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A CALORIMETRIC STUDY OF THREE LONG-CHAIN IONIC SURFACTANTS *

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ABSTRACT

Differential enthalpies of solution in water of crystalline sodium dodecyl sulphate (SDS), sodium *p*-octylbenzenesulphonate (SOBS), and hexadecyltrimethylammonium bromide (CTAB) have been measured as a function of concentration at temperatures between 25 and 50 °C. The concentration change was small in the experiments and the results give a good approximation to the partial molar enthalpy content of the surfactant in the monomer and micellar states relative to the crystalline state. The enthalpies of dissolution to give monomers showed a strong, linear increase with temperature for SDS and SOBS and a nearly linear increase for CTAB, while the enthalpy of dissolution to give micelles was constant between 25 and 50 °C for the first two surfactants and only slowly increased for CTAB. Partial molar heat capacities were derived for monomeric and micellar SDS and SOBS. The large positive partial molar heat capacities of the monomeric surfactants are characteristic for hydrophobic solutes and the large heat capacity change for micelle formation arises from the loss of hydrophobic hydration in the formation of micelles.

Results of microtitration experiments at 25 °C show that the micelle formation of CTAB is not a simple aggregation process, but indicate a secondary process taking place closely after the critical micelle concentration (CMC).

INTRODUCTION

The formation of micelles in aqueous solution is accompanied by a large negative heat capacity change ΔC_p(mic). This is in accordance with the expected change in hydration of the hydrophobic group upon micelle formation [1]. For ionic amphiphiles, a positive heat capacity contribution from ionic interactions counteracts, to some extent, the hydrophobic contribution and makes ΔC_p(mic) less negative than for nonionic amphiphiles having the same hydrophobic group [2]. Many ionic amphiphiles that have

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* Dedicated to Professor Syûzô Seki in honour of this contribution to Calorimetry and Thermal Analysis.

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been studied until now have enthalpies of micelle formation ΔH(mic) that are close to zero at room temperature [3]. This means that the critical micelle concentration (CMC) will have a minimum and vary only slowly with temperature in this region. However, the large C_p(mic) makes ΔH(mic) strongly temperature-dependent and CMC will vary significantly outside the room-temperature region. The influence of temperature on the micellization process is a reflection of the partial molar enthalpies and heat capacities of the monomer and micellar states in solution. As summarized in the review by Stenius et al. [3], previous calorimetric studies have mostly focused on the monomer–micelle equilibrium and provided ΔH(mic) and ΔC_p(mic) from measurements on the transfer of amphiphile molecules from the monomeric to the micellar state. A deeper understanding of the influence of temperature on the monomer–micelle equilibrium requires measurements of the individual partial molar enthalpies and heat capacities of the monomeric and micellar states relative to a common reference state. Heat capacity measurements on surfactant solutions leading to apparent molar heat capacities as a function of concentration have been made by Desnoyers and co-workers (see, e.g., ref. 4). Partial molar heat capacities of the amphiphiles $\bar{C}_{p,2}$ in monomeric and micellar state are deduced through differentiation of the results. The propagation of errors is unfavourable, leading to fairly large uncertainties in the derived partial molar heat capacities at low concentrations. The first attempt to determine separately the partial molar enthalpy of the monomer and micellar states appears to have been made by Mazer and Olofsson [5] in their study of the effect on the micellization of sodium dodecyl sulphate (SDS) of temperature variation and neutral salt (NaCl). The enthalpy of dissolution of small amounts of SDS crystals in SDS solutions above and below the CMC were measured at two different temperatures and in the presence of added NaCl. In this way, SDS in crystalline form provided a thermodynamic reference state. Both increase in temperature and addition of extra salt give a more exothermic ΔH(mic). However, the results showed the monomer, but not the micellar, state to be influenced by the temperature change, while the extra salt only affected the micellar state. This approach has been extended in the present study, which reports differential enthalpies of solution as a function of concentration for three different crystalline amphiphiles at various temperatures. The surfactants studied have low CMC: at 25°C they are 8.0×10^{-3} mol l^{-1} for sodium dodecyl sulphate [6], 11×10^{-3} mol l^{-1} for sodium *p*-octylbenzenesulphonate [7] and 0.89×10^{-3} mol l^{-1} for hexadecyltrimethylammonium bromide [8]. The concentration change in each experiment was small and the measured enthalpy changes are good approximations of the partial molar enthalpy change for the dissolution process. The results show how the partial molar enthalpy content of monomeric and micellar amphiphile varies with concentration and temperature and give a detailed mapping of the micellization region.

EXPERIMENTAL

Specially pure (> 99%) sodium dodecyl sulphate (SDS) from BDH, and analytical grade hexadecyltrimethylammonium bromide (CTAB) from Merck, were used without further purification. A pure sample of sodium *p*-octylbenzenesulphonate (SOBS) prepared by Professor P. Botherel, Domain Universitaire, Talence, France, was used as received. For the enthalpy of dissolution measurements, the amphiphile crystals were gently mortared and sifted through a 45 mesh sieve. Reagent-grade water produced by a Milli-Q filtration system was used in the experiments. The enthalpy measurements were made using an LKB-8721 reaction-solution calorimeter with 100- or 25-cm^3 glass vessels [9]. Samples of amphiphile crystals were placed in cylindrical glass ampoules (1 cm^3 volume) which had thin end-walls and narrow necks which were sealed under a low flame and detached [5]. The measured enthalpy changes were corrected for a small endothermal background effect that was observed when breaking empty ampoules in the filled calorimetric vessel. The effect is due mainly to the introduction of a small air bubble (~ 1 cm^3) into the calorimeter liquid, which results in some evaporation. Its magnitude was 0.02 J at 25°C, 0.05 J at 30°C, 0.08 J at 40°C and 0.17 J at 50°C. The uncertainty in this correction is less than 0.02 J. A measurement of the heat capacity of crystalline SOBS was also conducted in the present study with a drop heat-capacity calorimeter [10].

RESULTS

Measurements have been made of differential enthalpies of solution of crystalline SDS, SOBS and CTAB as a function of the total amphiphile concentration. The experiments consisted of measuring the enthalpy changes when breaking a series of ampoules containing a small amount of amphiphile in the calorimeter which initially contained 100 cm^3 of pure water. In the first few experiments, the final concentration in the calorimeter liquid was below the CMC and the measured enthalpy change was equal to the difference between the enthalpy content of the monomeric amphiphile at that concentration and the enthalpy content of the crystalline amphiphile:

$$\mathrm{A(cr)} + \mathrm{aq}(m_i) \rightarrow \mathrm{A}(\mathrm{mon}, m_f); \qquad \Delta \bar{H}_{\mathrm{obs}} = \bar{H}(\mathrm{mon}) - H(\mathrm{cr}) \tag{1}$$

m_i and m_f denote the initial and final amphiphile concentrations expressed in mol kg^{-1} H_2O.

In the micellization region a fraction $(1 - \alpha)$ of added amphiphile will dissolve as monomers while the fraction α will form micelles:

$$\mathrm{A(cr)} + \mathrm{aq}(m_i) \rightarrow (1 - \alpha)\mathrm{A}(\mathrm{mon}, m_f) + \alpha/n\,\mathrm{A}_n(\mathrm{mic}, m_f) \tag{2}$$

$$\Delta \bar{H}_{\mathrm{obs}} = (1 - \alpha)\bar{H}(\mathrm{mon}) + \alpha\bar{H}(\mathrm{mic}) - H(\mathrm{cr}) \qquad (2)$$

At higher total amphiphile concentration all added amphiphile will dissolve to give micelles *:

$$\mathrm{A(cr)} + \mathrm{aq}(m_i) \rightarrow \frac{1}{n}\mathrm{A}_n(\mathrm{mic},\ m_f);\ \Delta H_{\mathrm{obs}} = \bar{H}(\mathrm{mic}) - H(\mathrm{cr}) \qquad (3)$$

Results of measurements on the three surfactants at 50°C are summarized in Fig. 1. In addition, experiments were made at 25 and 40°C for SOBS, 25°C for SDS, and 25, 30 and 40°C for CTAB. Measurements on the dissolution of SDS have been made previously at 30 and 40°C [5]. These values are included in the table, but the values of $\bar{H}(\mathrm{mic}) - H(\mathrm{cr})$ and, accordingly $H(\mathrm{mic})$, refer to final concentrations of 11.5 and 13 mmol kg^{-1} at 30 and 40°C, respectively. The dissolution enthalpy below CMC for SDS and SOBS shows a concentration dependence which appears to be the same at the different temperatures. Linear fits give slopes of about 130 kJ $\mathrm{mol}^{-1}/\mathrm{mol\ kg}^{-1}$ for SOBS at three temperatures and 100 kJ $\mathrm{mol}^{-1}/\mathrm{mol\ kg}^{-1}$ for SDS at 25°C. At 50°C the slope for SDS appears to be about half the value at 25°C but considering the experimental errors it is questionable if the difference is significant. Results of the dissolution measurements are summarized in Table 1 where values of the dissolution enthalpies below CMC extrapolated to zero amphiphile molality, $H^{\infty}(\mathrm{mon}) - H(\mathrm{cr})$, are shown in column three. The values of $\bar{H}(\mathrm{mic}) - H(\mathrm{cr})$ shown in column four relate to an amphiphile molality of 30 mmol kg^{-1} for SOBS, 20 mmol kg^{-1} for SDS and 10 mmol kg^{-1} for CTAB. The difference between the temperature variations of the two sets of values is clearly seen in Fig. 2, where the different enthalpies are plotted against temperature. Enthalpies of micelle formation, $\Delta H(\mathrm{mic})$, were calculated from the enthalpy values in columns three and four: $\Delta H(\mathrm{mic}) = [\bar{H}(\mathrm{mic}) - H(\mathrm{cr})] - [H^{\infty}(\mathrm{mon}) - H(\mathrm{cr})]$. The values of $\Delta H(\mathrm{mic})$ shown in the last column thus refer to the formation of micelles from monomers at infinite dilution to give micelles at the indicated molalities.

The micellization of CTAB has also been studied using the microtitration method described in ref. 2. Measurements have been made of differential enthalpies of dilution of a concentrated CTAB solution as a function of concentration at 25°C. In the experiments, 7–25 mm^3 portions of 17.08 wt% CTAB solution were added consecutively to the calorimeter which initially contained 24.9 g of pure water. Results of two different series of experiments are shown in Fig. 3. The results of the individual experiments are represented by bars whose length indicates the change in concentration, which varies between 0.14 and 0.47 mmol kg^{-1}. As the change in concentration is small in each experiment, the measured enthalpy is a good approximation of the partial molar enthalpy change. The results at low concentration are

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* The effect of decreasing monomer concentration with increasing micelle concentration [11–15] is not considered in this paper.

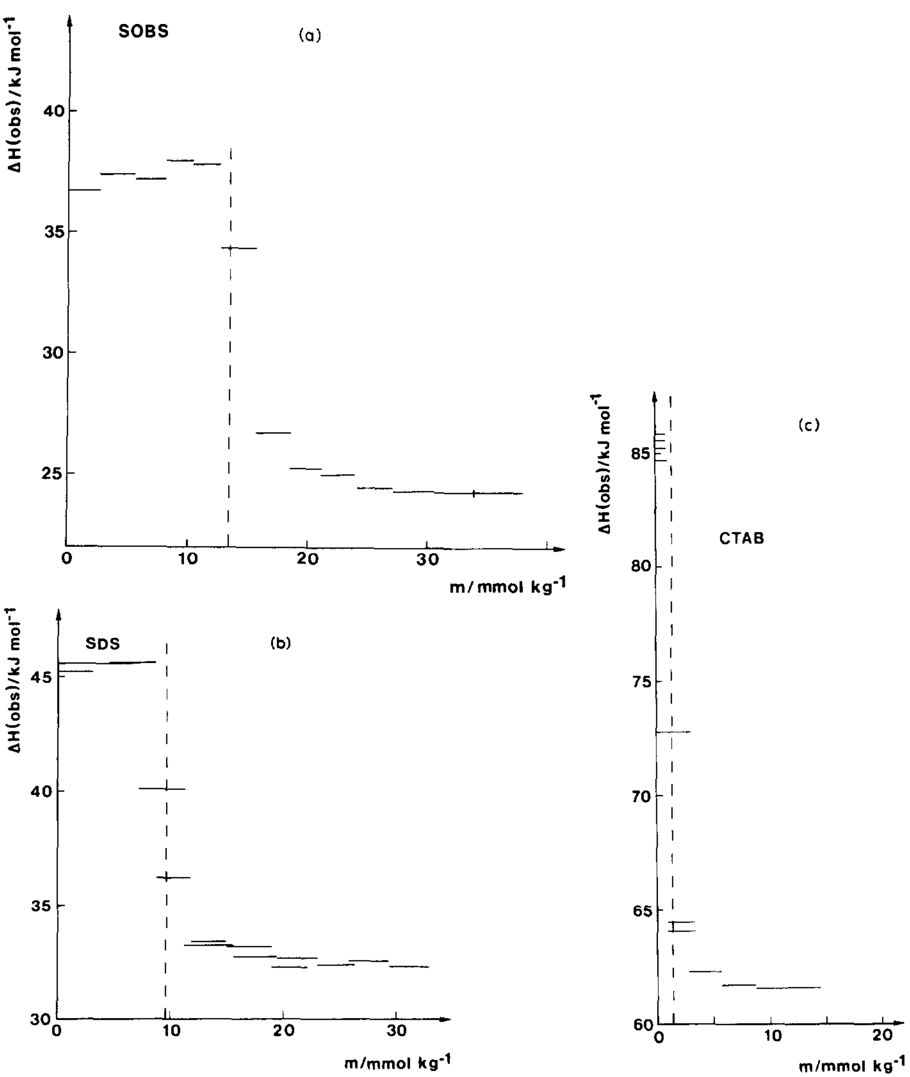

Fig. 1. Differential enthalpies of solution of crystalline amphiphiles as a function of amphiphile concentration at 50°C. The results of individual experiments are represented by horizontal lines whose end points indicate the concentration before and after each addition. The CMCs are indicated by the dashed vertical lines. Below the CMC the amphiphile dissolves to give monomers in solution, in the CMC region partial micellization takes place, and well above CMC all amphiphile added gives micelles.

consistent with the value for the CMC of 8.9×10^{-4} mol l^{-1} reported by Paredes et al. [8]. In the first couple of injections, the micelles in the concentrated solution are diluted and broken up to give monomers and the measured enthalpy stems from demicellization and dilution. In the region around CMC, only partial demicellization takes place and the measured enthalpy will decrease. In normal cases the titration curve would reach a "baseline" determined by the dilution enthalpy of the micelles at a total amphiphile concentration of about twice the CMC (see Figs. 1a and 1b and

TABLE 1

Results of measurements of enthalpies of solution of crystalline amphiphiles

Compound	t (°C)	H^{∞}(mon) − H(cr) (kJ mol^{-1})	$\bar{H}$(mic) − H(cr) [a] (kJ mol^{-1})	ΔH(mic) [a] (kJ mol^{-1})
SOBS	25.1	25.3 ± 0.2	24.44 ± 0.14	−0.9 ± 0.3
	40.0	32.0 ± 0.3	24.36 ± 0.16	−7.6 ± 0.4
	50.1	36.7 ± 0.3	24.42 ± 0.07	−12.3 ± 0.3
SDS	24.9	32.2 ± 0.1	32.3 ± 0.1	0.1 ± 0.2
	30.0 [b]	34.8 ± 0.1	(33.0 ± 0.1) [c]	(−1.8 ± 0.2) [c]
	40.0 [b]	40.1 ± 0.2	(33.4 ± 0.1) [c]	(−7.0 ± 0.2) [c]
	50.1	45.3 ± 0.1	32.4 ± 0.1	−12.9 ± 0.2
CTAB	25.0	66.0 ± 0.5	54.0 ± 0.5	−12.0 ± 0.7
	29.9	70.1 ± 0.5	56.5 ± 0.2	−13.6 ± 0.6
	40.0	78.7 ± 0.5	60.2 ± 0.1	−18.5 ± 0.5
	50.1	85.3 ± 0.5	61.5 ± 0.2	−23.8 ± 0.6

[a] The results relate to a concentration of 30×10^{-3} mol kg^{-1} for SOBS, 20×10^{-3} mol kg^{-1} for SDS in the present study and 10×10^{-3} mol kg^{-1} for CTAB.

[b] From ref. 5.

[c] The results were found at a final concentration of 11.5×10^{-3} mol kg^{-1} at 30°C and 13×10^{-3} mol kg^{-1} at 40°C.

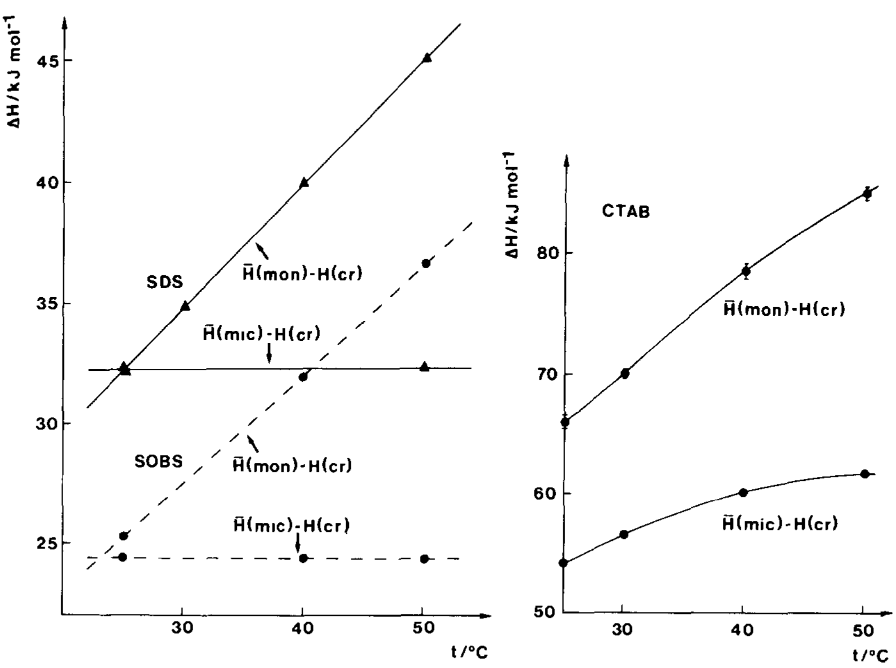

Fig. 2. Differential enthalpies of solution of crystalline surfactants to give monomers $\bar{H}$(mon) − H(cr) and micelles $\bar{H}$(mic) − H(cr), respectively, as a function of temperature.

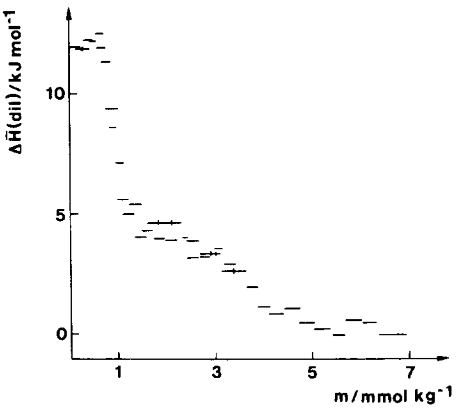

Fig. 3. Differential enthalpies of dilution of 17.1 wt% CTAB solution as function of CTAB molality at 25°C.

ref. 2). The behaviour of CTAB is atypical in that $\Delta\bar{H}$(dil) shows a plateau at about two times the CMC but then decreases further to become close to zero at concentrations above 5 mmol kg^{-1}. The hump in the $\Delta\bar{H}$ curve indicates a change in structure of the CTAB micelles close to the CMC; the nature of this change is unknown. The titration curve gives a plausible explanation for the discrepancy between the value of -12.0 kJ mol^{-1} for ΔH(mic) at 25°C found in the present study and the value of -9.2 kJ mol^{-1} reported by Paredes et al. [8,16]. Our value refers to a micellar concentration of about 10 mmol kg^{-1}, while their value probably refers to a concentration close to the CMC.

The heat capacity of crystalline SOBS C_p(cr), was found to be 415 ± 2 J K^{-1} mol^{-1} at 25°C. A value of 465 ± 2 J K^{-1} mol^{-1} for crystalline SDS was reported earlier [5].

DISCUSSION

The amphiphiles in the present study have low CMC (1–10 mmol kg^{-1} at 25°C) and they give fairly large micelles with an aggregation number of 60 or more. The micelle formation is highly cooperative, which means that micelle formation takes place over a narrow concentration range [17]. As seen in Figs. 1a and 1b, micelle formation appears to have a sharp onset and is completed at a concentration of about twice CMC. A more detailed description of the micellization region can be made using the thermodynamic model for the micellization of ionic amphiphiles developed by Gunnarsson et al. [11]. Such an analysis will be published elsewhere [18]. As was described in the Results section, the micelle formation of CTAB is more complex and the titration results at 25°C indicate that a secondary micellization process takes place close to the CMC in this system.

The enthalpy of micelle formation, ΔH(mic), is defined in the present study as the difference between the enthalpy content of the amphiphile in a micellar solution, of about twice the CMC for SOBS and SDS and 10 mmol kg^{-1} for CTAB, and of the monomeric amphiphile at infinite dilution. For both SOBS and SDS, ΔH(mic) is close to zero at 25 °C but fairly exothermic for CTAB, being -9 kJ mol^{-1} [8,16] or -12 kJ mol^{-1}, depending on the final concentration. As ΔH(mic) for dodecyltrimethylammonium bromide has been found to be -1.4 kJ mol^{-1} at 25 °C [19], the more exothermic ΔH(mic) for CTAB is primarily due to the longer alkyl chain and not to the difference between the character of the headgroups. Too few systems have been studied carefully enough to allow general conclusions to be drawn about the influence on ΔH(mic) and ΔC_p(mic) of alkyl chain-length and headgroup characteristics.

As seen from Fig. 2, the strong temperature variation of ΔH(mic) arises from the monomeric state. Within errors of measurements, H^{∞}(mon) $-$ H(cr) increases linearly with temperature for SOBS and SDS and nearly so for CTAB. From the slopes in Fig. 2, the heat capacity change for the dissolution of crystalline amphiphile to give monomers at infinite dilution, C_p^{∞}(mon) $-$ C_p(cr), is found to be 455 ± 15 J K^{-1} mol^{-1} for SOBS and 510 ± 10 J K^{-1} mol^{-1} for SDS. For CTAB a value of 840 ± 50 J K^{-1} mol^{-1} is derived at 25 °C. The partial molar heat capacity of the amphiphile at infinite dilution, C_p^{∞}(mon), is found by adding C_p(cr) to the above values. This gives C_p^{∞}(mon) equal to 870 ± 15 J K^{-1} mol^{-1} for SOBS and 975 ± 10 J K^{-1} mol^{-1} for SDS. The heat capacity changes, $\bar{C}_p$(mic)$-C_p$(cr), are within errors of measurement equal to zero for SOBS and SDS and on average 350 J K^{-1} mol^{-1} for CTAB between 25 and 50 °C. The partial molar hear capacity in the micellar state, $\bar{C}_p$(mic), then becomes 417 ± 10 J K^{-1} mol^{-1} for SOBS and 465 ± 10 J K^{-1} mol^{-1} for SDS. Heat capacity measurements on aqueous solutions of SOBS have been made at 25, 40 and 55 °C by Caron et al. [20] and apparent and partial molar heat capacities have been derived for monomeric and micellized SOBS. The agreement between their values and ours for C_p^{∞}(mon) and $\bar{C}_p$(mic) is satisfactory considering the different ways they were derived.

Hydrophobic solutes have large, positive partial molar heat capacities, $C_{p,2}^{\infty}$, in aqueous solution. A characteristic feature of $C_{p,2}^{\infty}$ of nonionic solutes is the group additivity, which allows the estimation of $C_{p,2}^{\infty}$ from the heat capacity increments of the constituent groups [21–24]. The contribution of the hydrophobic group to C_p^{∞}(mon) of SOBS and SDS can be estimated to be 986 and 1147 J K^{-1} mol^{-1}, respectively, using the scheme of Nichols et al. [21]. Sodium salts of anions of the same size as the headgroups have small $C_{p,2}^{\infty}$, -36 and -25 J K^{-1} mol^{-1} for $NaClO_3$ and $NaHSO_3$, respectively, and -30 and 8 J K^{-1} mol^{-1} for $NaClO_4$ and $NaHSO_4$ respectively [25,26]. The values of C_p^{∞}(mon) of SOBS and SDS are somewhat lower than the sum of these group contributions, which may at least in part be due to the effect of the ionic charge on the hydrophobic hydration. Also a larger part of the $\bar{C}_p$(mic) stems from the contribution of the hydrocarbon chains. If the interior of the micelles is assumed to be liquid-like, the C_p contribution of the chains can be estimated from the C_p for the corresponding liquid hydrocarbons. The C_p of dodecane is 375 J K^{-1} mol^{-1} at 25°C and can be estimated to be about 350 J K^{-1} mol^{-1} for octylbenzene [27]. This leaves about 70 and 90 J K^{-1} mol^{-1} for the contribution of the headgroup in SOBS and SDS respectively. An estimate of the headgroup contribution to $\bar{C}_p$(mic) can be made from the thermal behaviour of 2.5 mol l^{-1} solutions of $NaClO_3$ or $NaClO_4$ in which the interparticle spacing is about the same as the spacing between the head groups on the micellar surface [5]. Under these conditions $\bar{C}_p(NaClO_3)$ is 130 J K^{-1} mol^{-1} and $C_p(NaClO_4)$ is ~ 140 J K^{-1} mol^{-1} [25]. While there are indeed uncertainties involved in making these estimates, it is clear that in monovalent electrolyte solutions the partial molar heat capacity changes sign from dilute to concentrated solutions and probably gives the correct trend for the change in headgroup contribution between monomer and micelle. However, this comparison indicates that the hydrocarbon chain in the micelle has lost all the excess heat capacity originating from the water contact and has basically a liquid character in the hydrocarbon core. This is in accordance with Hartley's original view of micellar structure [28], as well as with the modern picture of ionic micelles [29].

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