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ORIGINAL ARTICLE

Surface and Aggregation Properties of Synthesized Cetyl Alcohol Based Bis-Sulfosuccinate Gemini Surfactants in Aqueous Solution

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Abstract A series of cetyl alcohol based anionic bis-sulfosuccinate gemini surfactants (BSGSCA1,4; BSGSCA1,6 and BSGSCA1,8) with different spacer lengths was prepared using dibromoalkanes. The surfactant structure was elucidated using elemental analysis, Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR). Surface tension measurements were used to determine the critical micelle concentration (CMC), the surface tension at the CMC (γ_{CMC}), surface pressure at the CMC (π_{CMC}) and efficiency of adsorption (pC20). On the basis of surface studies, the CMC and γ_{CMC} decreases with increasing length of the spacer group. The micelle aggregation number, determined by fluorescence quenching studies, increases with increasing surfactant concentration above the CMC. The micropolarity in the micelle increases with increasing length of the spacer and decreases with increasing surfactant concentration.

Keywords Bis-sulfosuccinate gemini surfactants · Surface active properties · Critical micelle concentration · Aggregation number · Micropolarity

Introduction

Gemini surfactants are dimeric surfactants with two amphiphilic moieties connected with a spacer group. Gemini surfactants are used in numerous fields, such as detergents and cleaning products, cosmetics and toiletries etc. due to good water solubility, low CMC, better wetting ability, foaming, aggregation and rheological properties as well as excellent surface activity in aqueous solution as compared to single chain conventional surfactants [1–6].

In recent years, researchers have investigated the properties of anionic dimeric surfactants [7–9]. Numerous reports have been published on the synthesis and surface properties of anionic gemini surfactants such as carboxylate [10–13], sulfate [14, 15], sulfonate [16], and phosphate [17–20]. The properties of anionic gemini surfactant with sulfosuccinate head groups have been comparatively less reported [21]. Anionic sulfosuccinate surfactants are amongst the mildest of all the anionic surfactants [22]. Sulfosuccinate surfactants have good performance properties as well as surface active properties viz. low critical micelle concentration, high effectiveness in reducing surface tension, strong wetting etc. and can used in numerous fields such as cosmetics, textile and polymers [23].

The purpose of this research work is to synthesize cetyl alcohol based gemini sulfosuccinate surfactants (BSGSCA1,4; BSGSCA1,6 and BSGSCA1,8). Three different α,ω-dibromo alkanes, i.e., 1,4-dibromo butane; 1,6-dibromo hexane and 1,8-dibromo octane were used as a flexible spacers. The surface and aggregation properties were investigated in aqueous solutions.

Experimental Section

Materials

Cetyl alcohol (99.0 %), maleic anhydride (99.0 %), ethylene glycol (99.0 %), sodium bisulfite (58.0 %), *p*-toluene sulfonic acid (98.0 %), benzophenone (99.0 %), chloroform

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(99.0–99.4 %), petroleum ether (60–800 C) and sodium chloride (99.5 %) were procured from Loba Chemie Pvt. Ltd., Mumbai (India). Toluene (99 %) was purchased from Merck specialities, Pvt. Ltd., Mumbai. 1,4-dibromo butane (98.0 %), 1,6-dibromo hexane (98.0 %) and 1,8-dibromo octane (98.0 %) were obtained from Spectrochem Pvt. Ltd., Mumbai (India). Pyrene (98 %) was purchased from Sigma–Aldrich Chemie GmbH, Riedstr. Steinheim. Absolute ethanol (99.9 %) was purchased from Changshu Yangyuan, Chemical, China. All the reagents and chemicals were used without any further purification. Surfactant solutions were prepared with deionized and doubled distilled water.

Preparation of the Monoester of Maleic Acid (STEP-1)

Equal molar ratio of maleic anhydride (0.4 mol) and cetyl alcohol (0.4 mol) were reacted to synthesize the monoester. Cetyl alcohol was heated to 40 °C for about 15 min and then reacted with maleic anhydride. The monoester was obtained after stirring for 2 h at a constant temperature 50–60 °C. Acid values were determined at different intervals to confirm the formation of ester bonds [22].

Preparation of the Mono Alkyl Sulfosuccinate Ester (STEP-2)

Mono alkyl sulfosuccinate ester was synthesized by reacting equal molar amounts of the maleic acid monoester (0.2 mol) and ethylene glycol (0.2 mol) for a 6-h duration. Toluene (100 ml) and *p*-toluene sulfonic acid (0.1 %) were used as a solvent and catalyst in the reaction, respectively. Water was completely removed azeotropically using a Dean and Stark assembly. After complete removal of solvent and water from the reaction mixture, it was washed with a chloroform/H_2O (50v/20v) and sodium chloride (30 % w/v) mixture using vigorous stirring. The reaction mixture was allowed to separate into two phases. The aqueous layer contained excessive amount of ethylene glycol was washed two or three additional times with chloroform. The chloroform layers were combined and distilled to isolate the mono alkyl maleate esters of ethylene glycol. The mono alkyl sulfosuccinate ester was obtained by refluxing equal molar amounts of alkyl maleate ester (0.26 mol) and aqueous sodium bisulfite solution (0.26 mol) for 2 h [21].

Preparation of Bis-Sulfosuccinate Gemini Surfactants by Using α,ω-Dibromo Alkanes(STEP-3)

Three different bis-sulfosuccinate gemini surfactants were prepared using three different α,ω-dibromo alkanes. Three different gemini surfactants symbolized as BSGSCA1,4; BSGSCA1,6; BSGSCA1,8 were synthesized by refluxing a mixture of monoalkyl sulfosuccinate ester (0.1 mol) and α,ω-dibromo alkanes (0.05 mol) in an ethanolic solution of sodium hydroxide (0.1 %) for 8 h at 70 °C. The three different end products, i.e., bis-sulfosuccinate gemini surfactants with different spacer lengths were obtained after the separation and crystallization of the product with petroleum ether (60–80 °C) [21].

Characterization of Synthesized Gemini Surfactants

The molecular structures of synthesized gemini surfactants (BSGSCA1,4; BSGSCA1,6; BSGSCA1,8) were confirmed by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR), i.e., ^{1}H NMR and ^{13}C NMR. The structural confirmation spectral techniques were performed at the Sophisticated Analytical Instrumental Facility (SAIF), Cochin, Kerala, India.

Surface Tension Measurements

The surface tension measurements were performed using a du Noüy tensiometer (Jencon, India) by the platinum ring detachment technique [24]. The tensiometer was calibrated or standardized against double distilled water. The platinum ring was completely cleaned and dried before every observation. The surfactants solutions for the surface tension measurements were prepared in the concentration range 10^{-2}–10^{-8} mol l^{-1} using double distilled water. The maximum force required to detach the ring from the interface was used to calculate the surface tension. The critical micelle concentration (CMC) and the surface tension at the CMC (γ_{CMC}) were determined from the sharp breakpoint of the surface tension *versus* concentration profile. All measurements were carried out at 25 °C. The results were accurate within +0.1 mN/m. Other important surface active properties like pC20 and π_{CMC} were also calculated. Efficiency of adsorption of the surfactant (pC20) was calculated by using the curve of surface tension *versus* the logarithm of the molar concentration [25–28]. The surface pressure at the CMC was calculated using Eq. 1:

$$\pi_{\mathrm{CMC}} = \gamma_o - \gamma_{\mathrm{CMC}} \tag{1}$$

where γ_o and γ_{CMC} are the surface tension of pure water and the surface tension at the CMC respectively [26].

Fluorescence Measurements

A very convenient and widely used technique to determine the aggregation number is fluorescence spectroscopy. In the current work, a Model RF-5301PC Spectrofluorophotometer (Shimadzu) and steady-state fluorescence quenching were used. Turro and Yekta [29] developed a technique for determining the aggregation number of micelles based on the assumptions of the Tachiya [30] model. The present studies were performed by using pyrene and benzophenone as the probe and quencher, respectively. To carry out the fluorescence studies successfully, the perceptive approach of many researchers' efforts [25, 29–36] were consulted. In current studies, pyrene was excited at 335 nm and the emission spectra were scanned from 340 to 600 nm [32]. All measurements were carried out at 22 ± 10 °C. The aggregation number was calculated using Eqs. 2–4 [25, 33]:

$$\ln\left[I_o/I_q\right] = N[Q]/C - \mathrm{CMC} \tag{2}$$

$$I_o/I_q = \exp([Q]/\ \mathrm{mic}) \tag{3}$$

$$N = (C - \mathrm{CMC})/\ \mathrm{mic} \tag{4}$$

where I_q and I_o are the fluorescence intensities with and without quencher, respectively, $[Q]$ is the concentration of quencher, N is the aggregation number, C is the surfactant concentration, CMC is the critical micelle concentration of the surfactant and 1/mic is the slope of the straight lines obtained from the plot of ln (I_o/I_q) *versus* quencher concentration. The I_q and I_o values were obtained from the fluorescence spectrum. Equations (2) and (3) can be solved and rearranged as Eq. (4). Finally aggregation number can be calculated by using the Eq. (4).

A stock solution of pyrene (5×10^{-4} mol/l) was prepared in ethanol. The surfactant solution was added and the pyrene concentration was kept constant at (5×10^{-6} mol/l) in the system [34]. The quencher concentration was used in the range of 2–8 × 10^{-4} mol/l [34, 35]. The study was carried out with the surfactant concentrations of 3*CMC, 5*CMC and 9*CMC for all the three synthesized gemini surfactants to investigate the variation of the aggregation number with surfactant concentration and to determine the effect of the spacer groups on the aggregation number.

Pyrene intensity ratio (I1/I3) is a well-established parameter which reflects the polarity experienced by the pyrene probe and found to be sensitive to the polarity of environment where the pyrene is located. In the present study, the fluorescence peak intensities of first (I1) and third (I3) vibronic bands were located at 376.0 and 387.0 nm respectively in the fluorescence spectrums. Pyrene intensity ratio was determined using a pyrene fluorescence probe to investigate the micropolarity of the micelle [33].

Results and Discussion

Synthesis of Gemini Surfactants

Cetyl alcohol based anionic bis-sulfosuccinate gemini surfactants (BSGSCA1,4; BSGSCA1,6; BSGSCA1,8) were prepared using the three steps in Scheme 1. The monoester of maleic acid was prepared using an equal molar ratio of cetyl alcohol and maleic anhydride. In this step, the acid value of the product was determined at repeated intervals after 1 h to confirm the complete conversion of alcohol into the ester. The second step was carried out with slight alteration, i.e., monoester of maleic acid (MMA) and ethylene glycol were used in equal molar ratios as compared to study carried out in [21]. The molar ratios were selected on the basis of stoichiometry. Benzene was replaced with toluene with a higher boiling point which is favorable to completely remove the water azeotropically with the help of a Dean and Stark assembly. The molecular formula, molecular weight and yield of synthesized BSGSCA's are shown in Table 1.

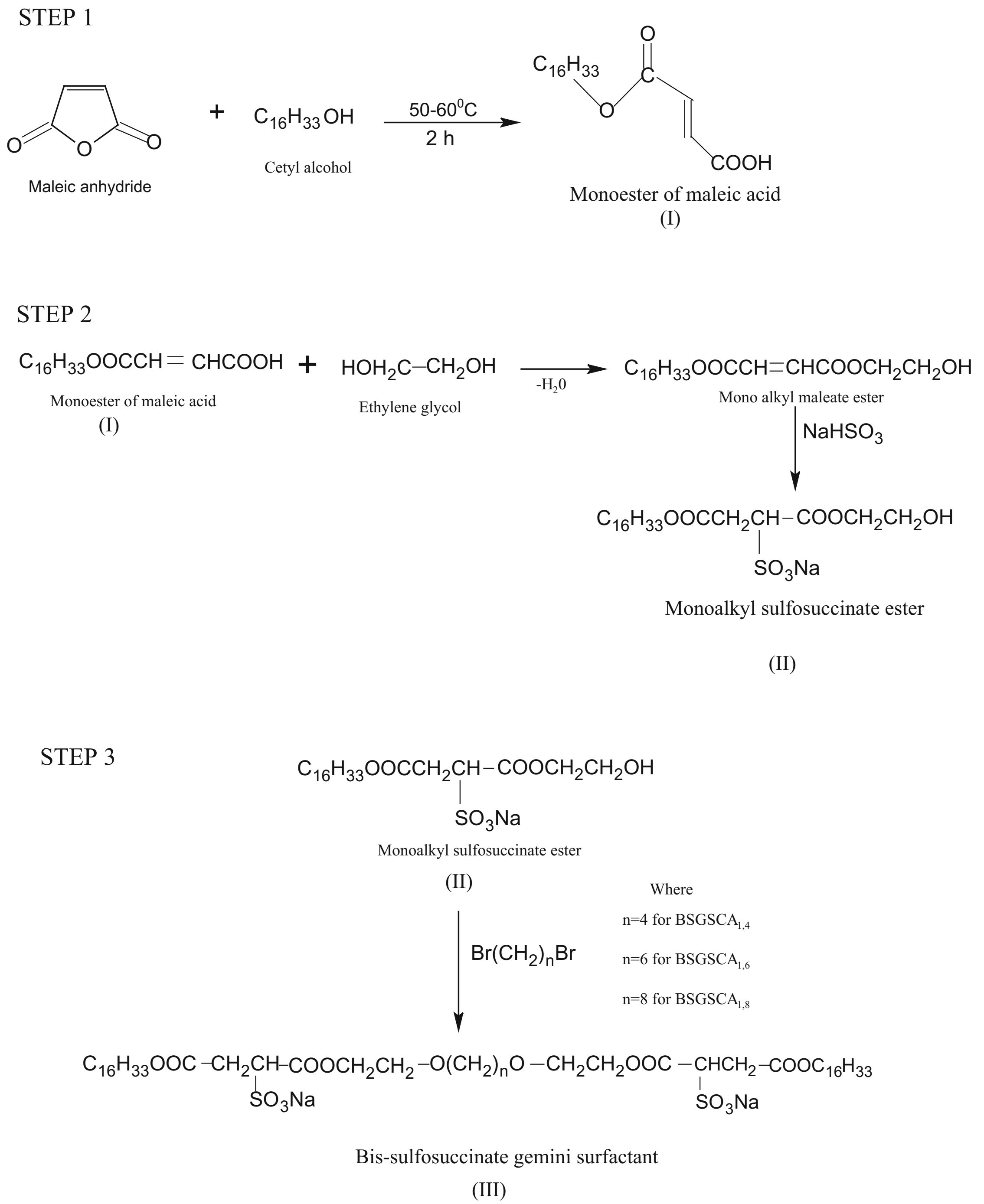
The chemical structures of the synthesized gemini surfactants were determined using elemental analysis, FT-IR and NMR. Table 1 shows the results of elemental analysis which is in good agreement with the theoretical calculated values for all carbon, hydrogen and sulfur elements. The result of FT-IR confirmed and satisfied the relevant frequency ranges of the functional groups present in the structures. The acceptable results of FT-IR were also corroborated and supported with the literature [37].

The bands appeared in the FT-IR spectrum {ν (cm^{-1})} of BSGSCA1,4; BSGSCA1,6 and BSGSCA1,8 displayed at 2919.75; 2921.11 and 2921.29 {CH3 (terminal) asymmetric bending}, 2851.25; 2851.99 and 2852.54 {CH_3 (terminal) symmetric}, 1147.38; 1147.26 and 1146.58 {C–O–C (Ether) asymmetric}, 1734.88; 1734.58 and 1734.18 {–C=O (Ester) stretching}, 1467.11; 1466.16 and 1465.05 {=CH_2 (Scissoring)}, 1225.54; 1233.44 and 1228.03 {C–O (Ester) stretching}, 721.36; 720.96 and 721.53{$(CH_2)8$} respectively [37].

Nuclear magnetic resonance spectroscopy was used to confirm the structures of the Gemini surfactants. The interpreted signals and peaks of ^{1}H NMR and ^{13}C NMR for all three synthesized gemini surfactants is shown in Table 2 [21, 38]. The ranges of 1H NMR peaks for BSGSCA1,8 appeared in δ (ppm) at 0.792–0.826 {t, 6H, $2CH_3$}, 1.251–1.279 {m, 60H, $2(CH_2)15$}, 1.384–1.511 {d,4H,$(CH_2\text{–}CHSO_3)_2$}, 1.806–1.823 {t, 8H, $(CH_2\ CH_2\ COO)_2$}, 2.099–2.244 {t, 2H, $(CHCO)_2$}, 3.320–4.314 {t, 16H, O–$(CH_2)8$–O}. The ^{13}C NMR peaks for BSGSCA1,8 displayed in the ranges δ (ppm) at 171.304 {ester –COO–}, 67.985 {ether C–O–C}, 31.932 {C–SO_2–R}, 22.690 {Terminal CH_3}, 25.746–29.763 {CH_2 chains of cetyl alcohol}.

Surface Properties of BSGSCA

The surface tension isotherms for the synthesized BSGSCA at different concentrations are shown in Fig. 1. The surface



Scheme 1 Synthetic steps for the preparation of cetyl alcohol based bis-sulfosuccinate gemini surfactants

tension at the CMC (γ_{CMC}) decreases with elongation of the spacer groups as shown in Table 3. This can be explained on the basis of enhanced flexibility. As the methylene chain length of the spacer group increases, the flexibility of the spacer group increases and reduces the γ_{CMC} [28].

The critical micelle concentration (CMC) is related to the concentration at which the surfactant monomers abruptly aggregate to form micelles. The CMC values shown in Table 3 indicate that the CMC decreases with increasing spacer length. The reduction in the CMC with increased spacer length may be result of the reduced electrostatic repulsion between the two polar head groups [28]. Similar results have been reported by Azira [27]. In the present study, the flexible spacers can easily bend and participate in the formation of the micelle hydrophobic

Table 1 Elemental analysis and yield of synthesized BSGSCA

Surfactant code	Molecular formula/molecular weight	Yield (%)	m *p* (°C)	Elemental analysis found/calculated (%)		
				C	H	S
$BSGSCA_{1,4}$	$C_{48}H_{88}O_{16}S_2Na_2$	76.93	66–68	55.98	8.72	6.34
	(1031.32)			55.90	8.60	6.21
$BSGSCA_{1,6}$	$C_{50}H_{92}O_{16}S_2Na_2$	74.80	72–74	56.79	8.92	6.14
	(1059.38)			56.68	8.75	6.05
$BSGSCA_{1,8}$	$C_{52}H_{96}O_{16}S_2Na_2$	84.36	77–79	57.56	8.99	5.97
	(1087.43)			57.43	8.89	5.89

Table 2 Interpretation [21, 38] of synthesized BSGSCA's by ^{1}H NMR and ^{13}C NMR

Surfactant code	^{1}H NMR δ (ppm)	^{13}C NMR δ (ppm)
$BSGSCA_{1,4}$	0.792–0.826, {t, 6H, $2CH_3$}	171.233 {–C=O}
	1.1–1.3, {m, 60H, $2(CH_2)_{15}$}	66.094 {ether C–O–C}
	1.478–1.531,{d,4H,$(CH_2–CHSO_3)_2$}	31.933 {$C–SO_2–R$}
	1.8, {t, 8H, $(CH_2\ CH_2\ COO)_2$}	22.692 {Terminal CH_3}
	2.100, {t, 2H, $(CHCO)_2$}	25.748–29.695{CH_2 chains of cetyl alcohol}
	3.087–4.314, {t, 8H, $O–(CH_2)_4–O$}	
$BSGSCA_{1,6}$	0.793–0.826, {t, 6H, $2CH_3$}	171.236 {–C=O}
	1.1–1.3, {m, 60H, $2(CH_2)_{15}$}	63.109 {ether C–O–C} 31.936 {$C–SO_2–R$}
	1.497–1.513,{d,4H,$(CH_2–CHSO_3)_2$}	22.690 {Terminal CH_3}
	1.803–1.827,{t, 8H, $(CH_2\ CH_2\ COO)_2$}	25.859–29.763 {CH_2 chains of cetyl alcohol}
	2.100, {t, 2H, $(CHCO)_2$}	
	3.328–4.237, {t, 12H, $O–(CH_2)_6–O$}	
$BSGSCA_{1,8}$	0.792–0.826, {t, 6H, $2CH_3$}	171.304 {–C=O}
	1.251–1.279, {m, 60H, $2(CH_2)_{15}$}	67.985 {ether C–O–C}
	1.384–1.511,{d,4H,$(CH_2–CHSO_3)_2$}	31.932 {$C–SO_2–R$}
	1.806–1.823, {t, 8H,$(CH_2\ CH_2\ COO)_2$}	22.690 {Terminal CH_3}
	2.099–2.244, {t, 2H, $(CHCO)_2$}	25.746–29.763 {CH_2 chains of cetyl alcohol}
	3.320–4.314, {t, 16H, $O–(CH_2)_8–O$}	

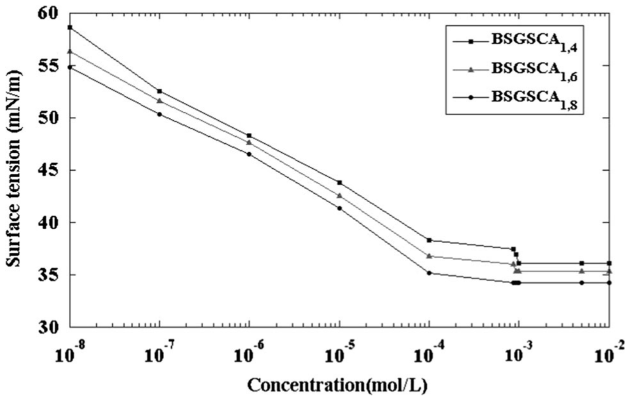


Fig. 1 Plots of surface tension *versus* surfactant concentrations at 25 ± 1 °C

Table 3 Surface active properties of BSGSCA's for different spacer chain lengths at 25 ± 1 °C

Surface active property	$BSGSCA_{1,4}$	$BSGSCA_{1,6}$	$BSGSCA_{1,8}$
Υ_{CMC} (mN/m)	36.1	35.3	34.2
CMC (mol/L)	0.0010	0.00093	0.00087
pC_{20} (mol/dm^3)	6.7	7	7.2
π_{CMC} (mN/m)	35.5	36.3	37.4

core. Due to enhanced flexibility with increased spacer length, more and more methylene groups contribute to micelle formation and as a result, free energy and CMC decreased for the gemini surfactants with longer spacer group [25]. The results in Table 3 show that BGSCA1,8 had the greatest reduction in CMC value out of the three synthesized surfactants due to the presence of a more flexible and elongated spacer group.

The efficiency or effectiveness of surfactant adsorption is given by the pC20 value, the negative logarithm of surfactant concentration required to reduce the surface tension of water by 20 mN/m. The efficiency of gemini surfactants to reduce the surface tension of water results in larger pC20 values because of the higher surface activity [25]. From Table 3, BSGSCA1,8 exhibited the highest pC20 value, i.e., 7.2 mol/dm3, due to its elongated spacer group.

Fluorescence Studies of BSGSCA

Micelle aggregation number was investigated using steady-state fluorescence quenching. In the present study, pyrene-benzophenone was used as a probe-quencher pair respectively which has been found to be appropriate to investigate the micelle aggregation number of anionic gemini surfactants [25, 33]. The experimental curves shown in Fig. 2 give the relationship between [*Q*] and ln (I_o/I_q) for the prepared gemini surfactants. These plots give straight lines for all the gemini surfactants and the slope of these straight lines was used to calculate the aggregation number.

Aggregation number was determined at different surfactant concentration (3*CMC, 5*CMC and 9*CMC) at 22 + 10 °C to investigate the effect of increased concentration. Figure 3 shows the variation of aggregation number with different surfactant concentrations (3*CMC, 5*CMC and 9*CMC). The increased aggregation number with increasing surfactant concentration indicates micelle growth and tighter packing of the molecules in the aggregate. Micellar growth with increased surfactant concentration is typical for ionic surfactants [35].

Micelle micropolarity can be determined from the intensity ratio (I1/I3) of pyrene molecules solubilized in the micelle. In general, reduced pyrene intensity ratio (I1/I3) reflects a less polar microenvironment. The pyrene intensity ratio (I1/I3) as a function of surfactant concentration is shown in Fig. 4. Increasing the surfactant concentration from 3*CMC to 9*CMC decreases the pyrene intensity ratio indicating a decrease in micropolarity. From the fluorescence quenching experiments we know that micelle aggregation number increases with increasing surfactant concentration. Micellar growth increases packing density causing pyrene to be solubilized towards the micelle core, consequently micropolarity decreases with increasing surfactant concentration [33].

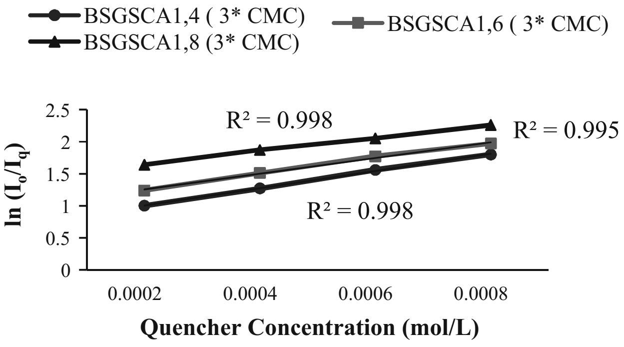


Fig. 2 Plot of ln (I_o/I_q) vs quencher concentration for different BSGSCAs at concentration 3*CMC at 22 ± 1 °C

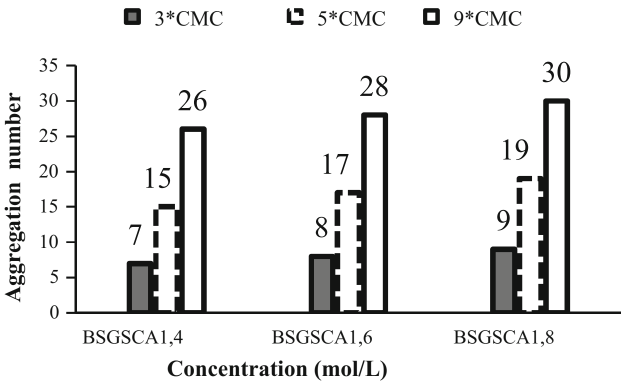


Fig. 3 Aggregation number for different BSGSCA's at different concentrations (3*CMC, 5*CMC, 9*CMC) at 22 ± 1 °C

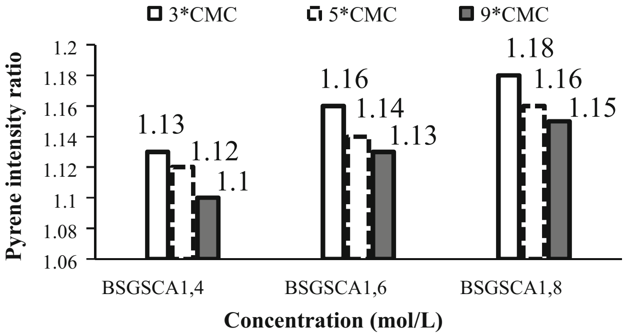


Fig. 4 Pyrene intensity ratio *versus* BSGSCA concentrations

Figure 4 also shows the increased micropolarity with elongated spacer length. The increase in polarity upon increasing the spacer chain length is likely due to progressive penetration of the spacer in the micelle hydrophobic core which allows water to enter the palisade layer of the micelle. The increased polarity is most noticed for BSGSCA1,8 having the longest spacer [39].

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