ORIGINAL CONTRIBUTION

Micellization of anionic gemini surfactants and their interaction with polyacrylamide

Lu Lai · Ping Mei · Xiao-Mei Wu · Cong Hou ·
Yan-Cheng Zheng · Yi Liu

Abstract A series of anionic gemini surfactants have been synthesized. The surface properties and micellization process of as-prepared sulfonate gemini surfactants (SGS) and carboxylate gemini surfactant (CGS) have been studied by surface tension measurement and isothermal titration microcalorimetry. Meanwhile, the interaction of these five surfactants with polyacrylamide (PAM) was investigated using surface tension, steady-state fluorescence measurement, and isothermal titration microcalorimetry. The results show that the critical micelle concentrations (CMCs) of above-mentioned surfactants are more than 1 order of magnitude lower than those of corresponding single chain surfactants. Moreover, the enthalpy of micelle formation (ΔH_{mic}) for the investigated gemini surfactants is negative. In the surfactant–PAM systems, the thermodynamic parameters of binding have also been determined. The conclusion may be drawn that the binding strength of SGS onto PAM is stronger than that of CGS, resulting from more compact structure of SGS aggregates. With increasing surfactant hydrophobicity, the values of ΔH_{agg} become more exothermic and a ΔS_{agg} decrease was observed. Therefore, the interaction between SGS and PAM is enthalpy-driven.

L. Lai · P. Mei (✉) · X.-M. Wu · C. Hou · Y.-C. Zheng
College of Chemistry and Environmental Engineering, Yangtze University, Jingzhou, Hubei 434023, China
e-mail: meipinghb@126.com

Y. Liu
State key laboratory of Virology and Key laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), College of Chemistry and Molecule Sciences, Wuhan University, Wuhan 430072, China

Introduction

Gemini surfactants represent a new class of surfactants made up of two identical or different conventional monomeric surfactants connected by a spacer group. Since gemini surfactants contain two hydrophobic alkyl chains per molecule and they are connected at the level of the head groups, hydrophobic interaction among the hydrocarbon side chains is enhanced and electrostatic repulsion among the head groups is reduced. Thus, gemini surfactants possess higher surface properties, could increase wetting, promote emulsification of oil in water, enhance dispersion of solids, and own unusual aggregation morphologies [1–5].

Surfactant-based formulations often contain water-soluble polymers that are introduced in the system to either improve its properties or obtain properties that neither the surfactant nor the polymer has when present alone. Nowadays, the mixtures of polymers and surfactants are widely applied in a variety of fields, including enhanced oil recovery [6], bioscience [7], and pharmaceuticals [8]. Therefore, it is important to investigate the interaction of gemini surfactants with water-soluble polymers in view of a future use of these surfactants in

formulations. So far, many important information on surfactant and polymer interaction at the air/water interface, the oil/water interface, or in the bulk are being provided by techniques such as surface tension, steady-state fluorescence measurement, isothermal titration microcalorimetry, neutron and X-ray reflection, ellipsometry, dynamic light scattering, transmission electron microscopy, and surface rheology [9–15]. The main types of polymer/surfactant interactions can be grouped into hydrophobic interactions between the polymer and the surfactant hydrocarbon chains, relatively weak interactions between the polymer chains and the surfactant head groups or strong electrostatic interactions between oppositely charged polyelectrolytes and surfactant head groups [16, 17]. Among these studies on surfactant–polymer interaction, uncharged polymer/ionic surfactant pairs and oppositely charged surfactant/polymer mixtures have received more attention [18–20]. The results indicated that hydrophobicity and surface activity of the polymer can be a dominant factor in the case of uncharged polymer/ionic surfactant pairs, while oppositeness of charge can be dominant in polyelectrolyte/ionic surfactant systems [21].

Isothermal titration calorimetry (ITC) is the only technique that can directly measure the binding energetics in solution [22]. It is most often used to study the binding of small molecules (such as medicinal compounds, surfactants) to larger macromolecules (polymer, proteins, DNA, etc.). The binding affinity (K_a), enthalpy changes (ΔH), and binding stoichiometry (n) of the interaction between two or more molecules in solution can be determined by ITC [23]. This thermodynamic information has contributed a great deal to our current understanding of the interaction mechanism at the molecular level. In recent years, microcalorimetric measurements have been used successfully to identify the factors and driving forces that govern the interactions in surfactant/polymer systems [24]. In these studies, Wang et al. [25–27] achieved a series of significant original findings, which have been widely accepted. For example, they studied the micellization of the surfactants SBPBS and AOT and their interaction with hydrophobically modified PAM. The information obtained from the calorimetric curves show that the interaction of SBPBS with HMPAM is much stronger than that of AOT/HMPAM, which may result from the π–π interaction among SBPBS molecules [28].

Although many studies of the interaction between oppositely charged surfactants and polymers have been reported, there have been few reports about those of the mixtures of anionic gemini surfactant and anionic polymer. However, such mixtures are widely applied in enhanced oil recovery, bioscience, and so on. Therefore, it is urgently required to examine the interaction mechanism of above-mentioned mixtures. In this work, we investigated the surface properties and micellization of as-prepared sulfonate gemini surfactants (SGS) and carboxylate gemini surfactant (CGS). Meanwhile,

the interaction of these five surfactants with polyacrylamide (PAM) was investigated using surface tension, steady-state fluorescence measurement, and isothermal titration microcalorimetry.

Experimental

Materials

1-Bromooctane, 1-bromodecane, 1-bromododecane, 1-bromotetradecane, 1,3-propanesulfonate, and pyrene were obtained from Sigma-Aldrich. Ethylenediamine and succinic anhydride were obtained from Tianjin Chemical Reagent Company. All of the above reagents were used as received without further purification. PAM was purchased from Tianjin Fuchen Chemical Reagent Company. The average molecular weight of PAM is 5,000,000. All other reagents were of analytical reagent grade. Ultrapure water with 18.2 MΩ cm^{-1} (Millipore Simplicity) was used throughout the whole experiment.

Synthesis and structure characterization

The reaction route for the synthesis of anionic gemini surfactants is shown in Fig. 1. The SGS were synthesized from bromoalkane, ethylenediamine and 1,3-propanesulfonate.

Synthesis of N,N′-bis(alkyl)-ethylenediamine

Ethanediamine (0.05 mol), bromoalkane (0.11 mol) and ethanol (150 ml) were introduced into a 250-ml three-necked round flask. The mixture was refluxed at 80 °C for 48 h with constant stirring. The resulting mixture was distilled under reduced pressure to remove ethanol. The residue was washed several times with diethylether to obtain white powder, and then it was recrystallized twice from ethanol and water (1:1) to yield N,N′-bis(alkyl)-ethylenediamine in the form of white solids.

Synthesis of sulfonate gemini surfactants

A mixture of N,N′-bis(alkyl)-ethylenediamine (0.01 mol) and 1,3-propanesulfonate (0.03 mol) in 50 ml of methanol was refluxed at 70 °C for 24 h under nitrogen protection. The resulting mixture was distilled under reduced pressure to obtain powder, and then it was separated with column chromatography from trichloromethane and methanol. The product was recrystallized twice from ethanol and water (2:1) to afford SGS as white powder.

The synthesis process of CGS (CGS-12) is similar to the above-mentioned process. The chemical structures of the synthesis products were confirmed by IR spectra, ^{1}H NMR and elemental analysis.

Fig. 1 The synthetic route of anionic gemini surfactants

$C_nH_{2n+1}Br \xrightarrow[EtOH]{NH_2CH_2CH_2NH_2}$

(SGS-8,10,12,14)

(CGS-8, 10, 12, 14)
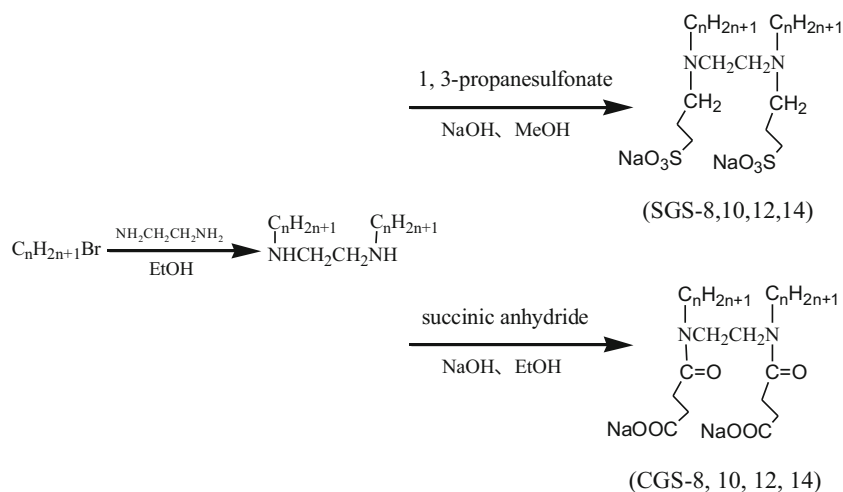
Surface tension measurements

Surface tension measurements were carried out using an automated drop tensiometer (Tracker, Teclis-IT Concept, France). Temperature was controlled at 25±0.1 °C using a thermostatic bath. In this instrument, an air bubble forms in a syringe tip placed in a glass cell filled with the solution, and the bubble is imaged with a video camera. The bubble shape is analyzed by a computer program that solves the Laplace equation (describing the mechanical equilibrium under capillary and gravity forces) and enables the monitoring of surface tension variations over time. A bubble volume of 3 µl was used. Each sample was equilibrated for at least 30 min under the test temperature to reach equilibrium before the measurement.

Fluorescence measurements

Fluorescence spectra were measured on a LS-55 Spectrofluorimeter (Perkin-Elmer Corporation, USA) equipped with a 1.0-cm quartz cell and a thermostatic bath. Pyrene was introduced in the investigated system under the form of a small amount of a stock solution in methanol. The labeled solutions were stirred overnight before use. The pyrene concentration used was 1.0×10^{-6} mol l^{-1}. Pyrene was excited at 335 nm, and the emission spectra were recorded from 360 to 460 nm. The widths of the excitation and emission slits were set to 5.0 and 10.0 nm, respectively. Each measurement was repeated three times. These spectra were used to determine the value of the I_1/I_3 ratio (the intensities of the first and third vibronic emission peaks) in the spectra. This ratio (polarity index) characterizes the polarity of surfactant aggregates and of hydrophobic microdomains formed by the polymers. The plots of I_1/I_3 versus surfactant concentration were used for the determination of the critical micelle concentration (CMC) and critical aggregation concentration (CAC).

Isothermal titration microcalorimetry (ITC)

The calorimeter used in this work was a Nano-ITC^{2G} (TA, USA) isothermal titration microcalorimeter with a 1-ml sample cell. The isothermal titration was performed as an incremental titration with a 1-ml cell and a 250-µl syringe. All the experiments were conducted at 298.15 K, while the stir speed was set to 150 rpm. The time settings in the titration were as follows: data interval, 1.0 s; injection interval, 600 s; start delay, 1,800 s; initial baseline, 1,800 s. The injection number was 50 and the injection volume was set as 5 µl. The control experiment for each system was conducted under the same conditions, using SGS as titrant and ultrapure water as the titrand. The baseline of the thermogram was manually set and then the peak area was integrated using NanoAnalyze software provided by TA Instruments. Subtracting the control experiment in Average Area mode gave the corrected reaction heat for each injection. Then we used the Independent mode to fit the data to get the parameters for the interaction.

Results

Characterization of as-prepared anionic gemini surfactants

The reaction routes for the synthesis of the anionic gemini surfactants are shown in Fig. 1. Spectral characterization including FT-IR, ^{1}H NMR and elemental analysis confirmed the structures and purity of these surfactants. All of the above corresponding spectral data are also presented in the Supplementary Material.

Surface properties of as-prepared anionic gemini surfactants

The surface tension curves of the investigated surfactant solutions at 298.15 K are shown in Fig. 2. The CMC
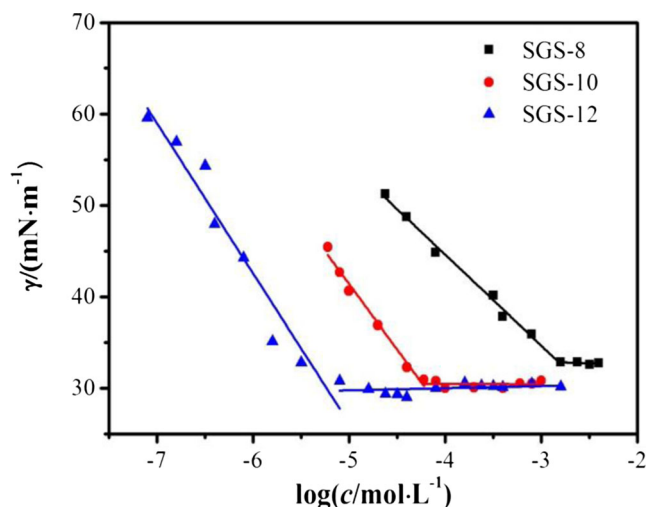
Fig. 2 Variation of surface tension as a function of surfactant concentration for the investigated surfactants (SGS-8, -10, -12) at 298.15 K

was taken as the concentration beyond which the surface tension of the aqueous solution does not decrease any more. In each of the curves, surface tension decreases as the surfactant concentration increases, reaching obvious breakpoints, and then almost becomes constant. The breakpoints correspond to the CMC values of anionic gemini surfactants. The CMC values and the surface tensions at the CMC (γ_{cmc}) for the investigated surfactants were obtained from the curves and presented in Table 1.

From the γ–log c curve just below the CMC, maximum surface excess concentration (Γ_{max}) is determined using the Gibbs equation,

$$\Gamma = -\frac{1}{2.303nRT}\left(\frac{\partial\gamma}{\partial\log c}\right)_T$$

where γ denotes surface tension, c is the concentration of surfactants, and R is the gas constant (T=298.15 K). n is a constant and depends on the number of species constituting the surfactant absorbed at the interface. The value of n is assumed to be 2 (one surfactant molecule and one

counterion) and 3 (one surfactant molecule and two counterions) without salt and to be 1 with salt [29]. Therefore, n=3 is taken in this work.

The minimum area occupied per surfactant molecule (A_{min}) at the air/water interface is calculated from the maximum surface excess concentration (Γ_{max}) using the following equation:

$$A_{min} = \frac{10^6}{N_A \Gamma_{max}}$$

where N_A is the Avogadro constant. The Γ_{max} and A_{min} of anioinc gemini surfactants are listed in Table 1.

The fluorescence emission spectrum of pyrene is very sensitive to solvent polarity, so pyrene has been used as a probe to determine the micropolarity of surfactant aggregates. The plot of the pyrene I_1/I_3 ratio as a function of SGS (SGS-12) concentration is shown in Fig. 3. Below the CMC, the I_1/I_3 ratio is about 1.80, indicating that the pyrene is located in a polar environment. With the increasing of the surfactant concentration, the I_1/I_3 ratio decreases rapidly. Above the CMC, the I_1/I_3 ratio reaches a roughly constant value because of the incorporation of probe into the hydrophobic microdomain of the micelles [30]. The averaged I_1/I_3 ratio of the aggregates for SGS-12 beyond CMC is 1.25, and the CMC determined by fluorescence is 0.013 mM.

In the present study, ITC was also employed to investigate the CMC values and the micellization process of SGS (SGS-12). Figure 4 presents the calorimetric curves of SGS-12 titrated into ultrapure water, where the observed enthalpies (ΔH_{obs}) are plotted against the final surfactant concentrations. The titration processes was found to be endothermic and show an abrupt decrease at a critical concentration [31]. The CMC value can be determined from the intercept of the two linear extrapolations of each plot, and the enthalpy of micellization (ΔH_{mic}) can be obtained from the difference between the observed enthalpies of the two linear segments of the plot, as shown in Fig. 4. The CMC values and the enthalpies of micellization are also summarized in Table 1.

Table 1 CMC, surface property parameters, ΔH_{mic} for anionic gemini surfactants at 298.15 K

	CMC[a] (mM)	CMC[b] (mM)	CMC[c] (mM)	ΔH_{mic} (kJ mol^{-1})	γ_{cmc} (mN m^{-1})	Γ_{max} (mol m^{-2})	A_{min} (nm^2)
SGS-8	1.778	2.015	9.145	−14.04	32.83	0.60	2.76
SGS-10	0.068	0.091	0.540	−15.68	30.49	0.87	1.92
SGS-12	0.008	0.013	0.070	−17.19	29.77	1.11	1.50
CGS-12	0.017	0.022	0.082	−8.07	28.57	1.30	1.25

[a] By surface tension

[b] By fluorescence

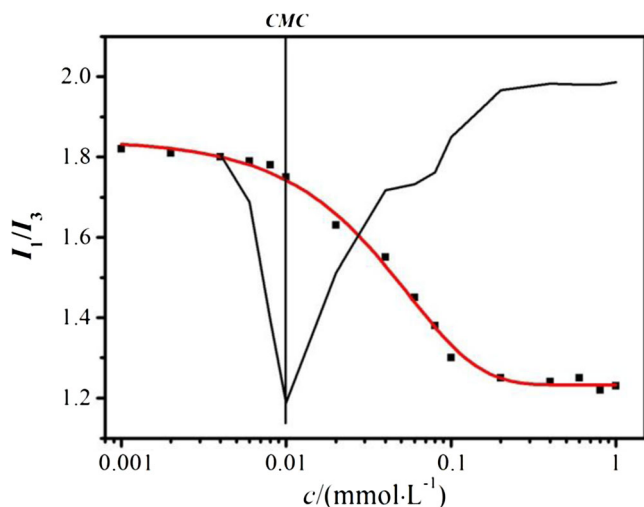[c] By isothermal titration calorimetry (ITC)

Fig. 3 The pyrene I_1/I_3 ratio as a function of SGS-12 concentration at 298.15 K

The interaction between aionic gemini surfactants and PAM

Calorimetric curves for the addition of concentrated surfactant solutions to 0.3 % PAM solution at 298.15 K are shown in the inset of Fig. 5, and then the observed enthalpies (ΔH_{obs}) of the above titration process are plotted against the total final concentrations of these investigated surfactants. As shown in Fig. 5, the interaction of these investigated surfactants with PAM are exothermic process. Moreover, as the length of hydrophobic chains of SGS increases, the thermal power increases. However, the thermal power is negligible when CGS-12 was titrated into the PAM solution.

We used the Independent mode to fit the data to get the parameters for the interaction. Independent Set of Multiple Binding Sites is the most common model for a binding
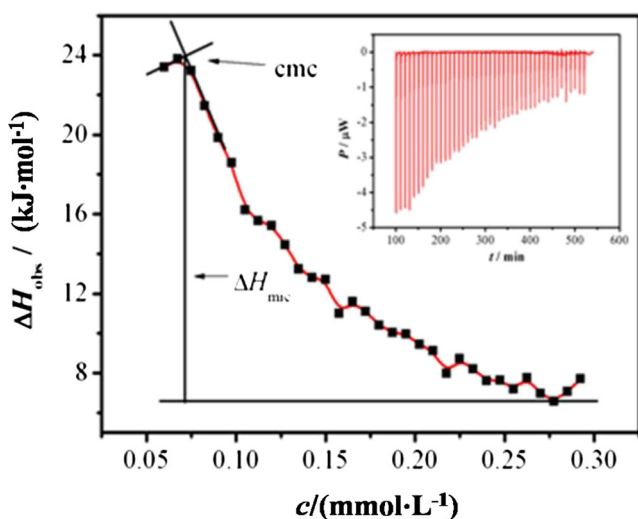

Fig. 4 Variation of the observed enthalpies(ΔH_{obs}) with the final concentrations for SGS-12 diluted into ultrapure water at 298.15 K. The *inset* shows a record plot of power (heat flow) versus time when SGS-12 is titrated into H_2O

experiment. The total heat of the analytical solution is determined by Eq. 1

$$Q = V \cdot \Delta H \left[[L] + \frac{1 + [M]nK_a - \sqrt{\left(1 + [M]nK_a - [L]K_a\right)^2 + 4K_a[L]}}{2K_a} \right] \quad (1)$$

where ΔH is the enthalpy of binding, K_a is the binding constant, n is the number of binding sites, V is the volume of the cell, $[L]$ is the total surfactant concentration, $[M]$ is the PAM concentration. From the determination of binding constant and enthalpy, the dissociation constant $K_d = 1/K_a$, the total free energy $\Delta G = -RT \ln K_a$ and entropy $\Delta S = (\Delta H - \Delta G)/T$ could be derived, providing a complete thermodynamic profile of the interaction. Thermodynamic parameters for the investigated surfactants in the presence of PAM at 298.15 K are listed in Table 2. However, thermodynamic parameters of interaction between CGS-12 and PAM have not been obtained because of the negligible thermal power.

Pyrene has been used as a probe to study the interaction between surfactant and polymer. The intensity ratio of the first to the third vibronic bands (I_1/I_3) can be taken as a measure of the polarity of the environment, being high in polar media and low in hydrophobic environment. Additionally, the CAC values of the surfactants can be obtained from the variation of the pyrene I_1/I_3 ratio with the surfactant concentration in the presence of polymer [30]. Figure 6 shows the variation of the pyrene I_1/I_3 ratio in the absence and present of PAM with the concentration of SGS-12 and CGS-12. As shown in Fig. 6a, in the absence of polymer, I_1/I_3 decreased steeply in the CMC range from the value in pure water (1.80) to a lower value (1.25), corresponding to a fairly hydrophobic environment characteristic of the SGS-12 micelles. In the presence of PAM, in the low surfactant concentration range below the CMC, the I_1/I_3 ratio is lower than in the absence of polymer, indicating the occurrence of an interaction between SGS-12 and PAM. Also in this system the CAC value is lower than the CMC in pure water. Further addition of surfactant SGS-12 to the PAM solution results in a decrease in I_1/I_3, revealing the presence of a hydrophobic environment due to the increase in attraction between surfactant molecules and polymer chains, and the polymer chains tend to a more compact form. Moreover, the final value of the I_1/I_3 ratio of the SGS-12/PAM mixture are very small. The interior of the mixed systems exhibits lower polarity than surfactant micelles [30]. On the contrary, as shown in Fig. 6b, whether in the concentration range below or above the CMC, there is no appreciable difference between CGS-12/PAM and CGS-12/water. Furthermore, the CAC value of the CGS-12/PAM mixture is higher than the CMC. The above-mentioned results thus reflect a weaker interaction between CGS-12 and PAM.

The surface tension curves of SGS-12 in the absence and presence of PAM are shown in Fig. 7. For the surfactant–
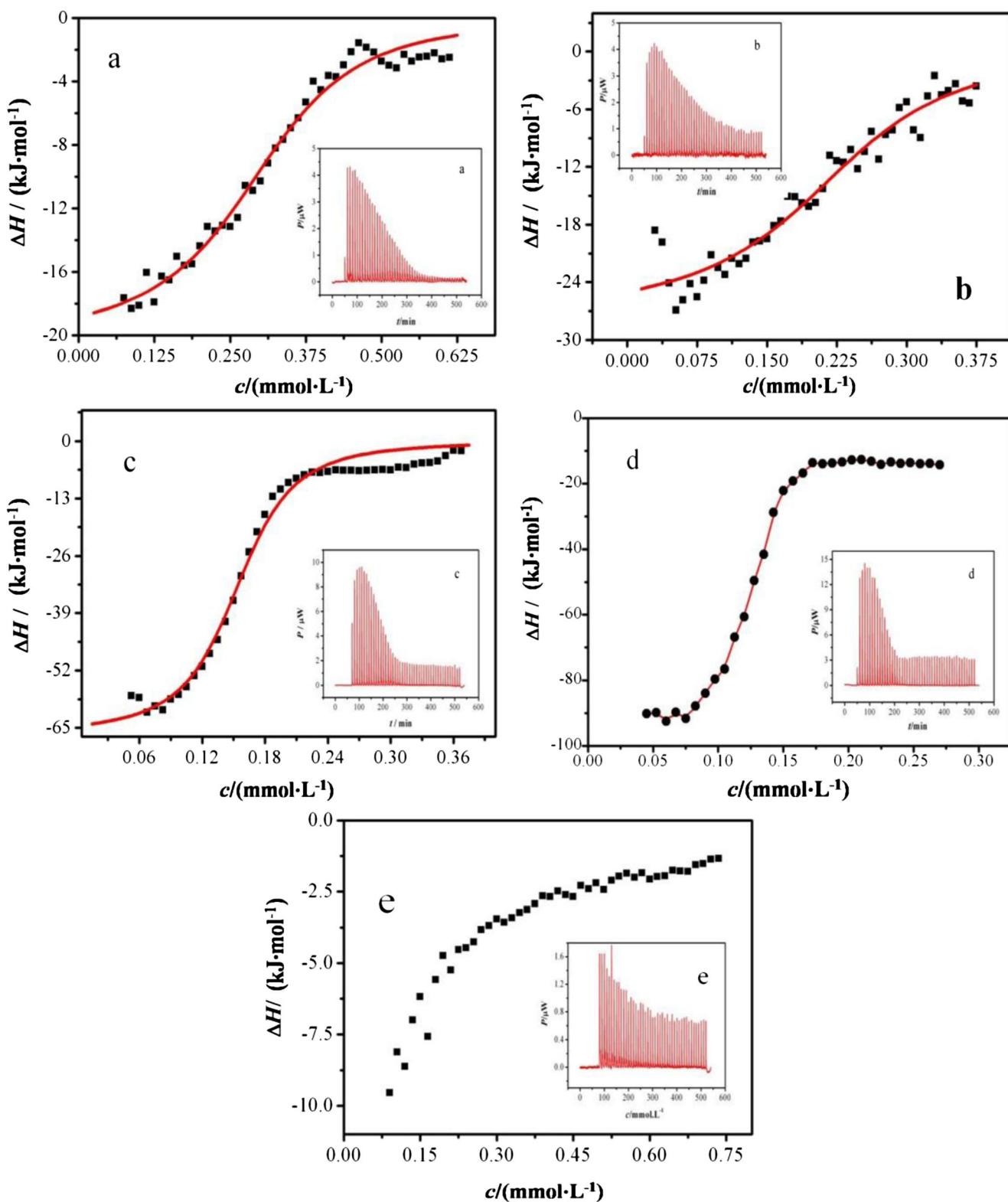
Fig. 5 Variation of the observed enthalpies (ΔH_{obs}) with the final concentrations for the investigated surfactants (**a** SGS-8; **b** SGS-10; **c** SGS-12; **d** SGS-14; **e** CGS-12) diluted into 0.3 % PAM solution at 298.15 K. The *inset* shows a record plot of power (heat flow) versus time when the investigated surfactants are titrated into PAM solution

polymer system, two transition points are observed in the surface tension curve. The first break point corresponds to

the beginning of the aggregation of surfactant molecules with polymer hydrophobes, which is defined as the CAC. The

Table 2 Thermodynamic parameters for the investigated surfactants in the presence of polyacrylamide (PAM) at 298.15 K

Surfactants	K_a (1/M)	n	K_d (M)	ΔH_{agg} (KJ/mol)	ΔG_{agg} (KJ/mol)	ΔS_{agg} (J/mol)
SGS-8	3.55×10^4	563	2.81×10^{-5}	−20.54	−26.84	21.13
SGS-10	3.79×10^4	436	2.64×10^{-5}	−27.42	−27.01	−1.37
SGS-12	2.81×10^5	287	3.59×10^{-6}	−57.98	−32.15	−86.63
SGS-14	8.45×10^5	123	1.18×10^{-6}	−76.56	−35.00	−139.40

second one represents the saturation of surfactant molecules binding to the polymers, which is normally called C_2 [28, 32]. As shown in Fig. 7, the surface tension before the CAC is lower than the case without polymer. This is probably ascribed to the participation of PAM hydrophobes in the surface monolayer. However, beyond the CAC, some of the added surfactants will form aggregates with polymer, and then, the amount of surfactant molecular adsorbed on to the surface becomes less than the case without polymer, which leads to a gradual decrease in surface tension. Therefore, the surface tension of SGS-12/PAM mixture decreases more slowly compared to the linear down curve in the absence of PAM.

Discussion

Surface properties and micellization of anionic gemini surfactants

As shown in Table 1, we found that the CMC values of SGS-10, SGS-12 and CGS-12 are more than 1 order of magnitude lower than those of corresponding single chain surfactants, resulting from the structural difference between the gemini surfactants and the conventional single chain surfactants. Since the gemini surfactants contain two hydrophobic alkyl chains per molecule and they are connected at the level of the head groups, hydrophobic interaction among the hydrocarbon side chains is enhanced and electrostatic repulsion among the head groups is reduced. Thus, the gemini surfactants possess

higher surface properties and are packed more closely than the single-chain surfactants.

Direct calorimetric measurements of ΔH_{mic} have become easy, accurate, and fairly rapid with the advent of isothermal titration microcalorimetry. Figure 4 shows that the titration process for SGS-12 in pure water was endothermic; thus, the enthalpy of micelle formation in the absence of polymer is negative (Table 1). It is generally accepted that there are mainly four contributions to the thermodynamic functions for the gemini surfactants, including the van der Waals interaction between the chains, the head group repulsion, the hydrophobic interaction, and the configuration of the spacer chain [33]. Among these interactions, the van der Waals and hydrophobic interaction will tend to make ΔH_{mic} negative at 298.15 K, whereas the dehydration process of hydrophilic head groups during micellization results in endothermic effects. Since the spacer chain enhances the hydrophobic interaction among the hydrocarbon chains of gemini surfactant, the enthalpy of micelle formation (ΔH_{mic}) of gemini surfactants is negative [28, 34].

The A_{min} values for SGS-8, SGS-10 and SGS-12 are 2.76, 1.92 and 1.50 nm^2, respectively (Table 1). With increasing surfactant hydrophobicity, the as-prepared SGS are packed more closely.

Thermodynamic parameters and mechanism of the interaction between anionic gemini surfactants and polyacrylamide

Surfactant-based formulations often contain water-soluble polymers that are introduced in the system to either improve

Fig. 6 Plots of the pyrene I_1/I_3 ratio as a function of the concentration of the investigated surfactants (**a** SGS-12; **b** CGS-12) in the absence and presence of polyacrylamide (*PAM*) at 298.15 K
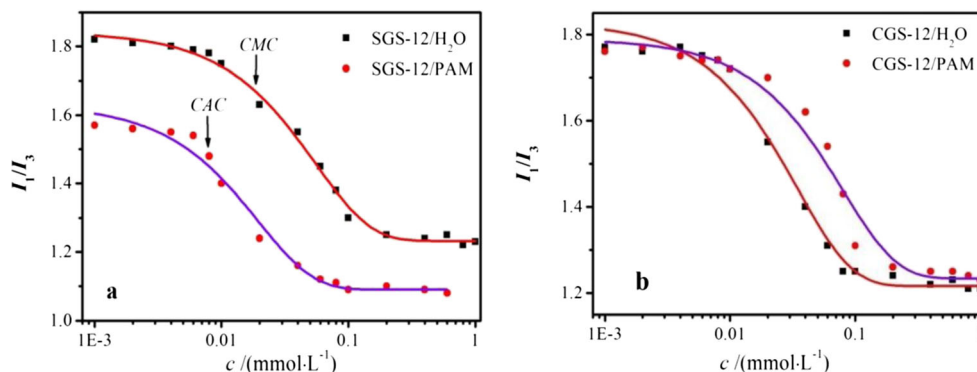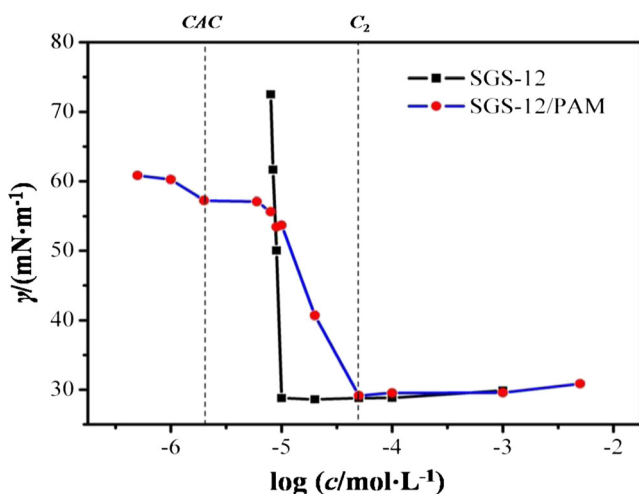
Fig. 7 Variation of the surface tension with the surfactant concentration for SGS-12/0.3 % PAM at 298.15 K

its properties or obtain properties that neither the surfactant nor the polymer has when present alone [35]. Therefore, it is important to investigate the interaction of gemini surfactants with water-soluble polymers in view of a future use of these surfactants in formulations.

Calorimetric curves for mixing SGS of different hydrocarbon chain length with 0.3 % PAM solution at 298.15 K are shown in the insets of Fig. 5. Subtracting the mixing enthalpy curves of SGS with water, the variations of the observed enthalpies (ΔH_{obs}) with the final concentrations for surfactants are shown in Fig. 5, which are ascribed to the polymer–surfactant interactions. As shown in Fig. 5, in the presence of PAM, the observed enthalpy increases rapidly with the initial addition of surfactants. Before the CAC, the added surfactant aggregates dissociate into monomers and the monomers are adsorbed onto polymer hydrophobic microdomains through the hydrophobic interaction between the surfactant hydrocarbon chains and the polymer hydrophobes [36, 37]. Thus, a large exothermic effect is found initially [38]. Beyond the CAC, more surfactant monomers are adsorbed onto the hydrophobes of PAM to form bound micelles. Because of the electrostatic repulsion between the charged surfaces of micelles, the polymer backbones may stretch out, resulting in the gradual increase of the observed enthalpies [39]. When the surfactant concentration continues to increase, the surfactant molecules will saturate the polymer and free micelles begin to form [40]. Beyond the C_2, the only thermal effect is the dilution of the micelles, and thus the ΔH_{obs} values are hardly changed [28].

Then we used the independent mode to fit the data to get the thermodynamic parameters for the interaction. Table 2 shows that ΔH_{agg} is negative for SGS-PAM. As suggested by other works, there are four main enthalpy contributions to the aggregation enthalpy: (1) the hydrophobic interaction between polymer side chains and the hydrophobic chains of

surfactants, (2) the electrostatic repulsion between the hydrophilic groups of surfactants, (3) the ion–dipole interaction between the hydrophilic moieties of polymer and the hydrophilic group of surfactants, and (4) the conformational changes of the polymer induced by surfactants [28]. It is widely recognized that the first and third factors from above mainly result in the exothermic effect [38]. As shown in Table 2, with increasing surfactant hydrophobicity, the values of ΔH_{agg} become more exothermic. Because the first factor become more pronounced for the increasing hydrophobic interaction. At the same time, the binding constant gradually increases with the increase in the hydrophobicity of surfactants.

Additionally, the thermal power for CGS-12/PAM interaction is so small that we have not obtained the value of ΔH_{agg} (Fig. 5e). Therefore, a conclusion may be made that the interaction of SGS with PAM is stronger than that of CGS-PAM. It is possible that the packing of SGS aggregates is more compact, which is proved by the values of ΔH_{mic} (Table 1). The more positive values of enthalpy of micellization is not favorable for aggregation of surfactants [31]. The more compact aggregates of SGS may have a higher surface charge density, which would strengthen the ion–dipole interaction of the hydrophilic groups with the hydrophilic segment of PAM [28.31]. Furthermore, the more compact aggregate may strengthen the hydrophobic interaction between surfactant and polymer. Meanwhile, the following results of fluorescence measurement also suggested that the interaction of SGS with PAM is stronger than that of CGS-PAM [41].

Table 2 shows a ΔS_{agg} decrease with increasing the surfactants hydrophobicity, that is, the entropy becomes more unfavorable for the aggregation when the surfactant hydrophobicity increases. The negative and small positive values of ΔS_{agg} and the large negative values of ΔH_{agg} indicate that the interaction between SGS and PAM is indeed enthalpy-driven [31, 39].

Conclusion

The micellization of as-prepared SGS and CGS and their interaction with PAM have been investigated. The CMCs of the above-mentioned surfactants are more than 1 order of magnitude lower than those of corresponding single chain surfactants. Moreover, the enthalpy of micelle formation (ΔH_{mic}) for the investigated gemini surfactants is negative. For SGS binding to the PAM, the polymer may promote the aggregation of surfactant with its hydrophobic segments. The binding strength of SGS onto PAM is stronger than that of CGS, resulting from more compact structure of SGS aggregates. With increasing surfactant hydrophobicity, the values of ΔH_{agg} become more exothermic and a ΔS_{agg} decrease was

observed. Moreover, the interaction between SGS and PAM is enthalpy-driven.

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