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A microcalorimetric titration study on the micelle formation of alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactants at a 283.15–343.15 K temperature range

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Abstract The aim of this study was to investigate the self-assembly process for *m*-8-*m* gemini surfactants, for $m = 8$ and 12, in water, using the microcalorimetric titration method within the temperature range of 283.15–343.15 K. The enthalpy of micellization (ΔH_{mic}) and critical micelle concentration (c.m.c.) have been calculated by using modified sigmoidal Boltzmann equation. Other thermodynamic parameters ΔG_{mic}, ΔS_{mic}, and $\Delta C_{\mathrm{p,mic}}$, associated with micellization process were determined on the basis of the calorimetric results by applying the pseudo-phase separation model. The c.m.c. and ΔH_{mic} values strongly depend on the temperature and the alkyl chain length. The enthalpy of micellization decreases and then changes its sign and becomes negative when temperature increases. The temperature dependence of the c.m.c. for the surfactants investigated exhibits typical U-shape. The results obtained are compared with literature data for other gemini cationic surfactants with a different alkyl chain length. The differences are analyzed in terms of differences in the hydrophobic interactions between the hydrocarbon chains.

Keywords Microcalorimetric titration · Alkanediyl-α,ω-bis(dimethylalkylammonium bromide) surfactants · *m*-8-*m* · Enthalpy of micellization

Introduction

As the name implies, gemini surfactants of general formula *m*-*s*-*m*, consist of two surfactant moieties with alkyl chain-*m* covalently connected by a spacer unit *s*. The chain length governs many of the properties of these surfactants and similarly as temperature does, the chain length determines the association process in aqueous solutions of gemini surfactants. The temperature dependence of the properties of surfactant solutions is relevant to their applications in many fields of science and industry [1–6] while thermodynamic information is indispensable to understand the phenomenon of self-organization of surfactants into micelles. A powerful and useful technique for obtaining thermodynamic parameters of association is the isothermal titration microcalorimetry (ITC). It has been successfully applied in a growing number of studies of surfactant systems [7–19]. The major advantage of ITC for micellization studies is the ability to perform direct determination of the heat of demicellization and the c.m.c. in a single isothermal titration experiment and to carry out the experiment within a wide range of temperature. In this study we examined the thermodynamics of micellization process of aqueous solutions of alkylene-α,ω-bis(dimethylalkylammonium bromides) with the general formula: *m*-8-*m* for $m = 8$, 12 within the temperature range of 283.15–343.15 K using the ITC. We used this method to determine the enthalpy of micelle formation (ΔH_{mic}) and the critical micelle concentration (c.m.c.) within the temperature range investigated. In order to describe the plots of the enthalpy of dilution versus surfactant concentration we adopted the sigmoidal Boltzmann equation (SBE) but with some modifications. The aqueous solutions of 8-8-8 gemini surfactant were earlier investigated by means of densimetric and DSC III methods [20], but no information on the temperature dependence of the enthalpy of micellization for the mentioned system is available. There are also some literature data on the micellization process of 8-12-8 in aqueous solutions obtained by means of conductometric [21], dilatometric [22], and calorimetric methods [11, 23] but they concern only few temperatures. We expected that our results

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together with appropriate literature data concerning other gemini surfactants would make it possible to analyze the effect of the alkyl chain length as well as that of temperature change on the value of enthalpy of micellization and on the c.m.c value of the systems under question.

Experimental section

Materials

Octylene-1,8-bis(dimethyloctylammonium bromide) was synthesized as it was described in our earlier paper [20].

Octylene-1,8-bis(dimethyldodecylammonium bromide), (surfactant 12-8-12) was carried out according to procedure given by Zana [21] for the preparation of surfactants but methanol was used as solvent. The obtained crude product was purified by crystallization from ethyl acetate/propan-2-ol (95/5) mixture (m.p. 202–204 °C, yield 58%).

^{1}H NMR (600 MHz, D_2O) 3.45–3.34 (8H, m, *N*-dod-1-CH_2 and *N*-oct-1,8-CH_2), 3.19 (12H, s, *N*-CH_3), 1.84–1.73 (8H, br s, *N*-dod-2-CH_2 and *N*-oct-2,7-CH_2), 1.50–1.28 (44H, m, *N*-dod-3,4,5,6,7,8,9,10,11-CH_2 and *N*-oct-3,4,5,6-CH_2), 0.93 (6H, t $J = 7{,}2$ Hz, *N*-dod-12-CH_3).

^{13}C NMR (150 MHz, D_2O) 65.41, 65.20, 54.42, 34.63, 32.53, 32.48, 32.43, 32.18, 32.14, 31.76, 30, 79, 28.71, 28.18, 55.29, 24.71, 16.53.

Before measurements, the synthesized surfactants were dried under vacuum at a temperature of 323.15 K. All solutions were made up using freshly boiled double distilled water. Solution concentrations were expressed by molarity (mol dm^{-3}).

Method

The experiments were carried out within the temperature range of 283.15–343.15 K using isothermal titration calorimeter (Microcal). Aliquots of the concentrated surfactant solution (from 1 to 12 μl, depending on the surfactant and the temperature) were added to 1.4 ml of water in the sample cell under constant stirring 307 revolutions per minute. The concentration of the surfactant in the syringe was 1.3 mol dm^{-3} for 8-8-8 and 0.018 mol dm^{-3} for 12-8-12 (~20 times larger than the c.m.c.). The rough c.m.c. values were determined by the trial and errors method.

Results and discussion

The typical experimental titration curves obtained for the dilution of micellar 8-8-8 and 12-8-12 solutions into water are given in Figs. 1a and 2a.

The enthalpies of dilution, ΔH_{dil} for aqueous solutions of the surfactants investigated, are plotted against the surfactant concentration at each the temperatures under investigation in Figs. 1b and 2b. In the case of 8-8-8 surfactant only every fifth point is presented in the plot.

The shape of the titration curves presented for 8-8-8 and 12-8-12 is not exactly the sigmoidal one particularly in pre- and post-micellar regions. As it is known, such behavior is often observed in the case of ionic surfactants [9]. For this reason we tried to fit the obtained experimental data to a modified version of Eq. 1 proposed by Király and Dekány [9].

$$\Delta H_{\mathrm{d}} = \Delta H_{\mathrm{d(f)}}\left[1+\left(\frac{\Delta H_{\mathrm{d(i)}}-\Delta H_{\mathrm{d(f)}}}{\Delta H_{\mathrm{d(f)}}}\right)\cdot\left(1+\frac{\exp(C_{\mathrm{S}}-C_{\mathrm{c.m.c.}})}{\Delta C_{\mathrm{S}}}\right)\right]^{-1} \qquad (1)$$

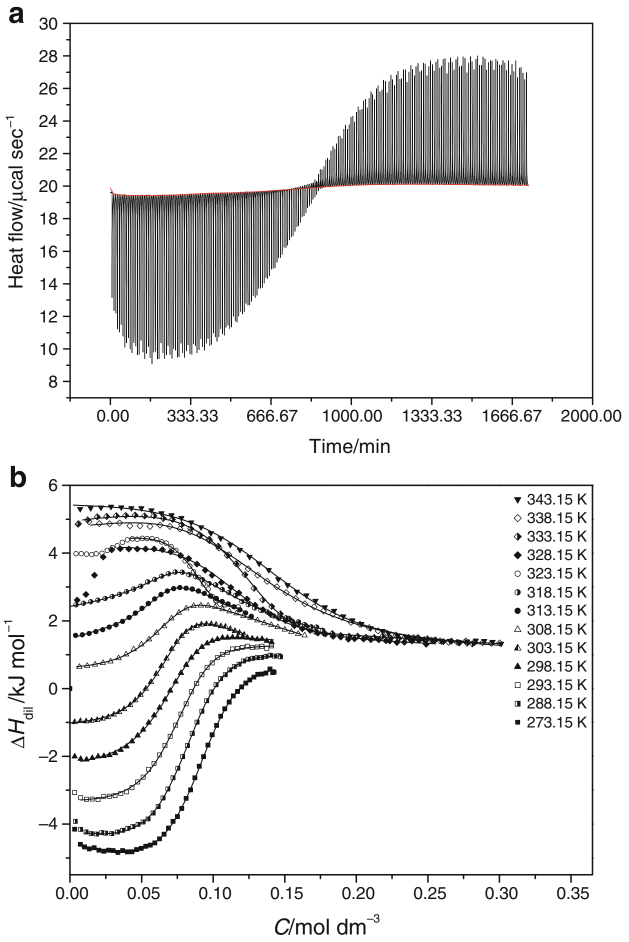

Fig. 1 **a** Typical thermogram obtained from ITC experiments for 8-8-8 surfactant at 298.15 K. **b** Enthalpies of dilution of 8-8-8 surfactant in water at different temperatures and results from a fit of the experimental data to the modified Boltzmann equation (*solid line*)

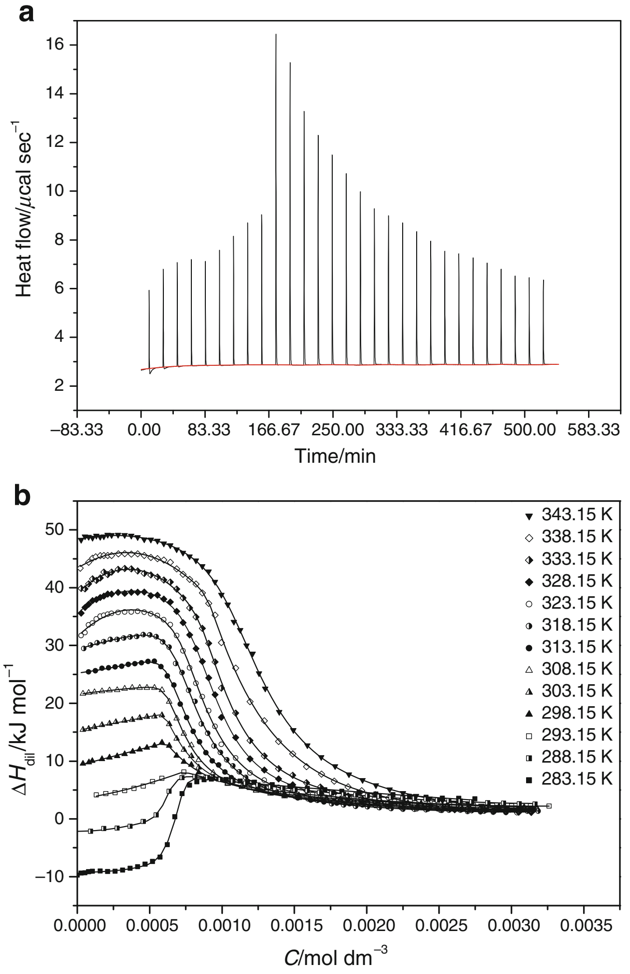

Fig. 2 **a** Typical thermogram obtained from ITC experiments for 12-8-12 surfactant at 298.15 K. **b** Enthalpies of dilution of 8-8-8 surfactant in water at different temperatures and results from a fit of the experimental data to the modified Boltzmann equation (*solid line*)

where C_s is the concentration of the surfactant in the system, ΔC_s is the constant interval of C_s, $C_{c.m.c.}$ was determined as described in article [9]. The $\Delta H_{d(i)}$ and $\Delta H_{d(f)}$ are linear functions of the C_s.

$$\Delta H_{d(i)} = f(C_S) = H_{ia} + H_{ib} C_s \tag{2}$$

$$\Delta H_{d(f)} = f(C_S) = H_{fa} + H_{fb} C_s \tag{3}$$

where H_{ia}, H_{ib}, H_{fa}, H_{fb} are fitting parameters.

Unfortunately, the fitting was not satisfactory for the 8-8-8 surfactant at all the temperatures examined and for 8-12-8 surfactant at temperatures above 293.15 K. Moreover, the values of ΔH_{mic} obtained seemed to be unrealistic. Therefore, we modified the Eq. 1 in the following way:we assumed that the equation describing the differential heat of dilution ΔH_d of a micellar solution takes the following form:

$$\Delta H_d = \Delta H_{d(f)} \left[1 + \left(\frac{\Delta H_{d(i)} - \Delta H_{d(f)}}{\Delta H_{d(f)}} \right) \cdot \left(1 + \frac{\exp(C_S - C_{c.m.c.})}{\Delta C_S} \right) \right]^{-n} \tag{4}$$

where C_s is the concentration of the surfactant in the system, ΔC_s is the constant interval of C_s, i and f mean the initial and final stages, n and $C_{c.m.c.}$ are fitting parameters. The $\Delta H_{d(i)}$ and $\Delta H_{d(f)}$ are functions of the C_s (Eqs. 5, 6), which describe the pre- and post-micellar range of titration curves, respectively:

$$\Delta H_{d(i)} = f(C_S) = H_{ia} + H_{ib} C_s + H_{ic} C_S^2 + H_{id} C_S^3 + \cdots \tag{5}$$

$$\Delta H_{d(f)} = f(C_S) = H_{fa} + H_{fb} C_s + H_{fc} C_S^2 + H_{fd} C_S^3 + \cdots \tag{6}$$

where H_{ia}, H_{ib}, H_{ic}, H_{id}, H_{fa}, H_{fb}, H_{fc}, H_{fd} are fitting parameters.

Because of many fitting parameters, it was impossible to determine all these parameters during a single optimalization. For this reason we separately fitted the data for pre- and post-micellar region to Eqs. 5 and 6, respectively. As low a polynomial degree as possible was used. The parameters obtained in this way were applied to Eq. 1 and they were not changed during subsequent fitting.

The enthalpy of micellization, ΔH_{mic}, was then calculated by taking the enthalpy difference between the two functions describing the pre- and post-micellar range corresponding to the c.m.c. value—Eq. 7

$$\Delta H_{mic} = \Delta H_{d(f)}(C_{c.m.c.}) - \Delta H_{d(i)}(C_{c.m.c.}) \tag{7}$$

The value of c.m.c., was regarded as the concentration where the second derivate of the ΔH_{dil} versus C_s curve displayed zero—Eq. 8.

$$\frac{\partial^2 \Delta H_{dil}}{\partial C_S^2}(C_{c.m.c.}) = 0 \tag{8}$$

The dilution enthalpy curve for ionic surfactants loses its sigmoidal shape. The determination of the c.m.c. for ionic surfactants within the temperature range where ΔH_{mic} is close to zero is often impossible, even by using modified SBE, as no jump in the enthalpy versus concentration curve is observed (Figs. 3, 4). According to Bijma et al. [14] this type of curve is a consequence of both micelle degradation during injection process and the non-ideal thermodynamic properties of the solution. For this shape of curve the determination of c.m.c. from the titration calorimetric plots becomes quite difficult. Therefore, the value of critical micelle concentration for this specific temperature range was obtained through the interpolation of data concerning other temperatures. To this aim the temperature

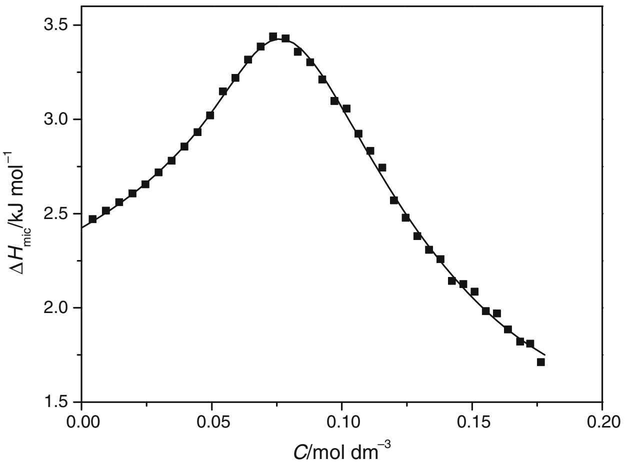

Fig. 3 Enthalpy of dilution of 8-8-8 surfactant in water at 318.15 K. The *solid line* is calculated from Eq. 1

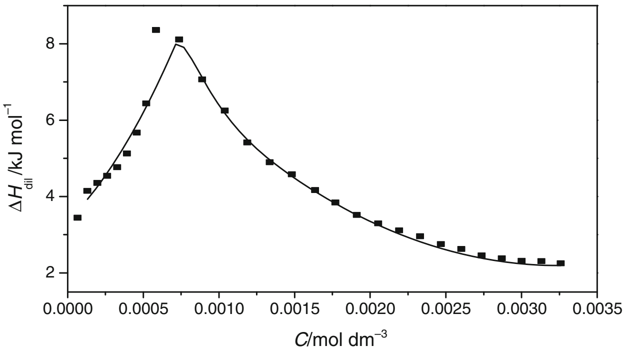

Fig. 4 Enthalpy of dilution of 12-8-12 surfactant in water at 293.15 K. The *solid line* is calculated from Eq. 1

dependences of the c.m.c. for both surfactants were fitted by the second degree polynomial [8, 9]. The values of c.m.c. determined are presented as a function of temperature in Figs. 6 and 7 and they are collected in Table 1 together with appropriate literature data.

As it is seen from Figs. 5 and 6 the c.m.c. versus temperature functions for both surfactants investigated exhibit characteristic U-shaped plot. In general, such behavior is frequently observed for the aqueous solutions of ionic surfactants [8, 9, 12]. It is a resultant of two opposing effects which influence the micellization process. The first effect is connected with the hydration of polar group of surfactant molecule and plays a key role in low range of temperature where hydrogen bond formation is more probably and the strong hydration of polar head disfavors the micelle formation process. The increase in temperature causes that the hydration of polar group decreases and thus the micellization can occurs at lower concentrations. The second effect is connected with the hydrophobic hydration of the alkyl chain, which changes the structure of water surrounding the hydrophobic tail. As is well known, the structure of water strongly depends on temperature. Because of that, the structure of water surrounding hydrophobic chains becomes looser and the hydrophobic interaction effect is weaker when the temperature increases. This phenomenon shifts the micellization process toward the higher concentration range. The competition between these two effects is the reason of the observed characteristic shape of the curve under question [12, 23].

The minimum temperatures of the c.m.c. T_{min}, were determined from the same c.m.c. as a function of temperature curves. The T_{min} values obtained for 8-8-8 and 12-8-12 are 304.92 and 294.81 K, respectively. This fact confirms that T_{min} systematically decreases as the hydrophobic alkyl chain length m increases in homologous series of surfactants with the same counter ions. This relation can be easily explained taking into consideration the previously discussed effects. In the case of surfactants with longer hydrophobic chains (12-8-12) the contribution of the hydrophobic hydration of alkyl group is more significant than for surfactants with shorter hydrophobic chain. Accordingly, the micellization process is hindered after crossing 295 K for 12-8-12 surfactant whereas for 8-8-8 micellization starts to be disfavored only for temperature higher than 305 K. In order to analyze the effect of hydrophobic chain length on critical micelle concentration, the c.m.c values for surfactants *m*-8-*m*, obtained by different methods, were set up in Table 2. The data presented confirms that the chain length—*m*, strongly influences the critical micelle concentration. An increase in the hydrocarbon chain length leads to stronger hydrophobic interactions between the hydrocarbon chains, hence the micelles can be formed easier and the c.m.c. value decreases. Moreover, the increase in *m* chain length causes that the micelles created are bigger and less dissociated [24]. A similar result was experimentally confirmed for other monomeric surfactants [25].

The experimental results of the ΔH_{mic} for 8-8-8 and 12-8-12 surfactants obtained from modified Sigmoidal–Boltzmann equation for the temperature range investigated were listed with some literature data in Table 2 and shown as a function of temperature in Figs. 7 and 8, respectively. The enthalpies of micellization for the temperature range where no jump in the enthalpy versus concentration curve was observed were calculated similarly as in the case of the c.m.c. Non linear regression yields a transition temperature where $\Delta H_{\text{mic}} = 0$ for 8-8-8 and 12-8-12. Consequently, the c.m.c has a shallow minimum near this temperature (Figs. 5, 6). As it can be seen from the presented data at low temperatures, the micellization enthalpy at temperatures below 313.15 K for 8-8-8 and below 288.15 for 12-8-12 is endothermic and then becomes exothermic as the temperature raises (Figs. 7, 8). As is well know, the enthalpy of micellization illustrates of energetic effect of

Table 1 C.m.c., enthalpy, and specific heat of the micellization of the surfactants investigated

Compound	T/K	c.m.c./mol/dm^3	ΔH_{mic}/kJ/mol	ΔG_{mic}/kJ/mol	$T\Delta S_{\mathrm{mic}}$/kJ/mol	$\Delta C_{\mathrm{p,mic}}$/kJ/mol/K
8-8-8	283.15	0.0922	5.66	−12.26	17.91	−0.178
	288.15	0.0823	5.80	−12.91	18.71	−0.181
	293.15	0.0769	4.52	−13.30	17.82	−0.183
	298.15	0.0709	3.67	−13.73	17.40	−0.185
	303.15	0.0671	3.29	−14.18	17.46	−0.188
	308.15	0.0638	2.29	−14.46	16.76	−0.190
	313.15	0.0635	1.39	−14.75	16.14	−0.193
	318.15	0.0697[a]	−0.13[a]	−14.69	14.57	−0.195
	323.15	0.0895	−1.77	−14.26	12.49	−0.198
	328.15	0.1134	−2.81	−13.84	11.02	−0.200
	333.15	0.1219	−4.00	−13.85	9.86	−0.202
	338.15	0.1300	−4.09	−13.88	9.78	−0.205
	343.15	0.1341	−4.05	−13.77	9.73	−0.207
12-8-12	283.15	0.000664	14.80	−24.03	38.83	−1.78
	288.15	0.000647	8.19	−24.52	32.71	−1.65
	293.15	0.000727[a]	−0.81[a]	−24.97	24.15	−1.52
	298.15	0.000703; 0.00083[b]; 0.000682	−9,32; −9.0[b]; −4.8[b]	−25.16	15.84	−1.39
	303.15	0.000682	−14.40;	−25.66	11.27	−1.26
	308.15	0.000695	−19.29; −17.3[b;]; −13.87[b]	−26.04	6.74	−1.13
	313.15	0.000714	−24.87	−26.39	1.52	−1.00
	318.15	0.000741	−33.13	−26.71	−6.41	−0.87
	323.15	0.000808	−33.46	−26.90	−6.56	−0.74
	328.15	0.000882	−36.70	−27.08	−9.62	−0.61
	333.15	0.000953	−44.65	−27.30	−17.37	−0.48
	338.15	0.001035	−43.55	−27.45	−16.09	−0.35
	343.15	0.001165	−42.45	−27.52	−14.92	−0.22

[a] Value calculated as indicate in the text

[b] Literature data Ref. [23]

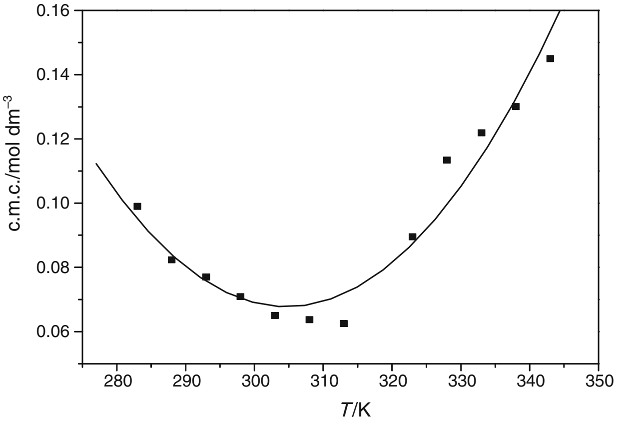

Fig. 5 Temperature dependence of the c.m.c. of 8-8-8 in water. Equation of fitted curve $y = 5.829 \times 10^{-5}\, x^2 - 0.0355x + 5.478$ $R^2 = 0.947$

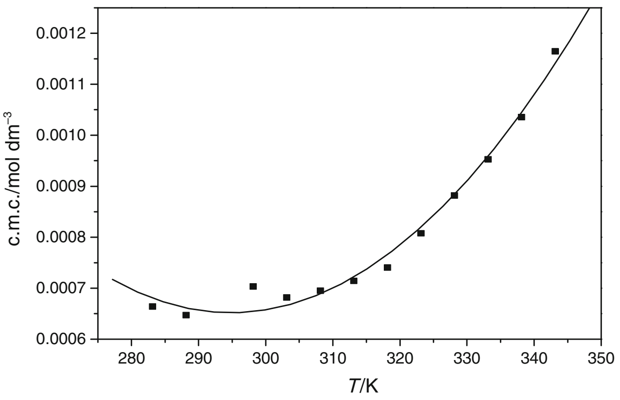

Fig. 6 Temperature dependence of the c.m.c. of 12-8-12 in water. Equation of fitted curve $y = 2.091 \times 10^{-7}\, x^2 - 0.000123x + 0.0188$ $R^2 = 0.985$

Table 2 The c.m.c. values of the *m*-8-*m* gemini surfactants at 298.15 K

Surfactant	c.m.c. × 10^{-3}/mol/dm^3
8-8-8	71.0^a, 75.0^b
10-8-10	5.8^c
12-8-12	0.703^a 0.80^c 0.83^d
14-8-14	0.018^d
16-8-16	0.038^d
18-8-18	0.0115^d

[a] This article

[b] Literature data Ref. [20]

[c] Literature data Ref. [21]

[d] Literature data Ref. [23]

the micelle formation process. It is a sum of several contributions which are connected with the structure of amphiphilic molecule [12, 23, 26]. The main contribution to this value comes from the transfer of the surfactant alkyl chains from aqueous solution to the micelle core while the water molecule surrounding hydrophobic chain are released to the bulk aqueous phase. This effect can be either exothermic or endothermic depending on temperature. At low temperatures, the destruction of structured water surrounding alkyl chains dominates over the condensation of alkyl chains into a micelle and in consequence the $\Delta H^{\circ}_{\mathrm{mic,chaintransf.}}$ is endothermic, and reversely at higher temperatures the $\Delta H^{\circ}_{\mathrm{mic,chaintransf.}}$ is exothermic. The second contributing effect, $\Delta H^{\circ}_{\mathrm{mic,elec}}$, describes the repulsion among the same charged heads of surfactant molecules and among the counter ions as well as attracting interactions between opposite charged ions and ionic groups. According to the opinion of Grosmaire et al. [23], the $\Delta H^{\circ}_{\mathrm{M,elec}}$ has negative contribution because of superior repulsive interaction.

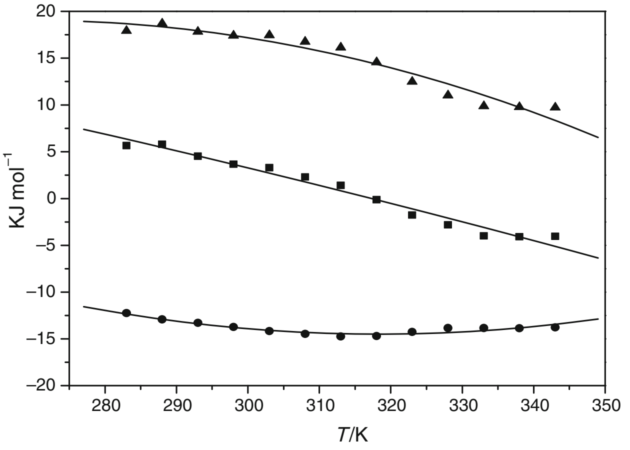

Fig. 7 Thermodynamic parameters for the micellization of 8-8-8 as a function of temperature where *filled square* ΔH_{mic}, *filled circle* ΔG_{mic}, *filled triangle* $T\Delta S_{\mathrm{mic}}$

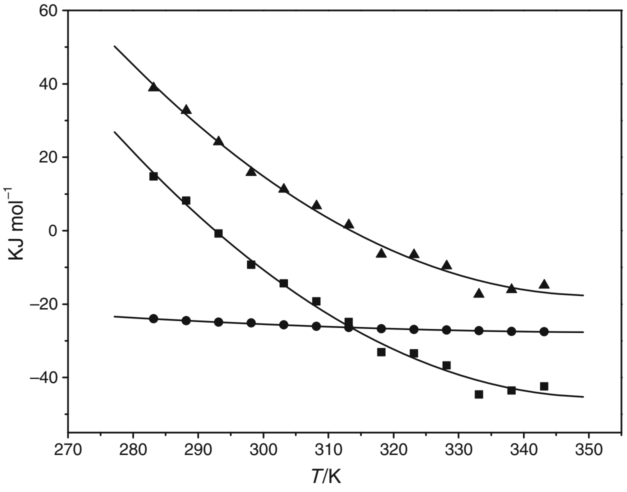

Fig. 8 Thermodynamic parameters for the micellization of 12-8-12 as a function of temperature where *filled square* ΔH_{mic}, *filled circle* ΔG_{mic}, *filled triangle* $T\Delta S_{\mathrm{mic}}$

The contributions connected with changes in the conformation of alkyl chain which take place during their transfer to the micelle core or with steric interaction between hydrophilic groups are unknown, but their magnitude is not meaningful [23]. Other effects that involve spacer chain length were not taken into account, because we compared compounds with the same spacer chain.

At low temperatures, the micellization enthalpy for 8-8-8 and 12-8-12 is endothermic and then becomes exothermic as the temperature raises (Figs. 7, 8). This behavior is determined by sign changes in the major contribution of the enthalpy of micellization—$\Delta H^{\circ}_{\mathrm{mic,chaintransf.}}$. Increasing temperature causes that the structure of water breaks down. As a result the positive effect related to destruction of structured water surrounding alkyl chains is dominated by the negative effect connected with the condensation of hydrophobic chains inside the micelle and the $\Delta H^{\circ}_{\mathrm{mic,chaintransf.}}$ becomes more exothermic upon increasing temperature [12, 23]. The effect of temperature on the enthalpy of micellization appears to be less visible at higher range of temperatures—333.15–343.15 K, as shown in Figs. 7 and 8. The above discussion leads to the conclusion that at 333.15 K the structured of water is so disturbed that any changes in temperatures do not significantly $\Delta H^{\circ}_{\mathrm{mic,chaintransf.}}$.

To calculate the other thermodynamics parameters of micellization for the systems examined, the pseudo-phase separation model was used. According to this model the free energy of micellization, ΔG_{mic}, corresponding to the standard free energy change for the transfer of one amphiphilic molecule from solution to the micellar phase can be calculated from the Eq. 9. [8]:

$$\Delta G_{\mathrm{mic}} = RT\ln X_{\mathrm{c.m.c.}} \tag{9}$$

where $X_{\mathrm{c.m.c.}}$ is the critical micellization concentration expressed in mole fractions, R is the gas constant, and T is temperature of the experiment. The entropy change ΔS_{mic} can be then obtained using the Gibbs–Helmholtz's equation:

$$\Delta S_{\mathrm{mic}} = \frac{\Delta H_{\mathrm{mic}} - \Delta G_{\mathrm{mic}}}{T} \tag{10}$$

The parameters ΔG_{mic}, and ΔS_{mic} calculated for the 8-8-8 and 12-8-12 micellization are listed in Table 1. The ΔG_{mic} values for both the 8-8-8 and 12-8-12 surfactants are negative and they are more negative for the surfactant with longer hydrocarbon chain length. It confirms the earlier observations that the micelle formation is more spontaneous when the alkyl chain in surfactant molecule is longer. A comparison of entropy and enthalpy of micellization values shows that the entropy term $T\Delta S_{\mathrm{mic}}$ gives a leading contribution to the negative value of the free energy of 8-8-8 surfactant within the whole temperature range examined. The same happens for 12-8-12 surfactant, but only for temperatures near room temperature. It means that in the mentioned cases, the association process of the gemini surfactants investigated is entropy driven, as for conventional surfactants. The positive values of the entropy of micellization are connected with the destruction of water structure in the neighborhood of alkyl chains, which causes an increase of freedom. For this reason, at low temperatures, where the hydrogen bonds between water molecules are strong, the micellization process results in larger gain in entropy than that at higher temperatures. In the case of 12-8-12 the entropic effects responsible for the association in water are reduced significantly at higher temperatures and then the micellization process becomes to be enthalpy driven [9, 27]. The similarity of the $\Delta H^{\circ}_{\mathrm{mic}}$ and ΔS_{mic} versus temperature curves suggests that in the examined systems the enthalpy–entropy compensation effect appears. This effect can be described as:

$$\Delta H_{\mathrm{mic}} = \Delta H^{*}_{\mathrm{mic}} + T_{\mathrm{c}}\Delta S_{\mathrm{mic}} \tag{11}$$

where the T_{c} is a compensation temperature. According to the opinion of some authors [e.g., 28] the "compensation temperature" characterizes the solute–solvent interactions and it is a measure of the "desolvation" part of the micellization process. The $\Delta H^{\circ}_{\mathrm{mic}}$, the heat effect corresponding to the $\Delta S_{\mathrm{mic}} = 0$ describes the solute–solute interactions and it can be interpreted as the "chemical" part of micellization process [28]. The enthalpy–entropy plots for the 8-8-8 and 12-8-12 surfactants are presented in Figs. 9 and 10, respectively. The linearity of the plot indicates that for the aggregation process, changes in ΔH_{mic} are compensated to a large extent by changes in ΔS_{mic}. The compensation temperatures for the gemini investigated surfactants are 269.78 K for 8-8-8 and 319.18 K for 12-8-12. It is noteworthy that T_{c} rises as the hydrocarbon chain length increases. The alkyl chain length influences also the $\Delta H^{\circ}_{\mathrm{mic}}$ value. As the hydrophobic chain m extends the intercept becomes more negative indicating that the chemical part of the effect plays a more significant role. The knowledge of micellization enthalpy as a function of temperature made it possible to calculate the value of isobaric heat capacity of micellization according to the following formula:

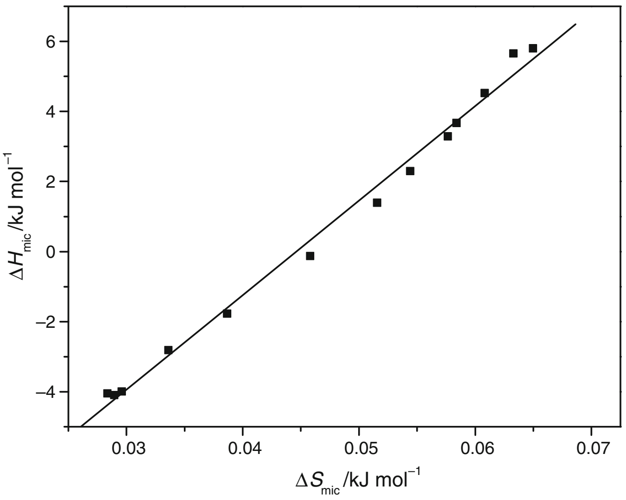

Fig. 9 Enthalpy–entropy compensation plot corresponding to the micellization of 8-8-8 in water at various temperatures. Equation of fitted curve: $y = 269.78x - 12.03$ $R^2 = 0.992$

$$\Delta C_{\mathrm{p,mic}} = \left(\frac{\partial \Delta H_{\mathrm{mic}}}{\partial T}\right)_{\mathrm{p}} \tag{12}$$

The isobaric heat capacity of micellization was found to be negative for both the surfactants investigated through the whole temperature range, as for most processes involving hydrophobic aggregation effects [8, 9] (Table 1).

Summary

This study proved that the isothermal titration microcalorimetry can be used as a sensitive research tool for the examination of the bulk behavior of gemini surfactants by determining the c.m.c. and enthalpy of micellization within a wide range of temperature. The modified Sigmoidal–Boltzmann equation, which was presented in the study, can be fruitfully employed for describing the titration curves and determining the thermodynamic parameters of micellization of surfactants. The thermodynamics parameters of the self-assembly process are indispensable for the

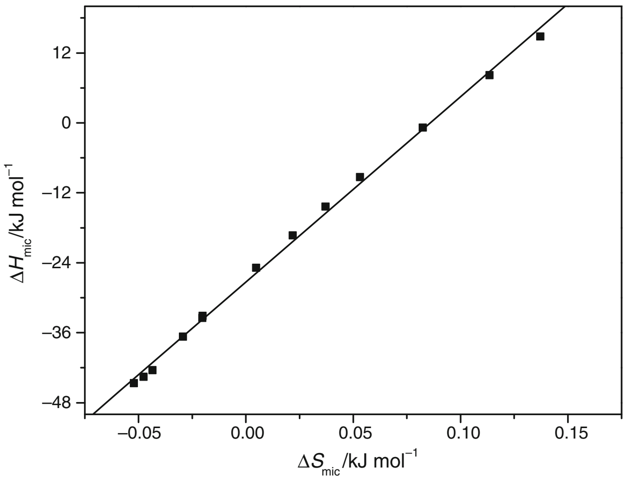

Fig. 10 Enthalpy–entropy compensation plot corresponding to the micellization of 12-8-12 in water at various temperatures. Equation of fitted curve: $y = -318.19x - 27.31$ $R^2 = 0.998$

determination of the factors that contribute to the aggregation process in solution: water structure, van der Waals interaction, hydrophobic hydration, etc. In the case of *m*-8-*m* surfactants, lengthening the alkyl chain results in a decrease in the c.m.c. values, which is consistent with the enhanced hydrophobic character of the surfactant molecule. The critical micelle concentration of 8-8-8 and 12-8-12 surfactants passes through a minimum with increasing temperature. This behavior is the outcome of two opposite contributions, one coming from the hydration of the hydrophobic chains and the other due to a partial hydration of the head group in the surfactant. The values of ΔH_{mic} obtained for the surfactants investigated indicate that the thermal effect of micellization is also dependent on the water structure and interaction between hydrophobic chains. The Gibbs free energy change was found to be negative, implying as expected that micellization occurs spontaneously. Further it was found that the changes in enthalpy and entropy almost compensate each other for surfactant with shorter chain lengths (8-8-8). In the case of 12-8-12 the entropy is the main factor responsible for micellization only at temperatures near 298 K, because at higher temperature the unique structure of water is broken down and, consequently, hydrophobic interactions becomes weaker. The experiments confirm that the micelle formation can be seen as a compromise of a variety of attractive and repulsive forces.

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