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Micellar structure of gemini cationic surfactants: influence of the spacer length

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Abstract

The enthalpies of micellisation of gemini and conventional cationic surfactants have been determined using calorimetric measurements as a function of temperature. The differential molar enthalpies of micellisation depend on the structure of the surfactants as well as on the temperature. As expected, a drastic increase of the enthalpies of micellisation are observed with an increase of the temperature. Moreover, calorimetric investigation of self-association process shows that the enthalpies of micellisation are much more exothermic for the gemini surfactants than for the conventional cationic surfactant. The higher values of the micellisation enthalpies are due to a higher micellar density of gemini surfactant micelles. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calorimetry; Micellisation; Cationic gemini surfactants

1. Introduction

The thermodynamics of micellisation processes for gemini and conventional cationic surfactants have been investigated by microcalorimetry at 25 and 35°C. This kind of investigation of micellar structure is a relatively new method, which allows the enthalpies of micellisation to be obtained. The gemini cationic surfactants studied are alkanediyl-α,ω-bis(dodecyldimethylammonium bromide). In these amphiphiles, two surfactant molecules are linked at the level of the head groups by an alkyl chain (spacer), containing *s* carbon atoms [1]. These surfactants can be formally considered as dimers of the corresponding quaternary ammonium surfactants. The aim of this study is to compare the behaviour of dimeric and monomeric cationic surfactants in aqueous solution, by their differential molar enthalpies of micellisation, with particular emphasis on the effect of the spacer length (*s*) and of the temperature (T) on the structure of the aggregates. These parameters *s* and T appear to be able to influence the surfactant properties in water.

2. Materials

The conventional surfactant investigated, dodecyltrimethylammonium bromide (DTAB), was supplied by Fluka. It is used as received (>98% purity). Its cmc is 15.6 mM at 35°C in water (Millipore Super Q System) [2].

The gemini surfactants studied, alkanediyl-α,ω-bis-(dodecyldimethylammonium bromide), are referred to as 12-*s*-12, with 12 being the number of carbon atoms of the amphiphilic moieties and *s* the number of carbon atoms of the alkanediyl spacer group. The gemini surfactants studied here 12-2-12, 12-4-12, 12-6-12,

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12-8-12, 12-10-12 and 12-12-12, were synthesised in our laboratory according to the method described previously [3]. Their respective cmcs in pure water at 35°C are 0.81, 1.17, 1.03, 0.83, 0.63 and 0.37 mM [3].

3. Calorimetric experimental procedure

The differential molar enthalpies of dilution ($\Delta_{dil}h$) were evaluated using the Calostar microcalorimeter. Fig. 1 represents the calorimetric cell with the devices for measuring the temperature, the constant stirring (250 rpm) and the addition of the reagents in use. The calorimetric device is placed into a metallic block where the temperature is controlled with a precision of 5×10^{-4}°C. The calorimeter is controlled by computer. It takes about 15 min to return to the base line, the sensitivity of the detector is 0.5 $\mu V \, \mu W^{-1}$ and the useful volume of the calorimetric cell is 5–15 cm^3. The Calostar microcalorimeter is perfectly adapted to studies on dilution, on adsorption and on micellisation. 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 solution of surfactant. Once the calorimeter reaches thermal equilibrium (around 12 h), one aliquot of the stock solution is injected into the calorimetric cell (from 5 to 100 μl). The dilution equilibrium is instantaneous, and the resulting endothermic effect is recorded.

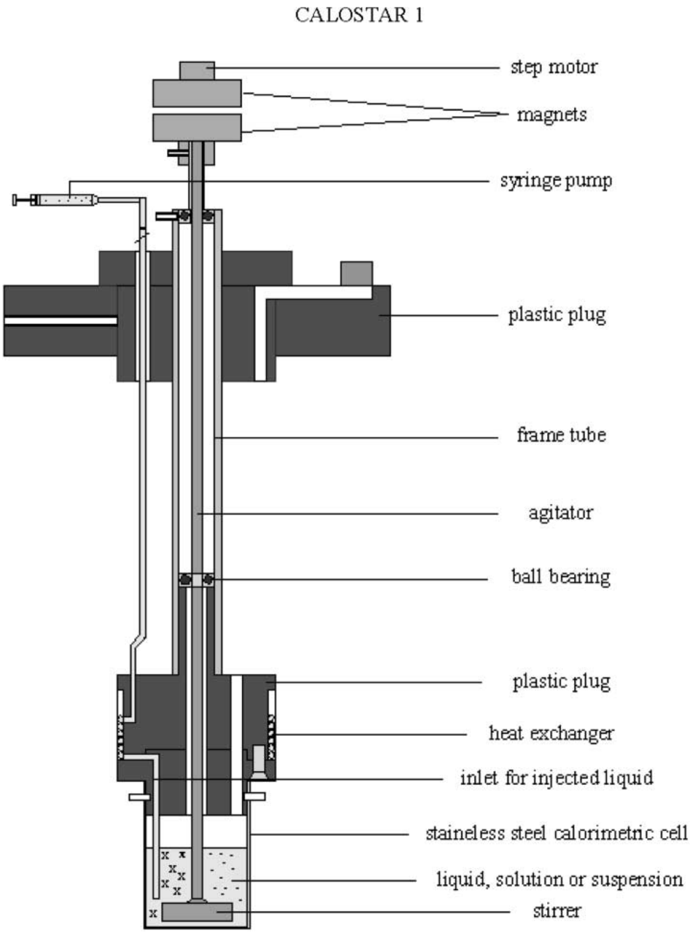

Fig. 1. Schematic representation of the Calostar microcalorimeter.

After return to the base line, another injection can be made and so on until the concentration in the calorimetric cell is higher than cmc. The differential molar enthalpies of dilution are determined by the integration of the endothermic peaks which are compared with calibration peaks obtained by the Joule effect.

4. Results

Fig. 2 shows typical differential molar enthalpies of dilution ($\Delta_{\mathrm{dil}}h$) which follow successive injections of a 12-2-12 stock solution into an initial volume of water in the calorimetric cell. This endothermic process encompasses three dilution domains as a function of C_e, the equilibrium concentrations obtained in the calorimetric cell after each injection.

1. At low concentrations, the enthalpy evolved, Δh_{I}, results from dissociation of all micelles and from dilution of the unmicellised species. The regime observed here for $C_e<0.7$ mmol kg^{-1} yields a constant molar enthalpic contribution in the experimentally accessible range.
2. A transition region is observed for $0.7 < C_e < 1.2$ mmol kg^{-1}. Here, addition of stock solution aliquots gives rise to stepwise shifts in the distribution of aggregates, involving changes in both size and total number of particles: dissociation and dilution of micelles occur simultaneously.
3. The last injections yield a constant and weakly endothermic enthalpic effect, Δh_{III}, which is related to the dilution of the stock solution micelles in the micellar solution.

The micelle formation enthalpy is evaluated as

$$\Delta_{\mathrm{mic}}h = \Delta h_{\mathrm{III}} - \Delta h_{\mathrm{I}}$$

The enthalpies of micellisation for each of the studied surfactants at 25 and 35°C are listed in Table 1.

Table 1
Differential molar enthalpies of micellisation, $\Delta_{\mathrm{mic}}h$, for gemini and conventional cationic surfactants studied as a function of the temperature

Surfactants	$\Delta_{\mathrm{mic}}h$ (kJ mol^{-1})	
	$T = 25$°C	$T = 35$°C
DTAB	−1.7	−4.1
12-2-12	−21.2	−28.5
12-4-12	−9.3	−17.7
12-6-12	−8.2	−17.5
12-8-12	−9.2	−17.3
12-10-12	−11.5	−17.6
12-12-12	−12.3	−19.9

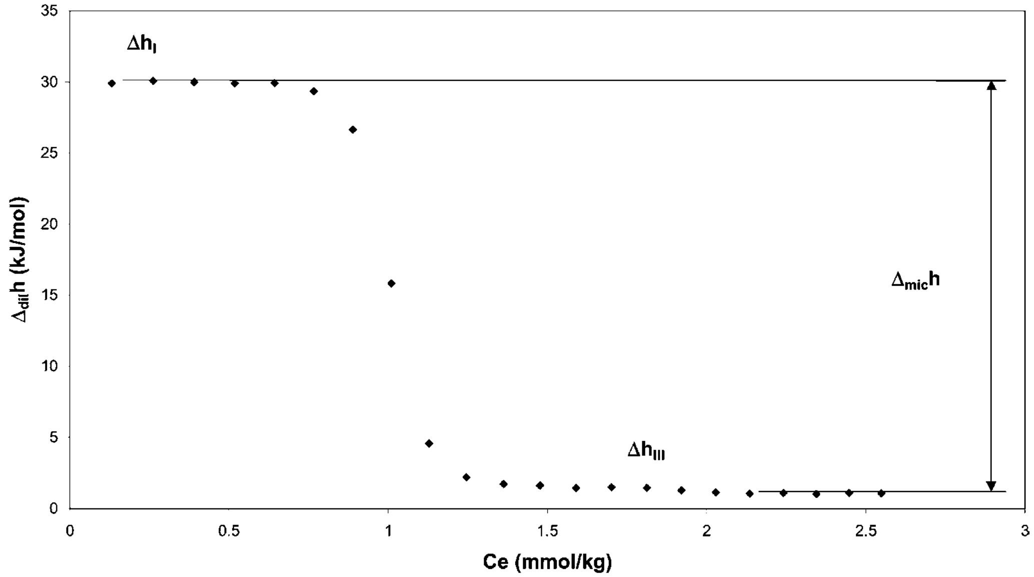

Fig. 2. Differential molar enthalpy of dilution for 12-2-12 at 35°C.

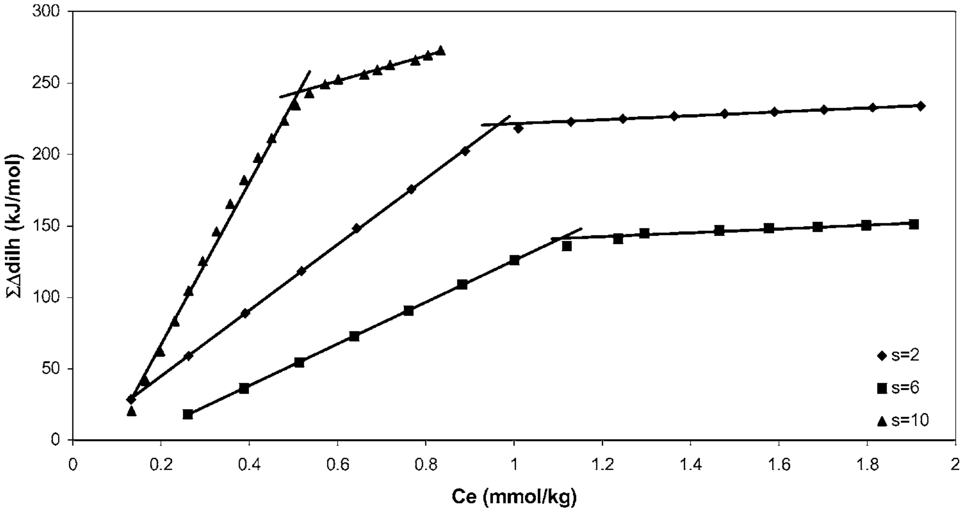

Fig. 3. Cumulative enthalpies of dilution for a 12-2-12 series at 35°C.

Fig. 3 shows the cumulative molar enthalpies of dilution for 12-2-12 at 35°C against the equilibrium concentrations. This other representation usually gives a change of slope at the cmc. The cmcs determined in this way give the same values as cmcs determined previously [3]. These results confirm that calorimetric measurements are reliable.

5. Discussion

5.1. Comparison of the micellisation of gemini and conventional surfactants

Fig. 4 displays the variation of the differential molar enthalpies of dilution ($\Delta_{\mathrm{dil}}h$) for DTAB and 12-2-12 at

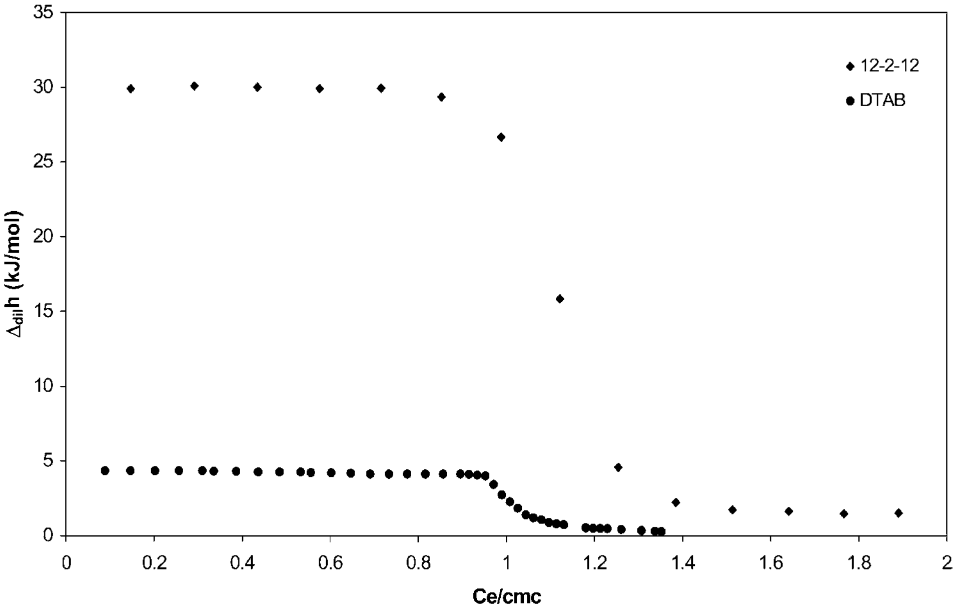

Fig. 4. Differential molar enthalpy of dilution for DTAB and 12-2-12 at 35°C using a reduced abscissa scale C_e per cmc.

35°C, using for the abscissa scale the reduced equilibrium concentration of surfactant C_e per cmc. This unusual abscissa scale facilitates comparison between the enthalpic data for surfactants which have very different cmcs. In this range of concentration, the micelles formed are spherical or spheroidal for both surfactants [4]. Fig. 4 shows also that the micellisation process is much more exothermic for the gemini than for its monomeric counterpart. Generally speaking, all the enthalpies of micellisation are much more exothermic for the gemini surfactants compared to DTAB (Table 1). This phenomenon gives some indication about the structure of the micelles of the studied surfactants. Indeed, gemini surfactants form more dense micelles which have slightly hydrated alkyl chains. The hydrophobic interactions due to the conformational change of the dimeric molecules and the interactions in the micellar core give a micellisation process strongly endothermic ($\geq 17\ \mathrm{kJ\ mol^{-1}}$ at 35°C). On the other hand, the less exothermic enthalpy of micellisation for DTAB indicates that the micelles which are formed have a less compact structure. In this case, the alkyl chains in the micelles are more hydrated, the hydrophobic interactions in the micellar core are relatively weaker. Then, the demicellisation process is easier, explaining the weak energy required.

5.2. *Influence of the spacer length*

Fig. 5 displays the variation of the cmc data and the molar enthalpies of micellisation ($\Delta_{\mathrm{mic}}h$) for the 12-*s*-12 series at 35°C as a function of the spacer length *s*. This representation facilitates the comparison of the different plots, as the cmc depends on the spacer group [5]. It may be seen that the values of the micellisation enthalpies decrease for $s < 4$, are quasi-constant for $4 < s < 10$ and increase for $s > 10$. For short spacers ($s < 4$), the surfactants have a *cis*-conformation which promotes micellisation [3]. In this case, when *s* varies from 2 to 4, $\Delta_{\mathrm{mic}}h$ becomes less and less exothermic in spite of the increase in cmc. Indeed, when the spacer becomes longer, the micelle is more easily hydrated and then $\Delta_{\mathrm{mic}}h$ decreases. For middle-length spacers ($4 < s < 10$), $\Delta_{\mathrm{mic}}h$ is quasi-constant. The cmc values decrease, but the aggregates which are formed have a similar structure. For long spacers ($s > 10$), one observes a slight increase of $\Delta_{\mathrm{mic}}h$ when the cmc continuously decreases. In this case, the spacer is more flexible and partly penetrates into the hydrophobic core of the micelles, restricting the hydration of the alkyl chains in the micelles. This organisation can explain the increase of the exothermic values of the micellisation enthalpy.

5.3. *Effect of the temperature*

Fig. 6 presents the differential molar enthalpies of dilution for 12-6-12 at 25 and 35°C. This weak variation in temperature does not influence the micellar region, but the molar enthalpy of micellisation is strongly affected. This phenomenon is observed for all surfactants studied (Table 1). Indeed, when the temperature

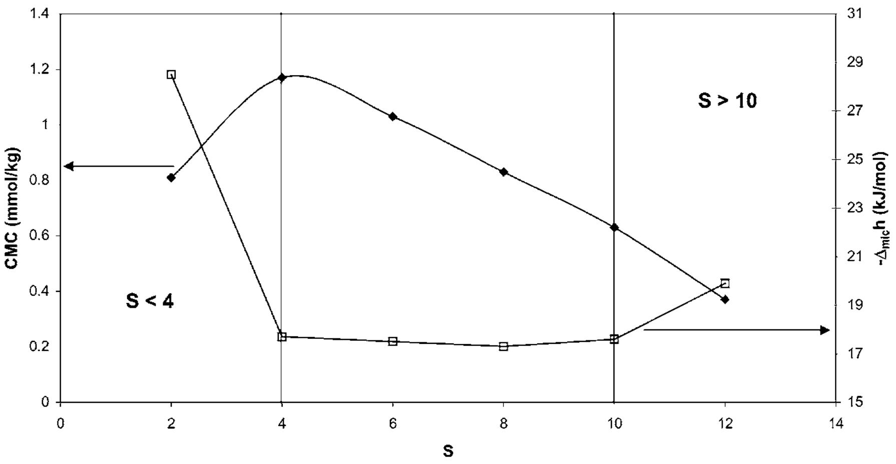

Fig. 5. Variation of the cmc and the differential molar enthalpy of micellisation vs. the spacer length *s* at 35°C.

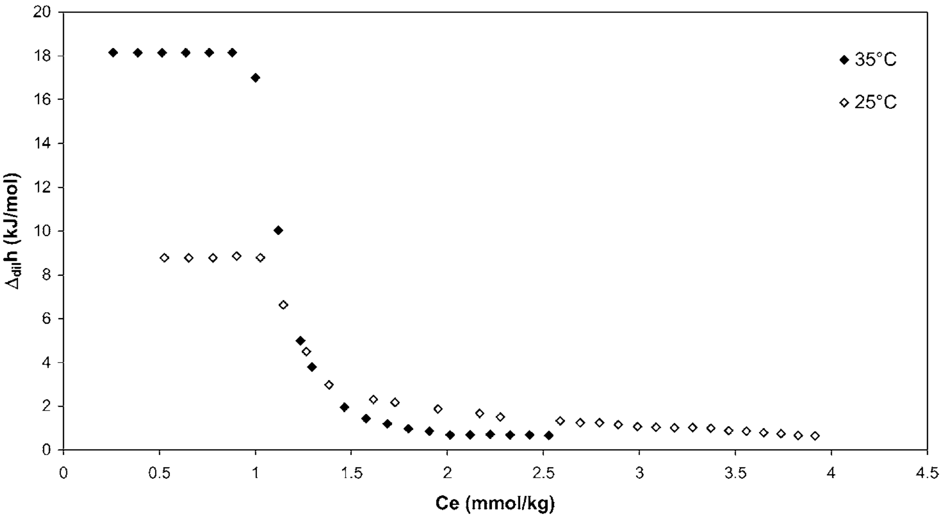

Fig. 6. Differential molar enthalpy of dilution of 12-6-12 at 25 and 35°C.

increases, the molar enthalpy of micellisation becomes more exothermic. The self-association behaviour of these surfactants have already been investigated by means of time-resolved fluorescence quenching [6]. The results show a decrease of the micelle aggregation number *N* upon increasing *T*. This variation may reflect then that the 12-*s*-12 micelles are more tightly organised and have a smaller size. For example, the aggregation number measured in the case of 12-6-12 is 25.8 at 25°C and 23.7 at 35°C. Consequently, the hydration of the alkyl chains inside the micelles is much more difficult. This behaviour at higher temperature explains the more exothermic values of $\Delta_{mic}h$ for gemini and conventional cationic surfactants.

6. Conclusion

The thermodynamics of the micellisation process of gemini and conventional cationic surfactants have been investigated by microcalorimetric techniques. The results obtained show that the micellisation process is more exothermic for the 12-*s*-12 series compared to the DTAB. The gemini surfactants form more compact micelles in solution than the monomeric counterpart. Moreover, this phenomenon is accentuated by an increase of the temperature. On the other hand, the length of the spacer group (*s*), which has an effect on the cmc, influences the organisation of the micellar structure. Overall, the results clearly demonstrate the utility of microcalorimetry for the precise description of micellisation processes.

References

[1] R. Zana, Specialist Surfactants, Chapman and Hall, London, 1997 (Chapter 4).
[2] M. Chorro, C. Chorro, O. Dolladille, S. Partyka, R. Zana, J. Colloid Interface Sci. 210 (1999) 134.
[3] R. Zana, M. Benrraou, R. Rueff, Langmuir 7 (1991) 1072.
[4] A. Bernheim-Groswasser, R. Zana, Y. Talmon, J. Phys. Chem. B 104 (2000) 4005.
[5] R. Zana, Surfactant Science Series, Esumi Ueno, Vol. 70 1997 (Chapter 6).
[6] D. Danino, Y. Talmon, R. Zana, Langmuir 11 (1995) 1448.