), 35 (o),40 (▲),45 (□) and 50 ^{0}C(Δ)

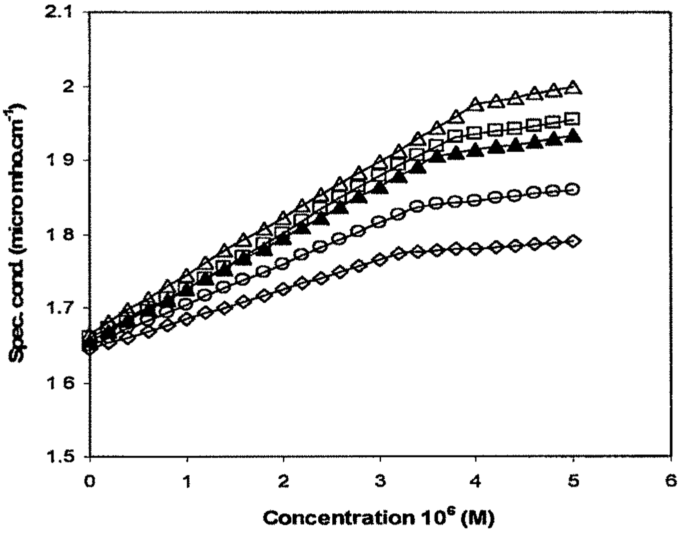


Figure 4.2(b) Effect of temperature on CMC of 16-6-16 MEA bis cationic surfactant,

at 30 (◇), 35 (o),40 (▲),45 (□) and 50 ^{0}C(Δ)

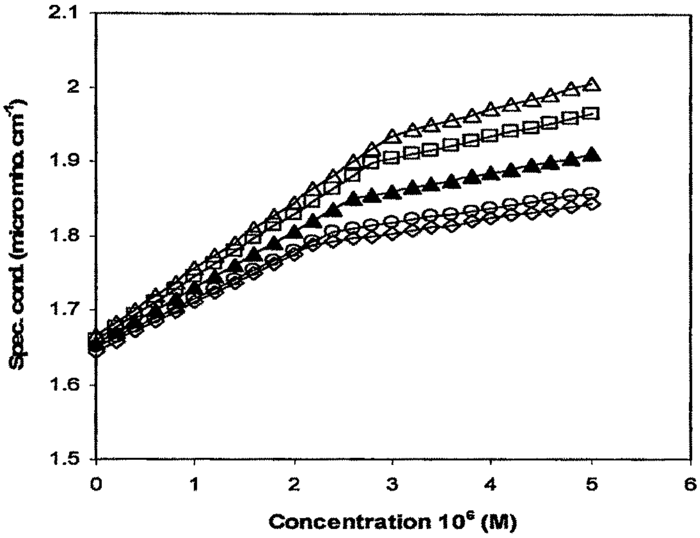


Figure 4.2(c) Effect of temperature on CMC of 16-8-16 MEA bis-cationic surfactant,
at 30 (◇), 35 (o),40 (▲),45 (□) and 50 ^{0}C(Δ)

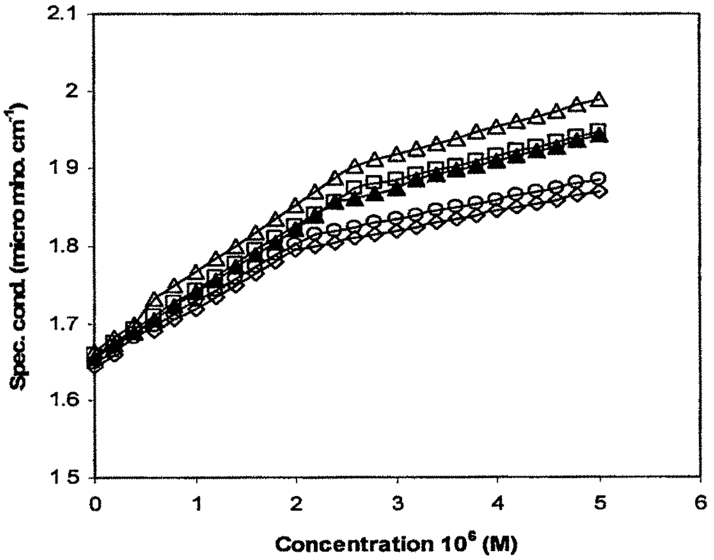


Figure 4.2(d) Effect of temperature on CMC of 16-10-16 MEA bis-cationic surfactant,
at 30 (◇), 35 (o),40 (▲),45 (□) and 50^{0}C(Δ)

Table 4.3 Effect of spacer chain length and temperature on thermodynamic parameters of micellization of 16-s-16 MEA bis-cationic surfactants

Surfactant system	Temperature (°C.)	Gibb's Free energy $(-\Delta G^{o}_{m})$ KJmol^{-1}	Enthalpy $(-\Delta H^{o}_{m})$ KJmol^{-1}	Entropy (ΔS^{o}_{m}) Jk^{-1}mol^{-1}
16-4-16 MEA	30	43.32 ±1.5	14.96 ±0.9	96.13 ±1.2
	35	42.69 ±1.5	14.44 ±0.9	91.72 ±1.2
	40	42.16 ±1.5	14.68 ±0.9	87.79 ±1.2
	45	41.92 ±1.5	14.91 ±0.9	84.90 ±1.2
	50	41.66 ±1.5	15.14 ±0.9	82.10 ±1.2
16-6-16 MEA	30	39.84 ±1.5	11.24 ±0.9	94.39 ±1.2
	35	39.65 ±1.5	11.42 ±0.9	91.63 ±1.2
	40	39.46 ±1.5	11.60 ±0.9	88.97 ±1.2
	45	39.26 ±1.5	11.78 ±0.9	86.39 ±1.2
	50	39.05 ±1.5	11.95 ±0.9	83.88 ±1.2
16-8-16 MEA	30	39.05 ±1.6	14.00 ±0.9	82.67 ±1.3
	35	39.09 ±1.6	14.35 ±0.9	80.32 ±1.3
	40	38.79 ±1.6	14.56 ±0.9	77.41 ±1.2
	45	38.48 ±1.6	14.77 ±0.9	74.56 ±1.2
	50	38.24 ±1.7	14.98 ±0.9	72.01 ±1.2
16-10-16 MEA	30	38.68 ±1.6	14.92 ±0.9	78.38 ±1.3
	35	38.68 ±1.6	15.28 ±0.9	75.94 ±1.3
	40	38.38 ±1.6	15.51 ±0.9	73.06 ±1.2
	45	38.08 ±1.6	15.73 ±0.9	70.28 ±1.2
	50	37.76 ±1.7	15.94 ±0.9	67.54 ±1.2

4.3.4 SANS and Micellar Solutions

Effect of Spacer Chain Length

SANS distributions for 50 mM solutions of 16-s-16 MEA gemini surfactants with spacer length 4, 6, 8 and 10 and at temperature 30 °C are shown in Figure 4.3. All distributions show well defined correlation peaks characteristic of suspension of charged particles. The peak arises because of intermicellar structure factor S(Q) irrespective of the spacer chain length. The correlation peak appears at around $Q_m \simeq 2\pi/D$, where D is average distance between the micelles. Since Q_m was found to vary with spacer, one can easily conclude that the number density (n) of micelles is not same in the above samples, even when they have identical surfactant concentrations. It is observed from Figure 4.3, that the peak position shifts towards higher Q values with the increase in the spacer chain length, indicating that the number density of micelles increases and aggregation number decreases with the increase in the spacer length. The shape and size of micelles also change with the increase in the spacer chain length. The micellar parameters aggregation number(N), fractional charge (α), semi minor axis(a) and semi major axis (b) as obtained from the SANS studies are compiled in Table 4.3. The micellar parameters for 100 mM solution of CTAB are also given in Table 4.3 for the sake of comparison. The aggregation number (N) was observed to decrease with the increase in spacer chain length. The observed high aggregation number for the shorter spacer s = 4 is in agreement with reports available in literature [14,15, 25]. The gemini surfactant having methylene spacer group with s = 4 is expected to show the formation of micelles with very low curvature. Hence in the process of balancing the intramolecular hydrophobic interaction and the intermolecular hydrophobic interaction, the micelles formed are compact. The decrease in aggregation number followed by the increase in fractional charge with the increase in spacer length (Table 4.3), can be attributed to conformational changes of spacer at micelle/water interface. The semi-minor axis (a) decreases as function of increase in spacer length, indicating increase in the folding of hydrophobic tail inside the micelle core.

The micellar parameters for 50 mM micellar solutions of conventional 16-s-16 DMA gemini surfactants are also given in Table 4.3 for comparison. It is observed that due to the change in head group polarity of conventional gemini surfactants, there are significant changes in micellar parameters. The decrease in fractional charge at the surface of micelles of gemini surfactants can be attributed to the increase in head group polarity which increases additional hydration of micelles and screens out the Coulombic repulsion between the heads at micelle/water interface. Overall the change in head group polarity and spacer length of gemini surfactants results in a significant change in micelle geometry. It is observed that the b/a ratio of the micelles decrease from 7.5 to 2.9 when the spacer length is increased from 4 to 10. Similarly, b/a ratio decreases from 7.5 to 3.8 as head group polarity of gemini surfactant decreases from 16-4-16 MEA to16-4-16 DMA.

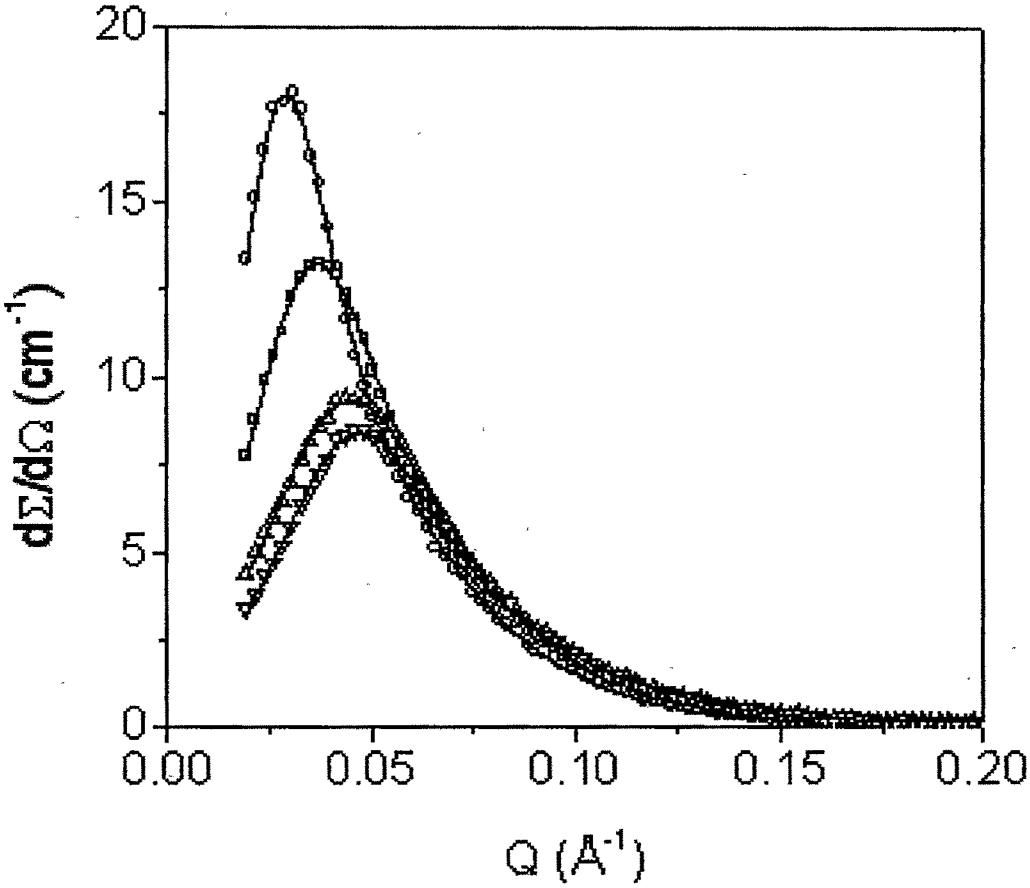


Figure 4.3 Effect of spacer chain length on SANS data for 16-s-16 MEA at 50 mM concentration and 30 °C.

s = 4 (o), 6 (□), 8 (Δ),10 (▽).

Table 4.3 Effect of spacer chain length on micellar parameters of 16-s-16 MEA bis-cationic surfactants at 50 mM concentration and temperature 30 °C.

Spacer length s	Aggregation number N	Fractional charge α	Semi-minor axis a (Å)	Semi-major axis b (Å)	b/a
CTAB (100 mM)	160±11	0.10±0.01	22.3±0.5	45.7±1.2	2.05±0.05
4	419±25	0.10±0.01	25.7±0.5	192.6±4.0	7.49±0.04
			(24.0)	(92.1)	(3.8)
6	170±12	0.08±0.01	23.9±0.5	94.0±2.4	3.93±0.05
	(97)	(0.10)	(21.5)	(66.2)	(3.1)
8	93±6	0.12±0.01	22.6±0.5	59.5±1.4	2.63±0.05
	(43)	(0.32)	(20.3)	(45.7)	(2.3)
10	84±6	0.16±0.01	21.7±0.5	60.4±1.4	2.78±0.05
	(50)	(0.24)	(20.1)	(49.2)	(2.4)

Note. The numbers given in brackets are the micellar parameters for conventional 16-s-16 DMA gemini surfactants as taken from Ref.[13].

Effect of Temperature

Effect of temperature on the size of micelle has been well reported for gemini surfactants [13,23]. Figure 4.4 shows SANS data for 50 mM 16-4-16 MEA surfactant at 30, 40 and 60 °C. It is observed that Q_{max} peak position shifts to the higher side with increase in the temperature (Fig. 4.4). The micellar parameters in these systems are given in Table 4.4. The aggregation number decreases and the fractional charge increases with increased temperature. Similar observations were made for conventional gemini surfactants by De et al [13].

Table 4.4 Micellar parameters of 16-4-16 MEA gemini surfactant at varying temperature at 50 mM concentration.

Temperature (°C)	Aggregation number N	Fractional charge α	Semi-minor axis a (Å)	Semi-major axis b (Å)	b/a
30	419 ± 25	0.10±0.01	25.7±0.5	192.6±4.0	7.49±0.04
40	402 ± 23	0.12±0.01	25.5±0.5	190.1±3.6	7.45±0.04
60	266 ± 17	0.18±0.01	23.8±0.5	140.7±2.8	5.9±0.04

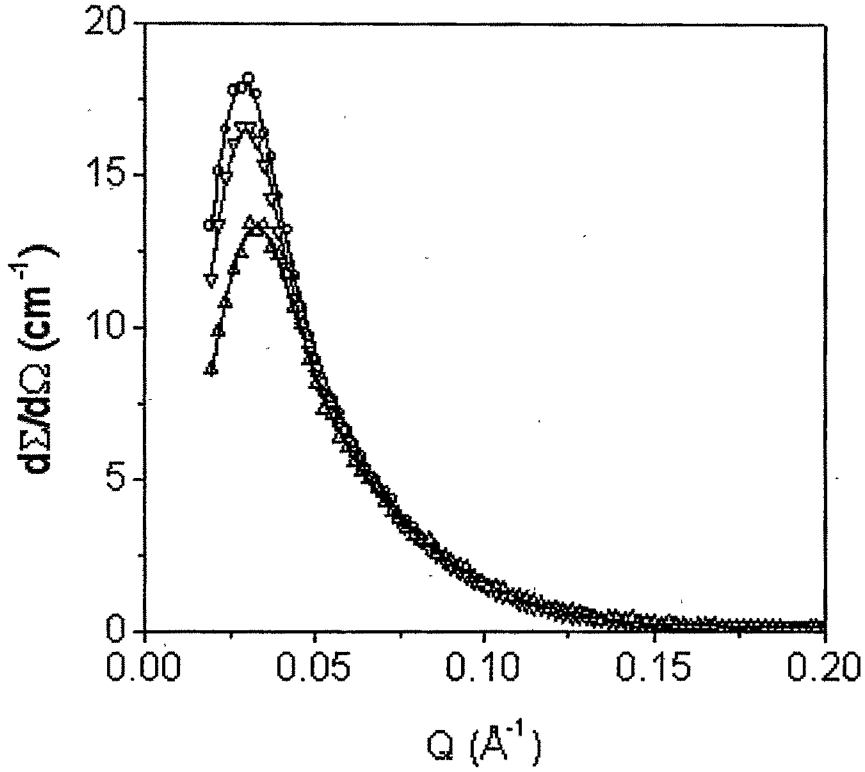


Figure 4.4 Effect of temperature on SANS data for 50 mM 16-4-16 MEA at different temperatures.

30 °C (o), 45 °C (▽) and 60 °C(△) .

4.4 Conclusions

- Critical micellar concentrations of the gemini surfactants 16-s-16 MEA were observed to be lower than those reported for conventional 16-s-16 DMA gemini surfactants.
- The CMC of the gemini surfactants increases as the spacer chain length increases from 4 to 6 and decreases further with increase in spacer length.
- SANS studies showed that micellar morphology depends on the molecular architecture.
- It is found that the micellar structure is sensitive to the spacer chain length and head group polarity.
- As the spacer chain length increases it suppresses the tendency of micellar growth, while the increase in head group polarity supports the micellar growth.

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