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Thermochimica Acta 434 (2005) 165–170

thermochimica acta

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Microcalorimetric studies of cationic gemini surfactant with a hydrophilic spacer group

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Received 20 August 2004; received in revised form 12 January 2005; accepted 20 January 2005
Available online 15 February 2005

Abstract

The aim of this work is to investigate the micellization thermodynamics for gemini surfactants with a hydrophilic spacer group, i.e. Br^- n-$C_{12}H_{25}N^+Me_2$—$CH_2(CH_2OCH_2)_xCH_2N^+Me_2$—$n$-$C_{12}H_{25}$ Br^-, referred to as 12-EO$_x$-12, where $x = 1, 3, 6, 7$. These oligooxaalkanediyl-α,ω-bis(dimethyldodecylammonium bromide) dimeric surfactants were synthesized by a two step reaction. Their physicochemical properties in aqueous solutions have been studied by microcalorimetry at 298 K, electrical conductivity and surface tension measurements. The critical micellar concentration (cmc) and the head-group area (a_0) per molecule at the air–water interface increase with increasing number of oxide ethylene moieties in the spacer and, consequently, with the enhanced hydrophilic character of the molecule. The calorimetric studies of the self-assembly process confirm this trend, since the exothermic values of the differential enthalpy of micellization ($\Delta_{mic}H^\circ$) decrease as the ethylene oxide moieties are lengthened. Moreover, the values of the free energy and entropy of micellization indicate an entropy driven phenomenon for all surfactants. These results are compared with those obtained for gemini cationic surfactants with a hydrophobic spacer and the differences observed are discussed in terms of the hydrophilic head-group conformation in the micelle.

Keywords: Gemini surfactants; Microcalorimetry; Thermodynamics of micellization

1. Introduction

Dimeric (gemini) surfactants and, generally, oligomere surfactants have been found to exhibit behaviour in aqueous solution significantly different from that of the corresponding monocationic compounds [1]. These surfactants provide a unique opportunity to control the aggregation behaviour in aqueous solution by the chemical nature of the spacer group linking the two head-groups together [2,3]. The evolution of the interfacial properties of dimeric surfactants with the nature of the spacer group (chemical structure, length, flexibility) is currently extensively studied in our laboratory in view of their possible use in specific detergency formulations.

The thermodynamics of micellization process for gemini cationic surfactants with a hydrophilic spacer group, made up of two hydrophobic chains and two polar head-groups connected covalently through a hydrophilic polyoxyethylene spacer, Br^- n-$C_{12}H_{25}N^+Me_2$–$CH_2(CH_2OCH_2)_xCH_2$ N^+Me_2–n-$C_{12}H_{25}$ Br^-, has been investigated in this work. These surfactants are referred to as 12-EO$_x$-12 with $x = 1, 3, 6, 7$ being the number of oxyethylene moieties. The aggregation properties of this new class of surfactants were recently reported [4,5] for the smallest spacer groups $x = 1, 2, 3$. The authors discussed their results with particular emphasis on the effect of the length spacer on the hydrophilic character of the spacer group and, consequently, on its conformation within the micelle.

In the present work, the emphasis is on the micellization properties of gemini homologue with long spacer groups. The calorimetric measurements of the dilution enthalpy were performed at 298 K using a batch microcalorimeter "Calostar". The free energies of micellization ($\Delta_{mic}G^\circ$) and the entropies of micellization ($\Delta_{mic}S^\circ$) were calculated in order to give

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doi:10.1016/j.tca.2005.01.034

a better insight on the micellization of the 12-EO$_x$-12 surfactants. This thermodynamic study has been completed by surface tension and electrical conductivity measurements at 298 K. The aggregation behaviour of these surfactants in aqueous solution is compared with that of the corresponding gemini cationics possessing a hydrophobic spacer.

2. Experimental procedures

2.1. Materials

All the reagents and solvents were commercial products of high purity and used purified, dried or freshly distilled as required. Phosphorus tribromide, poly(ethylene glycol) and *N*,*N*-dimethyldodecylamine were purchased from Aldrich Chemical Co.

The water used throughout the experiments was deionized and purified with a Millipore Super Q System.

2.2. Surfactant synthesis

The four 12-EO$_x$-12 gemini surfactants investigated, with x = 1, 3, 6, and 7, were synthesized by a two step reaction (a, b) as indicated in Fig. 1. All the surfactants (III) were obtained by the quaternization of the appropriate α,ω-dibromoalkoxyalkanes(II) with the *N*,*N*-dimethyldodecylamine in dry EtOH at 80 °C for 72 h [4]. The dibromo precursors (II) were synthesized by the addition of PBr_3 to the individual diol (I) at 0 °C. Then the mixture was stirred for 12 h at 60 °C. The purity of all dibromide precursors (II) was confirmed by ^{1}H NMR spectra in $CDCl_3$ (250 MHz) and electrospray ionization (ESI) mass spectrometry. Purification of the product III was performed by a repeated crystallization from acetone. Their purity and the previously established structure were ascertained by ESI and ^{1}H NMR spectra in $CDCl_3$ (250 MHz).

2.3. Characterization methods

The critical micellization concentration (cmc) of the synthesized surfactants was determined by measuring both the electrical conductivity and the surface tension of surfactant solutions. The measurements were performed at 25 ± 0.1 °C using a Multilab 540 conductimeter. The micelle ionization degree (α) at the cmc was determined as the ratio of the slopes of the plots above and below the cmc using the method of Evans [6].

The surface tension was measured at 298 K by the Wilhelmy plate method using a Krüss digital tensiometer K 12. From the plot of γ versus the logarithm of the surfactant concentration, the surface excess concentration Γ was determined, using the following Gibbs equation

$$\Gamma = \left(\frac{-3}{2.3nRT}\right)\left(\frac{d\gamma}{d(\log c)}\right)_T \qquad (1)$$

where $R = 8.32\ \mathrm{J\,mol^{-1}\,deg^{-1}}$, $T = 298$ K, with γ expressed in $\mathrm{Nm^{-1}}$, and n being the sum of the charge numbers of all ions resulting from the ionization of the surfactant molecule ($n = 3$ for the gemini surfactants). The cross-sectional area of one surfactant head group, a_0, was calculated from the maximum value of the surface excess of Γ_m, using the following equation

$$a_0 = (N_A \Gamma_m)^{-1} \qquad (2)$$

with N_A the Avogadro number.

The cmc was taken as the concentration at the point of intersection of the two linear portions of the $\gamma = f(\log c)$ plots.

2.4. Calorimetric experimental procedure

The differential molar enthalpies of dilution ($\Delta_{dil}H$) were determined using a Calostar microcalorimeter, which was described previously [7,8]. The Calostar microcalorimeter is perfectly adapted to studies on dilution, micellization and adsorption. For dilution, the experimental procedure for measuring $\Delta_{dil}H$ consists of filling up the calorimetric cell with water and the syringe with a micellar stock solution of the surfactant. Once the calorimeter reaches the thermal equilibrium (around 12 h), one aliquot of the stock solution is injected into the calorimeter cell. The dilution equilibrium is attained instantaneously and the resulting endothermic effect is recorded. After return to the base line, another injection can be made and this procedure is repeated until the equilibrium concentration in the calorimetric cell is higher than the cmc. The differential molar enthalpies of dilution are determined by integrating the endothermic peaks and comparing them with the calibration peaks obtained by the Joule effect procedure.

3. Results

The variations of the electrical conductivity K with the concentration C of the 12-EO$_x$-12 surfactants studied here are shown in Fig. 2. The plots of K versus C show a break corresponding to the critical micellar concentration (cmc). The

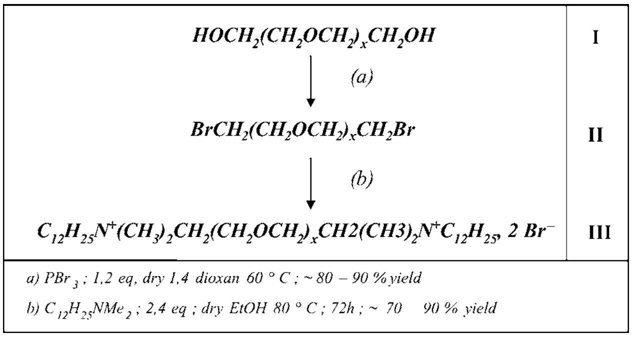

Fig. 1. The chart-flow of the synthesis of gemini surfactant.

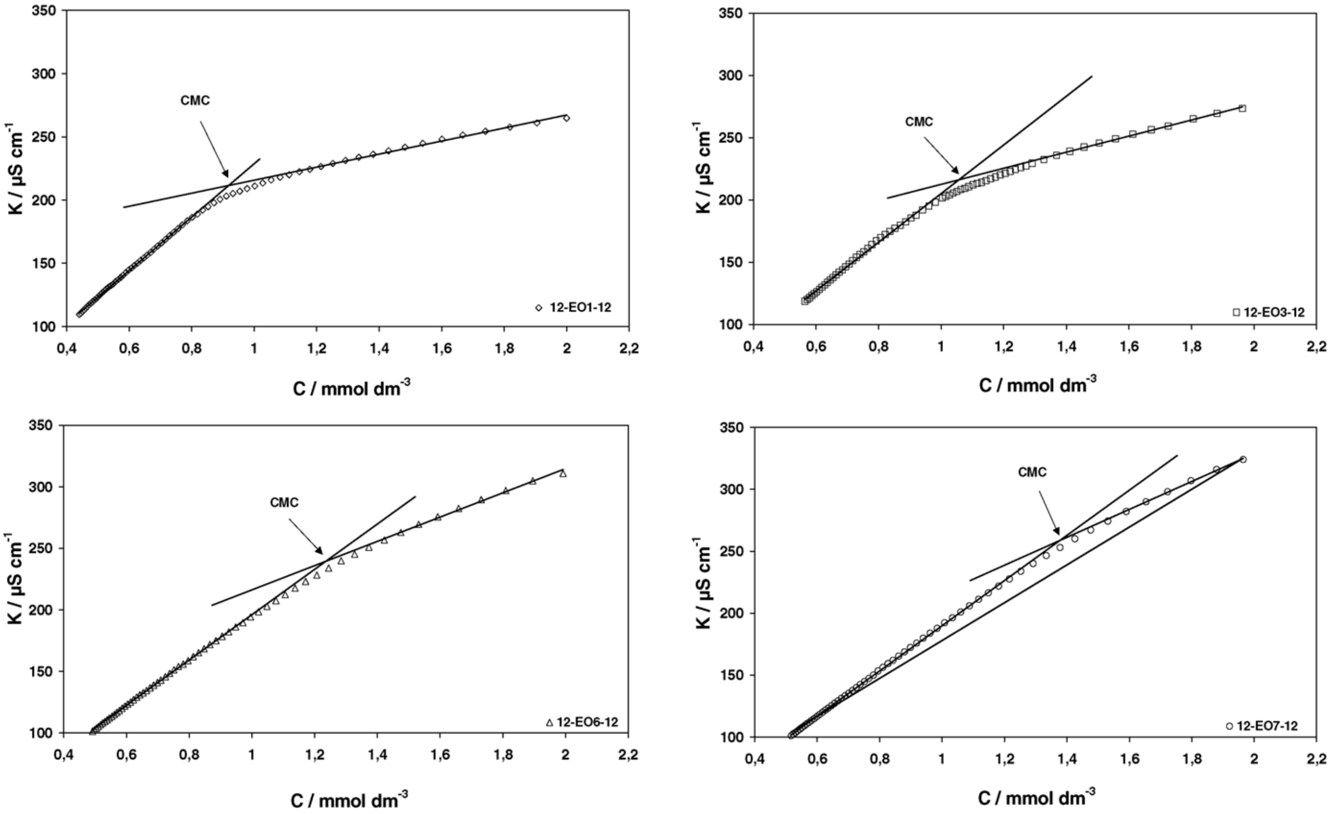

Fig. 2. Variations of the electrical conductivity (K) with the surfactant concentration (C) for 12-EO$_x$-12 surfactants at 298 K.

electrical conductivity K increases linearly with the surfactant concentration below and above the cmc. The two linear segments correspond to the monomeric and aggregate forms of the surfactant. The cmc and α values obtained from electrical conductivity measurements together with the cmc and the surface area per molecule at the air–water interface obtained from surface tension measurements are listed in Table 1.

The values of cmc, α and a_0 within the 12-EO$_x$-12 surfactant series increase with the oxyethylene number, x, in the spacer. This behaviour is consistent with the increase in the hydrophilic character of the spacer group [5].

Fig. 3 presents the variations of the differential molar enthalpy of dilution ($\Delta_{\rm dil}H$) at 298 K with the surfactant concentration C in the calorimetric cell corresponding to the successive injections of a micellar stock solution of a given 12-EO$_x$-12 surfactant. $\Delta_{\rm dil}H$ is always positive indicating an endothermic process in the whole range of concentration. The three ranges observed in Fig. 3 were previously discussed for conventional and gemini surfactants [7]. At low concentrations, each injection produces a nearly constant endothermic effect, $\Delta_{\rm dil}H_1$, which results from the dissociation of all micelles injected in the calorimetric cell and from the dilution of the monomer units. In the second region, the dilution enthalpies show a rapid decrease. This transition region corresponds to the cmc range. Here the addition of stock solution aliquots gives rise to changes in the aggregate distribution, involving both their size and their number. At concentrations higher than the cmc, each injection gives a nearly constant and weakly endothermic effect, $\Delta_{\rm dil}H_3$, which results

Table 1
Critical micellar concentration (cmc), micelle ionization degree (α), head group surface area (a_0) at 298 K

Surfactants	cmc[a] (mmol dm^{-3})	cmc[b] (mmol dm^{-3})	α[a]	a_0 (Å^2 molecule^{-1})
12-EO$_1$-12	0.92	0.95	0.24	109
12-EO$_3$-12	1.06	1.02	0.33	137
12-EO$_6$-12	1.23	1.49	0.53	162
12-EO$_7$-12	1.38	1.58	0.62	189

[a] From specific conductance measurements.
[b] From surface tension measurements.

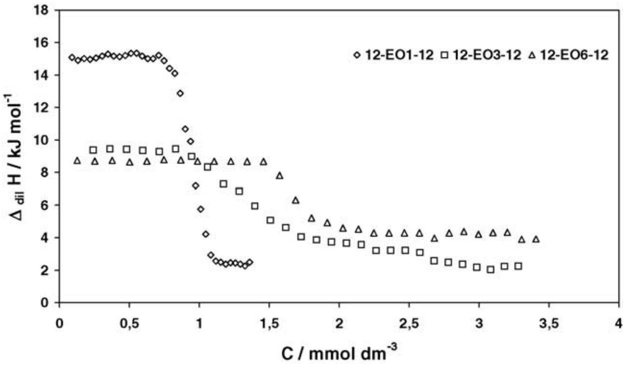

Fig. 3. Variations of the differential molar enthalpy of dilution for 12-EO$_x$-12 surfactants 298 K.

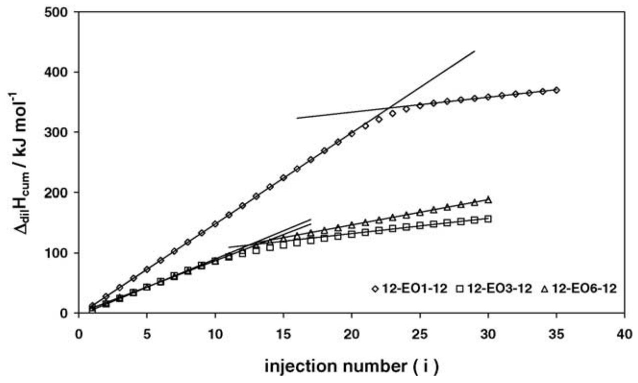

Fig. 4. Molar cumulative enthalpies of dilution for 12-EO$_x$-12 surfactants at 298 K.

from the dilution of the stock micellar solution into the micelle-containing solution inside the calorimetric cell.

The same behaviour is observed in Fig. 3 for other surfactants with a longer spacer group. However, the endothermic dilution enthalpy decreases as the number of EO moieties in the spacer increases and this effect becomes athermal for the 12-EO$_7$-12 surfactant.

Fig. 4 shows the cumulative molar enthalpies of dilution for the 12-EO$_x$-12 surfactant series determined from the dilution calorimetric measurements. This representation usually gives a change of the slope at the cmc. A new analysis of such data, recently proposed in [9], allows to calculate easily the enthalpy of micellization per mole of 12-EO$_x$-12, $\Delta_{\text{mic}}H^{\circ}$, and the cmc value. The plot of $\Delta_{\text{dil}}H_{\text{cum}}$ as a function of the injection number, i, is composed of two linear parts, their slopes providing the constant values of the apparent molal enthalpy of the surfactant in the premicellar and postmicellar regions. Within the framework of the pseudo-phase transition model, the micellization enthalpy is calculated straight from the difference between these two slopes. The intersection between the linear parts of the $\Delta_{\text{dil}}H_{\text{cum}}$ plot allows the cmc determination using the following equation [9]:

$$\text{cmc} = \frac{10^3 n_2^{\text{inj}} i_{\text{cmc}}}{m_0 + n_2^{\text{inj}} i_{\text{cmc}}/m_2^0} \tag{3}$$

where m_0 is the mass of the water initially placed in the calorimetric cell, m_2^0 is the molality of the stock solution; i_{cmc} is the number of injections necessary to attain the cmc corresponding to the intersection of the two linear parts; and n_2^{inj} is the number of moles of the surfactant solute injected into the calorimetric cell during each injection (n_2^{inj} was constant in all calorimetry experiments).

The values of $\Delta_{\text{mic}}H^{\circ}$ reported in Table 2, for surfactants with a spacer containing less than 7 EO moieties, are negative indicating that micelle formation is an exothermic process. The micellization enthalpy for the 12-EO$_7$-12 surfactant is close to zero indicating that the micellization process is entropy driven. The values of the free energy of micellization, $\Delta_{\text{mic}}G^{\circ}$, and those of the entropy of micellization, $\Delta_{\text{mic}}S^{\circ}$, give additional information on the thermodynamics of micellization of 12-EO$_x$-12 surfactants. These values (expressed in J per mole of the surfactant) can be obtained from the following equations:

Table 2
Thermodynamic properties of micellization at 298 K for the 12-EO$_x$-12 surfactant series

Surfactant	cmc[a] (mmol dm^{-3})	$\Delta_{\text{mic}}H^{\circ}$ (kJ mol^{-1})	$\Delta_{\text{mic}}G^{\circ}$ (kJ mol^{-1})	$T\Delta_{\text{mic}}S^{\circ}$ (kJ mol^{-1})
12-EO$_1$-12	0.93	−12.6	−43.63	31.03
12-EO$_3$-12	1.28	−6.9	−39.7	32.8
12-EO$_6$-12	1.45	−4.5	−32.2	27.7
12-EO$_7$-12	–	0	−28.7	28.7

[a] Calculated from cumulative enthalpies of dilution.

$$\Delta_{\text{mic}}G^{\circ} = 2RT(1.5 - \alpha)\ln(\text{cmc}) \tag{4}$$

$$T\Delta_{\text{mic}}S^{\circ} = \Delta_{\text{mic}}H^{\circ} - \Delta_{\text{mic}}G^{\circ} \tag{5}$$

The calculation of $\Delta_{\text{mic}}G^{\circ}$ requires the value of the micelle ionization degree α. The calculated values of α from the electrical conductivity are given in Table 1. The α values increase with lengthening the spacer. The values of $\Delta_{\text{mic}}G^{\circ}$ and $T\Delta_{\text{mic}}S^{\circ}$ calculated using Eqs. (4) and (5) are listed in Table 2. For all the surfactants investigated, $T\Delta_{\text{mic}}S^{\circ} > -\Delta_{\text{mic}}H^{\circ}$ indicating that the micellization process within the 12-EO$_x$-12 surfactant series is entropy driven.

4. Discussion

The chemical nature, structure and length of the spacer group of gemini surfactants is an essential feature in determining their behaviour in solution. The thermodynamic and aggregation properties in aqueous solution of gemini surfactants with a hydrophobic alkanediyl spacer, 12-s-12, were previously reported [8,10,11]. The variations of the cmc values and those of the molar enthalpy of micellization with the number of carbon atoms in the spacer were explained in terms of micelle structure modification, increase in the spacer length involving its location and conformation in the micelle. For small and medium spacers, $s < 10$, $\Delta_{\text{mic}}H^{\circ}$ was less and less exothermic despite the cmc values passing through a maximum for $s = 4$ and decreasing for $s > 4$. It was also stated that the spacer may not be long enough to be inserted into the hydrophobic micelle core and therefore it could be located only in the micelle palisade in contact with aqueous phase [11,12]. In this conformation, the micelle was more easily hydrated and the micelle formation less exothermic. For long spacers, $s > 10$, the cmc strongly decreased and the micellization enthalpy was more exothermic. In this case, the spacer was flexible enough to partly penetrates into the hydrophobic core of the micelles, decreasing the hydratation of the alkyl tails.

Table 3
Thermodynamic properties of micellization at 25 °C for the 12-*s*-12 surfactant series from reference [7]

Surfactants	cmc (mmol dm^{-3})	a_0 (Å^2 molecule^{-1})	$\Delta_{\text{mic}}H^\circ$ (kJ mol^{-1})	α	$\Delta_{\text{mic}}G^\circ$ (kJ mol^{-1})	$T\Delta_{\text{mic}}S^\circ$ (kJ mol^{-1})
12-2-12	0.84	72	−22	0.16	−47.3	25.3
12-4-12	1.17	117	−9.3	0.16	−45.1	35.8
12-6-12	1.03	140	−8.5	0.20	−44.6	36.1
12-8-12	0.83	176	−9.0	0.25	−44.2	35.2
12-10-12	0.63	217	−11.6	0.26	−45.5	33.9
12-12-12	0.37	223	−12.2	0.31	−46.8	34.6

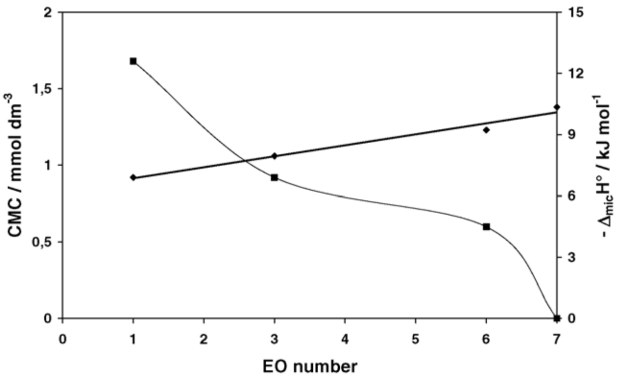

Fig. 5. Variations of the cmc and those of the micellization enthalpy as functions of the number of EO units in the spacer group.

4.1. *Influence of the spacer length and comparison of the aggregation properties for the 12-EO$_x$-12 and the 12-s-12 series.*

Fig. 5 shows the variation of the cmc values and the molar enthalpy of micellization for the 12-EO$_x$-12 surfactant series at 298 K in function of the spacer length *x*. This representation facilitates the comparison of the different plots, as the cmc and $\Delta_{\text{mic}}H^\circ$ depend on the spacer group. The cmc increases linearly with the number of oxyethylene moieties in the spacer group. This suggests that the location of the hydrophilic spacer is independent of the oxyethylene number, contrary to the behaviour of 12-*s*-12 surfactants. Indeed, for 12-*s*-12 surfactants with a long hydrophobic spacer, $s > 10$, the spacer group is flexible enough to partly penetrates into the hydrophobic core of the micelle. As a result, the cmc of the 12-*s*-12 series strongly decrease for spacers longer than 10 methylene units (Table 3). Furthermore, the increase in the cmc is associated with the head-group size and the effective micelle charge (Table 1). However, the surface areas obtained in the present work are smaller than those previously reported for the 12-*s*-12 series (Table 3), although the hydrophobic spacers containing methylene groups are shorter. This may suggest that the hydrophilic spacer with oxyethylene moieties is not fully extended at the air–water interface. Moreover, in order to obtain this closer packing, much energy is needed to overcome the electrostatic repulsion, as the two linked ammonium head-groups are closer. Notify that the interaction between the ethylene oxide group and water molecules does not exist in the case of gemini surfactants with a hydrophobic spacer. Therefore, this hydrophilic spacer is flexible enough to penetrate into the water phase, as was assumed by Wettig et al. [5], the effect being more pronounced when increasing the spacer length.

Decrease in the exothermic effect of micellization with increasing number of EO moieties (Fig. 5) is consistent with the enhanced hydrophilic character of the surfactant molecule and, consequently, the micelles formed are more hydrated. The results obtained for the longest spacer confirm the behaviour described by Wettig et al. [5] for shorter spacers (12-EO$_{1\text{–}3}$-12). It is interesting to note that similar trends in $\Delta_{\text{dil}}H$ with spacer length was monitored for zwitterionic surfactants of the [(dodecyldimethylammonium)alkyl] phenylphosphinate type [13]. The micellization phenomenon was found to be endothermic for intercharge chains containing 3 and 6 methylene units and athermal for the spacer with 10-CH$_2$ groups. The addition of methylene groups to the chain separating charged centers increased the polarity of the functional group. Long and flexible intercharge groups were postulated to penetrate into hydrophobic micellar core, thereby reducing both hydration number and repulsive dipole–dipole interactions.

The enthalpy of micellization equal to zero for the surfactant 12-EO$_7$-12 suggests that the enthalpy of micellization in the present case could result from two opposite contributions. The first one is an exothermic effect corresponding to the partial dehydration of the cationic part (the alkyl chains and the polar head) transferred from the aqueous environment to the micelle. The second contribution is an endothermic effect resulting from the partial dehydration of the oligo(oxyethylene) group in the spacer, as was reported and discussed for nonionic surfactants [14]. Moreover, the values of the $\Delta_{\text{mic}}S^\circ$ given in Table 2 for the four surfactants studied in the present work are roughly constant. As the hydrophobic tails are the same for the 12-EO$_x$-12 surfactant series, it may be deduced that the dominating entropic contribution to the free energy results from the dehydration of the alkyl chains transferred from the aqueous environment to the hydrophobic micelle core of the micelle.

5. Conclusion

Gemini surfactants containing two quaternary ammonium groups bound by an ethylene oxide spacer chain, referred to as 12-EO$_x$-12, have been synthesized and their properties in aqueous solution studied, mainly by calorimetry. This work illustrates the use of microcalorimetric methods to understand the bulk behaviour of such systems. The thermodynamic data obtained show that the micellization process for 12-EO$_x$-12 is entropy driven. Lengthening the spacer group results in an increase in the cmc and a decrease in the enthalpy of micellization, which is consistent with the enhanced hydrophilic character of the surfactant molecule producing more hydrated micelles. Moreover, the corresponding values of the head-group surface area suggest that the spacer remains in contact with water and penetrates into the water phase. At least, the values of the micellization enthalpy obtained for molecules with the longest spacers, 12-EO$_6$-12 and 12-EO$_7$-12, indicate that the thermal effect of micellization is the outcome of two opposite contributions, one coming from the dehydration of the hydrophobic chains and the other due to the partial dehydration of the oligo(oxyethylene) group in the spacer.

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