J Surfact Deterg (2012) 15:33–40
DOI 10.1007/s11743-011-1270-7

ORIGINAL ARTICLE

Aggregation and Thermodynamic Properties of Some Cationic Gemini Surfactants

Halide Akbaş · Aylin Elemenli · Mesut Boz

Received: 24 November 2010 / Accepted: 29 March 2011 / Published online: 20 April 2011

Abstract In this study, the gemini surfactants of the alkanediyl-α-ω-bis(alkyl dimethyl ammonium) dibromide type, on the one hand, with different alkyl groups containing m carbon atoms and an ethanediyl spacer, referred to as "m-2-m" (m = 10, 12 and 16) and, on the other hand, with n-C_{16} alkyl groups and different spacers containing s carbon atoms, referred to as "16-s-16" (s = 2, 6, 10 and Ar (8)) have been synthesized, purified and characterized. The critical micelle concentration (CMC), micelle ionization degree (α) and Gibbs free energy of micellization (ΔG_{mic}) of these surfactants and the monomeric cationic surfactants DTAB and CTAB have been determined by means of electric conductivity measurements. In addition, the temperature dependence of the CMC was determined for the 10-2-10 gemini surfactant. The CMCs of the gemini surfactants are found to be much lower than those of the corresponding monomeric surfactants and the effect of the hydrophobic alkyl chain length is more important than that of the spacer. The CMC of 16-s-16 passes through a maximum of (or around) s = 6 and then decreases for s = 10. The presence of a maximum CMC is explained by the contribution of a change of conformation of the surfactant with increasing spacer chain length. The changes of α with s and m are found qualitatively similar to those found for CMC values. The values of ΔG_{mic} are more negative for the dimers than for the monomers and also change with an increasing spacer carbon number, as CMC values do. The thermodynamic parameters of micellization indicate that the micellization of 10-2-10 is enthalpy driven.

Keywords Cationic gemini surfactants · Spacer group · Critical micelle concentration · Micelle ionization degree

Introduction

Surfactants are widely used in our daily life and in various industrial productions. For instance, they catalyze some reactions, act as solubilizers for water insoluble dyes, break down dye aggregates in order to accelerate adsorption processes on fibers, are auxiliaries for improving dye adsorption and are used as leveling agents [1–4]. Gemini or dimeric surfactants are rather novel surfactants that have become of considerable interest in the academic and industrial areas. Due to their different molecular structure with respect to monomeric surfactants, they have superior properties for special purposes [5–7]. Gemini surfactants show bioactivity as disinfectants and are used in skin care formulations, antipollution protocols, analytical separations, nanoscale technology and as paint additives.

Gemini surfactants consist of two amphiphilic moieties connected at the level of or very close to the head groups by a "spacer" group of varying nature namely hydrophobic, hydrophilic, rigid or flexible [8, 9]. As the spacer and alkyl groups play an important role in the properties of gemini surfactants [10–12], we focused on the effect of those moieties on the aggregation properties of some cationic gemini surfactants. For this purpose, a series of quaternary ammonium dimeric surfactants (C_m–s–C_m, 2Br, s = 2, m = 10, 12 and 16; m = 16, s = 2, 6, and 10) were synthesized in our laboratory. The characteristic parameters of these compounds and those of monomeric cationic surfactants (DTAB and CTAB), such as critical micelle concentration (CMC), micelle ionization degree (α) and Gibbs free energy of micellization (ΔG_{mic}) were determined

H. Akbaş (✉) · A. Elemenli · M. Boz
Department of Chemistry, Faculty of Sciences,
Trakya University, Edirne 22030, Turkey
e-mail: hakbas34@yahoo.com.tr

by means of electric conductivity measurements. In addition, a surfactant with m = 16 containing a *p*-xylylene spacer (–CH_2–C_6H_4–CH_2–), represented as 16-Ar (8)-16, was also examined. We compared the aggregation behavior and micellar properties of all these surfactants to study how their aggregation in aqueous solution is affected by both hydrophobic and spacer chain lengths of the surfactants.

It is widely recognized that the CMC is the most important parameter in studies dealing with the micellization of surfactants. Because the CMC value of a surfactant can be considered as a measure of the stability of the micellar form with regard to its monomeric form. Another important aspect is related to the thermodynamic studies of micellization. To obtain thermodynamic information on the micellization process, the CMC values of surfactants over a temperature range are used. The CMC values are usually determined from the abrupt change of a certain physical property over a very small concentration range.

Experimental

Materials

The monomeric cationic surfactants, dodecyl trimethyl ammonium bromide (DTAB, 98%) and hexadecyl trimethyl ammonium bromide (CTAB, 97%) were supplied by Merck and used without further purification. The original materials for the syntheses of the cationic geminis, alkanediyl-α-ω-bis(alkyldimethylammonium) bromides: 1-bromodecane (97%, Fluka), 1-bromododecane (95%, Fluka), 1-bromohexadecane (97%, Fluka), *N*,*N*,*N*′,*N*′-tetramethyl ethylene ediamine (98%, Fluka), 1,6-dibromohexane, (97%, Fluka), 1,10-dibromodecane, (95%, Fluka), *N*,*N*-dimethylhexadecylamine (98%, Fluka), were used without further purification. All solutions were prepared with double distilled water in an all-glass apparatus. The specific conductivity of this water was in the range of (1–2) × 10^{-6} S cm^{-1}.

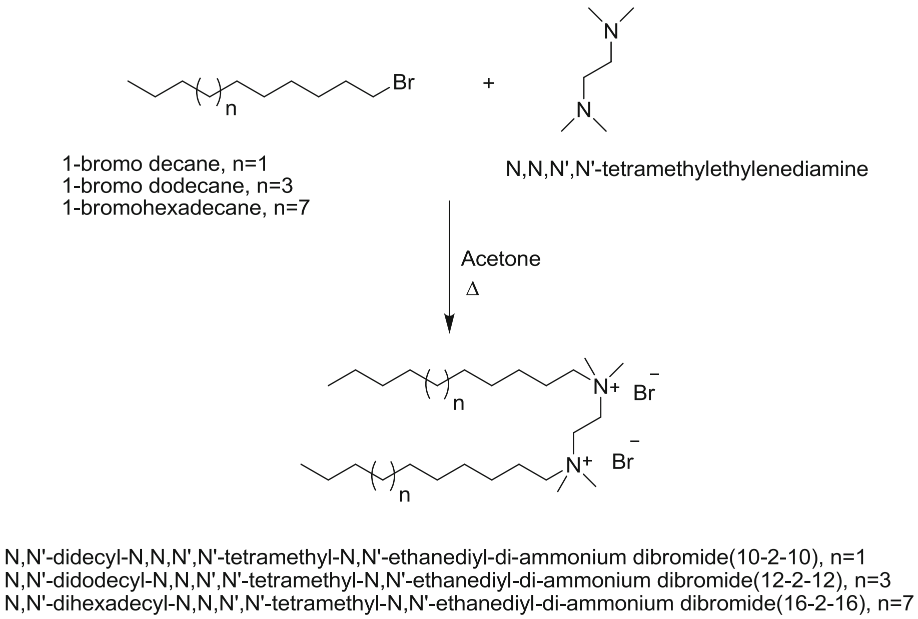
Synthesis Schemes

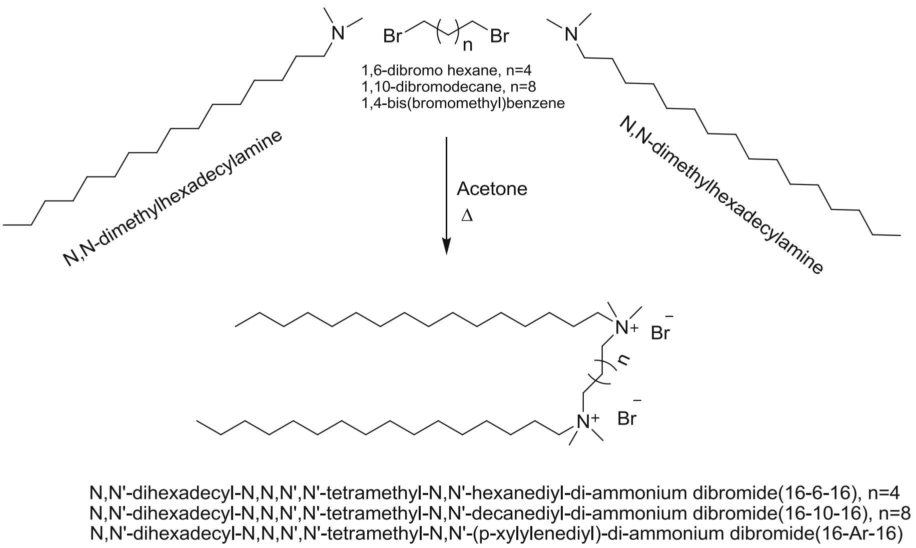
The cationic gemini surfactants were synthesized by using two different methods described by Zana et al. [12] (Schemes 1, 2). The preferred solvent for both methods was dry acetone [13]. The yields of the reaction were almost quantitative 90–97%. Surfactant purity was checked by nuclear magnetic resonance (NMR) and surface tension, all with excellent results. ^{1}H-NMR spectra were recorded in $CDCl_3$ solution with a Varian Mercury Plus 300 MHz spectrometer. ^{13}C-NMR spectra were recorded at 75 MHz.

Conductance Measurements

The conductance as a function of surfactant concentration was measured using a conductometer WTW Terminal 740 with a cell constant of 0.433 cm^{-1}. The conductometer was initially calibrated with standard KCl solutions in the appropriate concentration range. The experiments were performed at constant temperature by circulating water through a jacketed cell holding the solution under study. The experimental error in the temperature was minimized to ±0.1 °C.

Scheme 1 Synthesis procedure for gemini cationic surfactants types 10-2-10, 12-2-12 and 16-2-16





Scheme 2 Synthesis procedure for gemini cationic surfactants types 16-6-16, 16-10-16 and 16-Ar-16

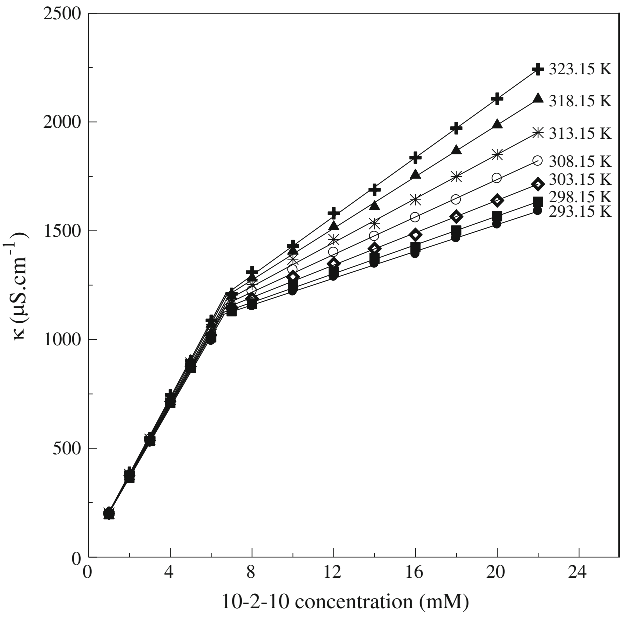


Fig. 1 Conductivity plots of (10-2-10) in pure water at different temperatures

Results and Discussion

Critical Micelle Concentration Determination

The CMC values of surfactant solutions were determined at sharp break points on specific conductivity versus concentration curves. Figure 1 depicts representative conductivity plots of 10-2-10 in pure water at seven temperatures ranging from 293.15 to 323.15 K. The increase of conductivity with concentration, which is observed for dilute solutions, is a direct result of the increasing number of free ions. The CMC values taken from Fig. 1 are given in Table 1. This table shows that the CMC of 10-2-10 increases insignificantly with temperature. The temperature effect on surfactants CMC in aqueous solution is usually a consequence of two opposite phenomena [14, 15]. First, as temperature increases, the degree of hydration of the hydrophilic groups decreases. This favors the aggregation process and micellization can occur at lower concentration. Second, with increasing temperature the breakdown of the structured water surrounding the hydrophobic group can occur. This does not favor micellization, as the low entropy of structured water is the key driving force of the self-association process. In addition, thermal motion also delays micellization [15, 16]. Here it seems that the second effect slightly predominates over the first in the narrow temperature range studied.

The conductivity values for other surfactant solutions were measured only at 303.15 K and the CMC values are given in Table 2. These values are in good agreement with reported values from the literature for 12-2-12, 16-2-16, 16-6-16, DTAB and CTAB. It can be seen from Table 2 that the micellization behavior of gemini surfactants is significantly different from that of conventional ones. Gemini surfactants have low CMC values compared with corresponding conventional surfactants of equivalent chain length. The CMC of 12-2-12 is about 15 times less than that of DTAB and that of 16-2-16 about 23 times less than that of CTAB (Figs. 2, 3). Doubling surfactant molecular weight decreases CMC values. This indicates that the studied dimeric species have a much better micelle-forming ability than single tail-single head ones, probably because the two hydrophobic chains of gemini surfactants break the water structure earlier and thus increase the tendency to form micelles.

The comparison of the results for the 10-2-10, 12-2-12 and 16-2-16 gemini surfactants shows that, as usually observed, CMC values decrease for longer alkyl chains

Table 1 Various micellization and thermodynamic parameters of (10-2-10) surfactant solutions at different temperatures

Temperature (K)	293.15	298.15	303.15	308.15	313.15	318.15	323.15
CMC (mmol/L)	6.62	6.63	6.65	6.67	6.69	6.70	6.71
Micelle ionization degree (α)	0.18	0.20	0.22	0.26	0.31	0.34	0.39
$-\Delta G^{0}_{\text{mic}}$ (kJ/mol)	58.1	58.2	58.3	57.4	55.9	55.4	53.8
$-\Delta G^{0}_{m,\text{tail}}$	29.1	29.1	29.1	28.7	28.0	27.7	26.9
$-\Delta H^{0}_{\text{mic}}$ (kJ/mol)	46.6	48.1	49.7	51.3	53.0	54.6	56.3
$T\Delta S^{0}_{\text{mic}}$ (kJ/mol)	11.6	10.1	8.5	6.0	3.0	0.7	−2.5

Table 2 Various micellization and thermodynamic parameters of m-s-m (s = 2, m = 10, 12 and 16 and m = 16, s = 2, 6, 10 and Ar(8)) surfactant solutions at 303.15 K

Surfactant	CMC (M)	Micelle ionization degree (α)	Gibbs free energy of micellization $\Delta G^{0}_{\text{mic}}$ (kJ/mol)	$\Delta G^{0}_{m,\text{tail}}$ (kJ/mol)
10-2-10	6.65×10^{-3}	0.22	−58.3	−29.1
12-2-12	9.6×10^{-4}	0.19	−71.4	−35.7
	9.3×10^{-4}[a]	0.19[a]		
	8.4×10^{-4}[b]	0.22[b]		
16-2-16	3.3×10^{-5}	0.18	−95.4	−47.7
	3.6×10^{-5}[c]	0.33[c]		
16-6-16	4.6×10^{-5}	0.39	−55.9	−27.9
	4.3×10^{-5}[b]	0.48[b]		
	4.6×10^{-5}[d]	–		
16-10-16	4.1×10^{-5}	0.37	−80.4	−40.2
16-Ar(8)-16	6.1×10^{-5}	0.47	−71.2	−35.6
DTAB	1.5×10^{-2}	0.31	−35.0	−35.0
	1.6×10^{-2}[a]	0.29[a]		
	1.6×10^{-2}[e]	0.28[e]		
CTAB	9.5×10^{-4}	0.32	−46.5	−46.5
	9.1×10^{-4}[e]	0.29[e]		

[a] Wang Y, Marques EF (2008) Non-ideal behavior of mixed micelles of cationic gemini surfactants with varying spacer length and anionic surfactants: A conductimetric study. J Mol Liquids 142:136–142

[b] From Ref. [12] at 298.15 K

[c] Junior PBS, Tiera VAO, Tiera MJ (2007) A fluorescence probe study of gemini surfactants in aqueous solution: a comparison between n-2-n and n-6-n series of the alkanediyl-a,w-bis (dimethyl alkyl ammonium bromides). Ecletica Quimica 32:47–54

[d] Khan IA, Khanam AJ, Khan ZA, Kabir-ud-Din (2010) Mixing behavior of anionic hydrotropes with cationic gemini surfactants. J Chem Eng Data 55:4775–4779

[e] Mata J, Varade D, Bahadur P (2005) Aggregation behavior of quaternary salt based cationic surfactants. Thermochimica Acta 428:147–155

(Table 2). These CMC values are quite different from each other. The stability of the m-2-m surfactant monolayer increases with the hydrophobic chain length, in direct relation to stronger hydrophobic interaction [17]. Due to their short spacer (–CH_2–CH_2–), the m-2-m double-headed dicationic surfactants bear a high charge density on their polar head (two ammonium cations close to each other). So, the proximity of alkyl chains in 12-2-12 greatly strengthens hydrophobic interaction, which results in small CMC [18]. As seen in Table 2 and Fig. 4, with increasing spacer length, the hydrophobic interaction is decreased and thus the CMC increases (here for 16-6-16 compared with 16-2-16), however remaining lower than that of CTAB. The maximum of CMC indicates a minimum stability of the surfactant in the micellar state. When the spacer is long enough (s = 10), it tends to bend towards the micellar core so as to reduce the Gibbs energy. By this way, the CMC decreases again. Therefore, the CMC of gemini surfactants is a non-monotonous function of the spacer length, with a maximum value around 6 methylene groups [12]. For 16-2-16 with short inter-charge spacer, the CMC values are only slightly lower than those of 16-6-16 and 16-10-16. As seen

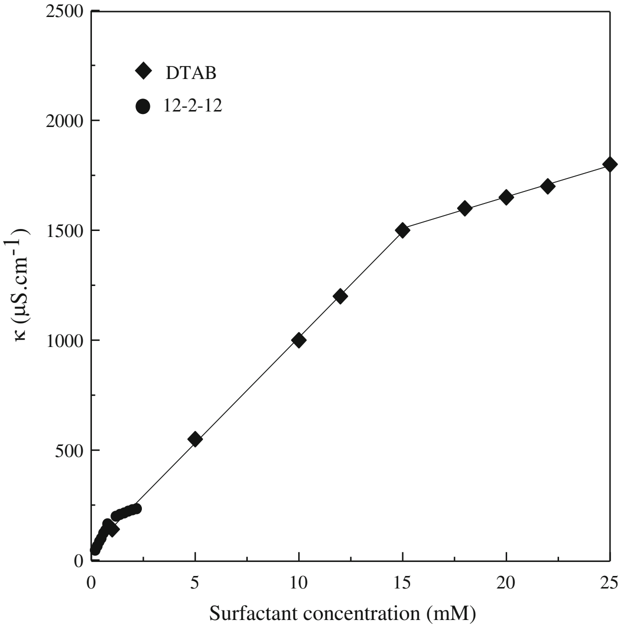


Fig. 2 Variation of the specific conductivity with concentration of 12-2-12 and DTAB solutions at 303.15 K

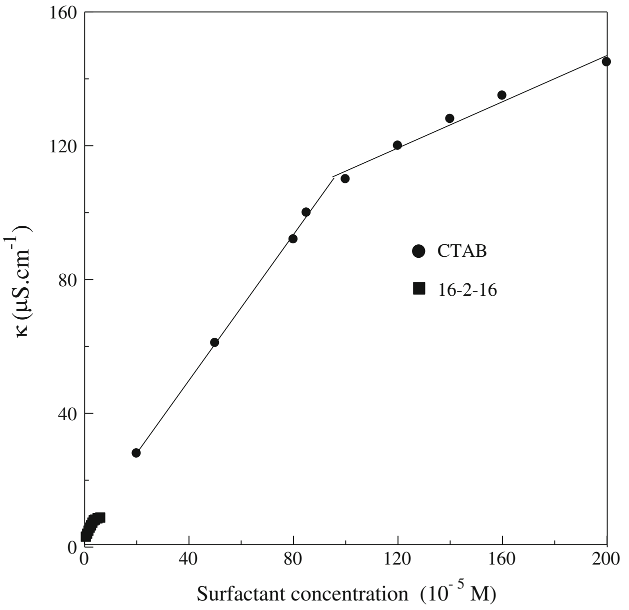


Fig. 3 Variation of the specific conductivity with the surfactant concentration for 16-2-16 and CTAB solutions at 303.15 K

as Table 2, CMC values depend significantly on the alkyl chain length and at a less important degree on the spacer chain length. Similar results have been found by Zana et al. [12] for a series of 12-s-12 (s = 2–16) at 25 °C.

If one considers that a benzene ring can be approximated as being equivalent to 3–3.5 methylene units in length, then the Ar(8) spacer is equivalent to 5–5.5 methylene units. The CMC of 16-Ar (8)-16 surfactant is found

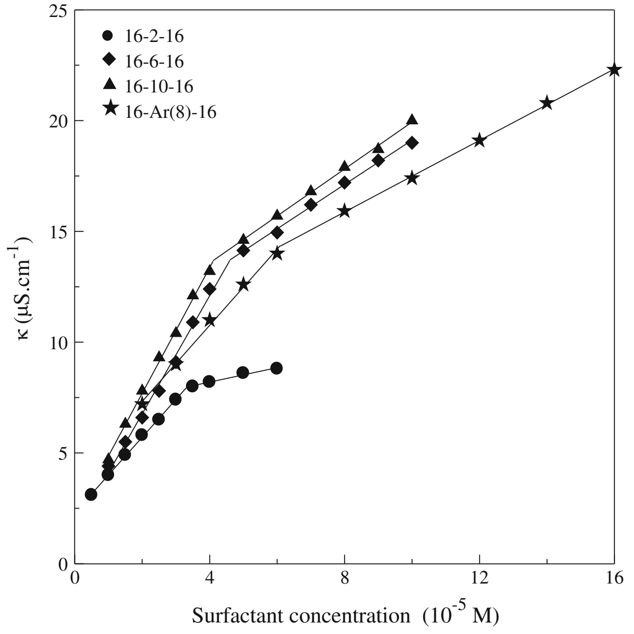


Fig. 4 Variation of the specific conductivity with the surfactant concentration for (16-s-16), s = 2, 4, 10 and Ar (8) solutions at 303.15 K

as 6.1×10^{-5} M, which is about 16 times smaller than that of CTAB. In fact, as expected, an aryl spacer is less hydrophobic than the corresponding alkyl one. Alternatively, it may be an indication of the packing arrangement of the corresponding surfactant at the air–water interface. That is to say, the interaction between surfactant monomers and the length and flexibility of spacer chain are the main factors that account for the behavior of the spacer [19, 20]. Similar observations have been made recently by researchers, who have examined both acetylenic spacers and the *p*-xylylene spacer [10, 13].

Micelle Ionization Degree (α)

In order to explain the aggregation behavior of gemini surfactants in aqueous solutions, the electric conductivity of these solutions was measured. As seen in Fig. 1, a temperature rise results in a conductivity increase, especially above the CMC. The pre-micellar slope ($S_1 = d\kappa/dC_{C>CMC}$) is always higher than the post-micellar one ($S_2 = d\kappa/dC_{C<CMC}$) and their ratio can be used for a rough evaluation of the micelle ionization degree ($\alpha = S_2/S_1$) [12, 21, 22].

The micelle ionization degree describes the number of counterions not bound to the micelle. The values of α for 10-2-10 at different temperatures are also given in Table 1. It can be seen that α increases from 0.18 to 0.39 as temperature rises from 293.15 to 323.15 K, Thus the degree of counterion binding to micelles β ($\beta = 1 - \alpha$) shows a trend to decrease with increase in temperature, suggesting that the binding of counterions to micellar surface is an exothermic process. Counterion binding is caused by an electrostatic interaction between opposite charges [23]. α values calculated for the dimeric and monomeric surfactant at constant temperature are listed in Table 2. They decrease gradually with increasing hydrophobic chain length.

According to the α values, we can obtain the β values as 0.72, 0.81 and 0.82 for 10-2-10, 12-2-12 and 16-2-16, respectively, at 303.15 K. All these values are larger than those corresponding to DTAB and CTAB (0.69 and 0.68, respectively). This suggests that, in (m-2-m) type surfactants, the binding ability of the Br^- counterion is stronger than in monomeric surfactants. The spacer may be responsible for this result. In (m-2-m) type surfactants, the hydrophilic head groups are closer to each other, resulting in a higher effective positive charge density on the micelle surface, thus increasing the attraction of counterions.

As mentioned before, with increasing spacer length, hydrophobic interaction is reduced: that is why CMC and micelle ionization degree increase: α is 0.18 for 16-2-16 and 0.39 for 16-6-16 (Table 2). Due to the above mentioned reason, when the spacer is long enough ($s = 10$), α decreases to a value (0.37) closer to that of CTAB (0.29–0.32).

Thermodynamics of Micellization

The temperature dependent values of CMC and α can be used to obtain information about the thermodynamics of micellization. The standard Gibbs free energies of micellization for ionic surfactants ($\Delta G^0_{\mathrm{mic}}$) were calculated from the relation derived for the charged phase separation model of micellization [22]:

$$\Delta G^0_{\mathrm{mic}}(\text{monomer}) = (2-\alpha)\,\mathrm{RT}\ln X_{\mathrm{CMC}} \qquad (1)$$

$$\Delta G^0_{\mathrm{mic}}(\text{dimer}) = (3-2\alpha)\mathrm{RT}\ln X_{\mathrm{CMC}} \qquad (2)$$

where X_{CMC} is the value of CMC expressed in mole fraction units ($X_{\mathrm{CMC}} = \mathrm{CMC}/(\mathrm{CMC} +$ number of moles of pure water)). The Gibbs energy of micellization per alkyl tail of dimeric surfactants ($\Delta G^0_{\mathrm{mic,tail}}$), was obtained according to $\Delta G^0_{\mathrm{mic,tail}} = \Delta G^0_{\mathrm{mic}}/2$. Table 2 summarizes both Gibbs energy values obtained by using Eqs. 1 and 2 for surfactants studied. As can be seen, Gibbs energy values were found to be negative in all the cases. At a constant temperature (303.15 K), $\Delta G^0_{\mathrm{mic}}$ decreases as the hydrophobic chain length increases, indicating that micellization is more spontaneous and that its driving force gets stronger due to hydrophobic interactions. It can be seen from Table 2 that the free energy value for 16-6-16 is much smaller than the others studied here. A very large decrease of—$\Delta G^0_{\mathrm{mic}}$ is observed in going from 16-2-16 to 16-6-16;

When the spacer is short enough, the free energy of micellization per chain of dimeric surfactant is the same as that for monomeric surfactants. This behavior reflects the fact that a short polymethylene spacer lies at the micelle/water interface [24], and does not contribute to the free energy of transfer. A different behavior is expected for a long spacer which folds into the micelle hydrophobic core.

On the other hand, the standard enthalpy change for the micellization of 10-2-10, $\Delta \mathrm{H}^0_{\mathrm{mic}}$ can be calculated by applying the Gibbs–Helmholtz equation to Eq. 2

$$\Delta \mathrm{H}^0_{\mathrm{mic}} = -\mathrm{RT}^2\left[(3-2\alpha)\left(\frac{\partial \ln \mathrm{X_{cmc}}}{\partial \mathrm{T}}\right)_P - \ln \mathrm{X_{cmc}}\left(\frac{\partial \alpha}{\partial \mathrm{T}}\right)_P\right] \qquad (3)$$

The values of $\ln X_{\mathrm{CMC}}$ were plotted against temperature, T. As seen in Fig. 5 a linear plot is obtained, whose slope is $\mathrm{d}\ln X_{\mathrm{CMC}}/\mathrm{dT}$,

The standard entropy values of micelle formation, $\Delta S^0_{\mathrm{mic}}$, were evaluated from the calculated $\Delta \mathrm{H}^0_{\mathrm{mic}}$ and $\Delta G^0_{\mathrm{mic}}$ values as follows:

$$\Delta S^0_{\mathrm{mic}\propto} = \frac{\Delta \mathrm{H}^0_{\mathrm{mic}} - \Delta G^0_{\mathrm{mic}}}{\mathrm{T}} \qquad (4)$$

The values of $\Delta G^0_{\mathrm{mic}}$, $\Delta G^0_{\mathrm{mic,tail}}$, ΔH^0_m, and $T\Delta S^0_{\mathrm{mic}}$, obtained by using above equations for 10-2-10 are listed in Table 1 and also the values of $\Delta G^0_{\mathrm{mic}}$, $\Delta G^0_{\mathrm{mic,tail}}$ for all surfactants studied here are listed Table 2. The $\Delta \mathrm{H}^0_{\mathrm{mic}}$ values are always negative, indicating that the micelle formation process is exothermic. Nusselder and Engberts [25] suggested that for the negative $\Delta \mathrm{H}^0_{\mathrm{mic}}$, dispersion forces play a major role in micelle formation. The

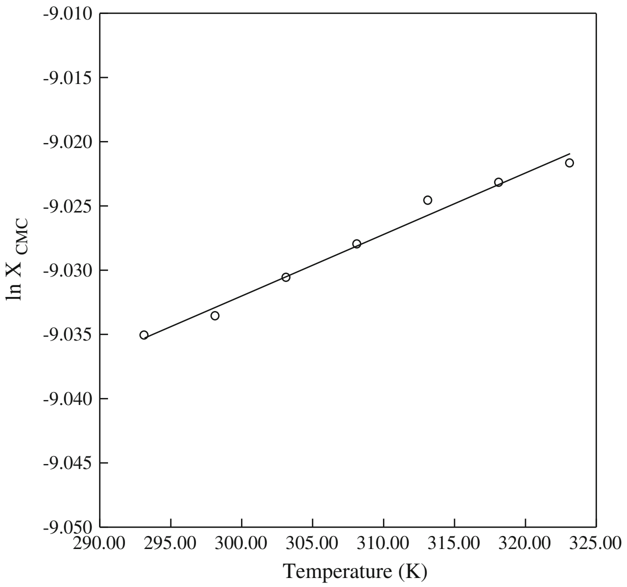


Fig. 5 Plots of $\ln X_{\mathrm{CMC}}$ versus temperature for 10-2-10 in water

ΔH^0_{mic} values do not vary significantly with temperature, indicating no significant variation in the environment surrounding the hydrophobic chain of the surfactant molecule with increasing temperature.

The ΔH^0_{mic} values for the gemini surfactants studied are more negative than those of the corresponding monomeric surfactants. These trends are similar to those found for the hydrophobic gemini surfactant 12-2-12 and the corresponding monomeric surfactant DTAB [12, 26]. In our previous study, we investigated the thermodynamic parameters of hexadecyltrimethylammonium bromide (CTAB) and dodecylpyridinium chloride (DPC) micellization in pure water and different cosolvents at different temperatures [27, 28]. The smallest enthalpy values were -13.1 kJ mol^{-1} for CTAB and -29.7 kJ mol^{-1} for DPC at 303.15 K. This difference in CMC and ΔH^0_{mic} between gemini and the corresponding monomeric surfactants mostly arise from the number of hydrophobic chains transferred from the aqueous phase to the micelle core.

It can be seen from Table 1 that the entropy values relative to 10-2-10 are positive over the whole temperature range studied, except at 323.15 K and that these values decrease with an increase in temperature. This decrease in entropy indicates that the tendency of micellization reduces at higher temperature. Also, the enthalpy of micellization is negative and becomes more negative with an increase in temperature. $T\Delta S^0_{mic}$ values are smaller than ΔH^0_{mic} values. So, the negative values of ΔG^0_{mic} are mainly due to ΔH^0_{mic}. With increasing temperature, the contribution of entropy to micelle formation becomes less with a sign change in the range from 318.15 to 323.15 K. The micelle formation process for 10-2-10 is enthalpy—entropy driven at low temperatures (the enthalpic contribution is 4 times larger than the entropic contribution) and enthalpy-controlled at high temperature. In our previous work, the study of the thermodynamic parameters of DPC indicated that its micellization is enthalpically controlled [28].

Conclusions

Gemini surfactants are superior in their properties and show better performance over conventional surfactants. While the CMC values of gemini surfactants decrease significantly with increasing alkyl chain length, those values change to a lesser degree with the spacer chain length but are still lower than those of the corresponding monomeric surfactants. At a constant temperature (303.15 K), ΔG^0_{mic} decreases as the hydrophobic chain length increases, indicating that micellization is more spontaneous and that a profound driving force due to hydrophobic interactions. The values of ΔH^0_{mic} show that the micellization of gemini surfactants is exothermic at all the temperatures studied. Micelle formation process for the 10-2-10 gemini surfactant is enthalpy-driven.

References

1. Sulthana SB, Rao PVC, Bhat SGT, Nakana TY, Sugihara G, Rakshit AK (2000) Solution properties of nonionic surfactants and their mixtures: polyoxyethylene (10) alkyl ether (C_nE_{10}) and MEGA-10. Langmuir 16:980–987
2. Akbaş H, İşcan M (1994) Effect of added salt on the solubilization of Sudan Red B in surfactant solution. Turk J Chem 18:80–83
3. Ribe J, Cegarra J, Aizgurua L (1983) The influence of ionic surface-active agents on the dyeing of Hercosett wool with α-bromoacrylamide dyes. Soc Dyers Colour 99:374–382
4. Sudbeck EA, Dubin PL, Curran ME, Skelton J (1991) Dye solubilization in polyelectrolyte-micelle complexes. J Colloid Interface Sci 142:512–517
5. Zana R (1998) Novel surfactants. In: C Holmberg (ed) vol 8, p 241. Dekker, New York
6. Rosen MJ (1993) Geminis: a new generation of surfactants. Chemtech 23:30–33
7. Swenson S (2004) Controlling surfactant self-assembly. Curr Opin Colloid Interface Sci 9:201–212
8. Menger FM, Keiper JS (2000) Gemini surfactants. Angew Chem Int Ed 39:1906
9. Fletcher PD (1996) Self-assembly of micelles and microemulsions. Curr Opin Colloid Interface Sci 1:101–106
10. Wetting SD, Verrall RE (2001) Thermodynamic studies of aqueous m–s–m gemini surfactant systems. J Colloid Interface Sci 235:310–316
11. Akbas H, Boz M, Batıgöç Ç (2010) Study on cloud points of Triton X-100-cationic gemini surfactants mixtures: a spectroscopic approach. Spectrochimica Acta A 75:671–677
12. Zana R, Benraou R, Rueff R (1991) Alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactants. 1. Effect of the spacer chain length on the critical micelle concentration and micelle ionization degree. Langmuir 7:1072–1075
13. Menger FM, Keiper JS, Azov V (2000) Gemini surfactants with acetylenic spacers. Langmuir 16:2062–2067
14. Chen L, Shi-Yow L, Chiung-Chang H, En-Ming C (1998) Temperature dependence of critical micelle concentration of polyoxyethylenated non-ionic surfactants. Colloid Surf A 135:175–181
15. Hunter RJ (1989) Foundations of colloid science. Oxford University Press, New York
16. Hiemenz PC, Rajagopalan R (1997) Principles of colloid and surface chemistry. Marcel Dekker, New York
17. Wang Y, Marques EF, Pereira CM (2008) Monolayers of gemini surfactants and their catanionic mixtures with sodium dodecyl sulfate at the air–water interface: chain length and composition effects. Thin Solid Films 516:7458–7466
18. Danino D, Talmon Y, Zana R (1995) Alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactants (dimeric surfactants). 5. aggregation and microstructure in aqueous solutions. Langmuir 11:1448–1456
19. Diamant H, Andelman D (1994) Dimeric surfactants: spacer chain conformation and specific area at the air/water interface. Langmuir 10:2910–2916
20. Diamant H, Andelman D (1995) Dimeric surfactants: a simplified model for the spacer chain. Langmuir 11:3605–3606

21. Chlebicki J, Wegrzynska J, Wilk KA (2008) Surface-active, micellar, and anti electrostatic properties of bis-ammonium salts. J Colloid Interface Sci 323:372–378
22. Zana R (1996) Critical micellization concentration of surfactants in aqueous solution and free energy of micellization. Langmuir 12:1208–1211
23. Inoue T, Ebina H, Dong B, Zheng LQ (2007) Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution. J Colloid Interface Sci 314:236–241
24. Alami F, Beinert G, Marie P, Zana R (1993) Alkanediyl-α,ω-bis(dimethyl alkyl ammonium bromide) surfactants. 3. Behavior at the air-water interface. Langmuir 9:1465–1467
25. Nusselder JJH, Engberts JFN (1992) Toward a better understanding of the driving force for micelle formation and micellar growth. J Colloid Interface Sci 148:353–361
26. Grosmaire L, Chorro M, Chorro C, Partyka S, Zana R (2002) Alkanediyl-α,ω-bis(dimethyl alkyl ammonium bromide) surfactants 9. Effect of the spacer carbon number and temperature on the enthalpy of micellization. J Colloid Interface Sci 246:175–181
27. Akbaş H, Kartal Ç (2006) Conductometric studies of hexadecyltrimethylammonium bromide in aqueous solutions of ethanol and ethylene glycol. Colloid J 68:125–130
28. Akbaş H, Batığöç Ç (2008) Micellization of dodecylpyridinium chloride in water–ethanol solutions. Colloid J 70:127–133

Author Biographies

Halide Akbaş is an associate professor of physical chemistry, in the chemistry department at Trakya University. She graduated from the Technical University of Istanbul and received her Ph.D. at Trakya University in 1993. Her research area focuses on novel surfactants, their thermodynamic properties and interactions, and surface chemistry.

Aylin Elemenli was a master student in physical chemistry, in the chemistry department at Trakya University. She received her master's degree in 2010 from this university. Her research focuses on dimeric surfactants and their interaction with dyes.

Mesut Boz is an assistant professor of organic chemistry, in the chemistry department at Trakya University. He received his M.Sc. in 1996 and his Ph.D. in 2005 at this University. His main research interests are in organic synthesis, characterization, spectroscopy, and recently, dimeric surfactants.