Calorimetric study of SDS micelle formation in water and in NaCl solution at 298 K

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Abstract

The enthalpies of micellization for the anionic surfactant sodium dodecylsulphate (SDS) in water and in NaCl solution have been studied by calorimetry at 298 K. The calorimetric experiments were carried out by measuring the heat of solution of SDS in both monomeric and micellar phases. From these data the enthaply of micelle formation was derived. The enthalpy of solution of SDS below and above the critical micellar concentration was found to be endothermic. The results indicate that the enthaply of micelle formation in water at 298 K is -1.42 ± 0.30 KJ mol^{-1}.

The micellization process becomes more exothermic with addition of salt and the enthalpy of micelle formation in 0.50 mol dm^{-3} of NaCl is -8.90 ± 0.15 kJ mol^{-1}. The calorimetric ampoule-breaking technique was adopted in this work for the investigation of the enthalpy of SDS micelle formation. Titration microcalorimetry using the TAM was unsuccessful. The enthalpy of micellization of SDS in water obtained in this work corresponds to the sign of the majority of the values reported in the literature, although very different values are found as well. An evaluation of the thermodynamic parameters is given.

Keywords: Surfactant; Micelle formation; Enthalpy of micellization

1. Introduction

The formation of surfactant micelles is one of the most interesting phenomena in the physical chemistry of solutions. Micelle formation is characteristic of molecules in

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which both hydrophilic and lipophilic groups (hydrocarbon or fluorocarbon chains usually play the function of such groups) are present [1]. The formation of an ionic micelle from monomeric ions results from a balance between hydrophobic interactions between the hydrophilic part of the amphipathic micelle forming ions and electrostatic interactions and their hydrophilic charged parts, as well as with and between counterions. The strength and importance of these various interactions depend, in part, upon factors such as temperature, ionic strength, the properties of the particular ions involved, and also upon the concentration and structure of the resulting micelle (or more exactly, the distribution of micelles), in particular, its association number, its shape, and the compactness of its electrical double layer. Needless to say, the micelles that actually exist correspond to the lowest free energy state of the system.

Micelles correspond to the formation of aggregates usually at a defined concentration, the critical micelle concentration or CMC [2]. The great importance of micelles in the textile industry in detergents, biological actions, membrane mimetic chemistry, etc., is due to this peculiar property. Applications of surface active agents have been increasing rapidly, and an understanding of the physico-chemical properties of micelle formation is becoming more and more important to scientists in various fields [3]. We have recently studied the partition of a homologous series of biologically active compounds into micellar solutions [4].

A positive ΔS is the dominant driving force behind micelle formation. The key to understanding this entropy increase is the extensive hydrogen bonding that occurs in water. Because water forms no hydrogen bonds with the surfactant hydrophobic tail, the latter merely occupies a cavity in the liquid water structure and, as a result, water molecules become more ordered around the hydrocarbon with an attendant decrease in entropy [5].

On the formation of micelles, surfactant molecules are removed from water and form a micellar environment, which allows the cavity to revert to the structure of bulk water. The highly organized water structure involved in the cavity returns to normal hydrogen-bonded liquid water with an increase in entropy. Incidentally, enhanced hydrogen bonding at the walls of the cavity largely compensates for the breaking of hydrogen bonds to form the cavity, so the enthalpy of micellization is small. Also, the increase in entropy when a CH_2 group is transferred from water into a micelle arises from the breakup of this structured water [6]. The heats of solution of SDS in water and in salt solution in the monomeric and micellar phase were measured by ampoule-breaking calorimetry. The aim of the present work is a calorimetric study of the micellization of SDS to clarify and comment upon the values of its micellization enthalpy in water and in the presence of salt as found in the literature. The enthalpy of micelle formation was derived from these experimental data.

1.1. Thermodynamics of micelle formation

Micelle formation has been treated theoretically either by applying the law of mass action to the equilibrium between monomers and aggregates or by considering the micelle as a separate but soluble phase. The law of mass action [2] can be applied to the equilibrium between n detergent ions D^{-1} and m counterions C^+ and monodisperse

micelles $M^{(n-m)-}$ as

$$nD^- + mC^+ \rightleftharpoons M^{(n-m)-} \tag{1}$$

where each micelle $[M^{(n-m)-}]$ is assumed to contain n detergent ions D^- and m free counterions C^+, so that a fraction m/n (or degree of ionization α) of the charge of the detergent ions in each micelle is neutralized.

The equilibrium constant for micelle formation is then

$$K_{mic} = \frac{[M^{(n-m)-}]}{[D^-]^n[C^+]^m} \tag{2}$$

Activity coefficients are usually omitted, although even in dilute solutions ($< 10^{-2}$ mol dm^{-3}) the departure from ideality is probably significant [7, 8].

From this model, it can be shown [9] that a relatively rapid increase in $[M^{(n-m)-}]$ occurs over a narrow range of $[D^-]$, provided that n is large, i.e. the model predicts a CMC.

From Eq. (2), the standard free energy of micelle formation per mole of monomer is given by the usual thermodynamic argument as

$$\Delta_f G^\ominus_{mic} = -(RT/n) \ln K_{mic} \tag{3}$$

$$\Delta_f G^\ominus_{mic} = (RT/n)\{n \ln[D^-] + m \ln[C^+] - \ln[M^{(n-m)-}]\}$$

At the CMC, $[D^-] \cong [C^+] \cong CMC$. If the term containing $\ln[M^{(n-m)-}]$ can be neglected [10] we get the useful approximation

$$\Delta_f G^\ominus_{mic} = RT(1 + m/n) \ln CMC \tag{4}$$

As the lifetime of a surfactant molecule in a micelle is of the order of 10^{-7} s and the half-life of a micelle is between 10^{-9} and 1 s [11], the reaction described by Eq. (1) should be assigned to the class of fast reactions [1]. This condition justifies the approximation necessary in the mass action approach, because the process involves not only a chemical reaction, but also a process of segregation of a new phase [1]. The values of these equilibrium constants for surfactants in electrolyte solutions are influenced by the ionic strength of the environment. The CMC of ionic surfactants decreases markedly upon addition of a simple salt of the counterion. Mukerjee et al. [12] have studied the effect of counterion specificity on ionic micelle size hydration and hydrophobic bonding effects, and, through consideration of the CMC and the free energy values in salt-free systems, have shown that micelles form more easily as the size of the hydrated counterion becomes smaller. Their general conclusions are that micelle formation is facilitated as the double layer becomes more compact, which corresponds to a reduction in the effective degree of ionization as shown by conductance and light-scattering, especially for the alkali metals [13].

2. Experimental

2.1. Materials and methods

The initial calorimetric technique involved the use of the thermometric activity monitor (TAM) microcalorimeter in its titration mode. However this technique proved unsuccessful.

An ampoule-breaking technique was then used to measure the enthalpies of solution of SDS in water and in salt solution (LKB-8700 precision reaction calorimeter in which the reaction vessel was immersed in a thermostatted bath maintained at 25.0 ± 0.05°C). In each calorimetric experiment, enthalpies of solution of SDS in the monomeric and micellar phases were determined by breaking an ampoule containing the appropriate quantity of SDS into 100 cm^3 of distilled water and in salt solution to give final concentrations below and above the CMC over the concentration range of $[(1–20) \times 10^{-3}$ mol dm$^{-3}]$. The enthalpies of solution below and above the micellar concentration were plotted against SDS concentration and the values of $\Delta_{sln}H^{\ominus}_{mon}$ and $\Delta_{sln}H^{\ominus}_{mic}$ contained in Table 1 were obtained by extrapolation at the CMC concentration. The same procedure was used to determine the heat of pre-micellar formation or aggregates. Even taking this procedure, we have observed that on increasing the concentration of SDS below and above the CMC the heat effect of solution changes very little. Each experiment was repeated at least three times, and a correction was made for the small heat change (0.10 ± 0.02 J) associated with the breaking of the ampoules.

A test of the accuracy of the calorimeter was performed according to the experimental procedure proposed by Wadsö [14]. This is based on the determination of the enthalpy of solution of tris(hydroxymethyl)aminomethane, 0.01 mol dm^{-3} in 0.1 mol dm^{-3} hydrochloric acid. The value obtained in the present work of -29.7 ± 0.1 kJ mol^{-1} is in agreement with that measured by Sunner and Wadsö of -29.75 ± 0.01 kJ mol^{-1} [15]. As recommended by Koch et al. [16], tris(hydroxymethyl)aminomethane (Riedel-de Häenag) was sublimed and recrystallized under vacuum. The purity was determined by potentiometric titration with hydrochloric acid. Sodium dodecylsulphate (SDS) (Sigma) was purified by reflux extraction with diethyl ether using a Soxhlet extractor, dried under vacuum and stored in a desiccator. The CMC of SDS was measured spectrophotometrically following the procedure described by Ray and Némethy [17] and the result, 8.2×10^{-3} mol dm^{-3}, is in agreement with the literature [2, 18].

3. Results and discussion

The literature contains extensive data relating to the enthalpy of micellization of SDS in water obtained from both calorimetric and van't Hoff methods. However, these

Table 1
Thermodynamic parameters of micellization of SDS in water and in salt solution at 298 K [a]

NaCl mol dm^{-3}	$\Delta_{sln}H^{\ominus}_{mon}$ kJ mol^{-1}	$\Delta_{sln}H^{\ominus}_{mic}$ kJ mol^{-1}	$-\Delta_f H^{\ominus}_{mic}$ kJ mol^{-1}	$-\Delta_f G^{\ominus}_{mic}$ kJ mol^{-1}	$\Delta_f S^{\ominus}_{mic}$ J mol^{-1} K^{-1}
0.00	31.13 ± 0.30	29.71 ± 0.16	1.42 ± 0.30	16.40	50.30
0.01	33.34 ± 0.10	24.97 ± 0.30	8.37 ± 0.30	19.40	37.00
0.05	33.23 ± 0.10	24.73 ± 0.11	8.50 ± 0.15	21.30	42.90
0.50	29.16 ± 0.10	20.26 ± 0.11	8.90 ± 0.15	28.50	65.80

[a] $\Delta_{sln}H^{\ominus}_{mic}$ and $\Delta_{sln}H^{\ominus}_{mic}$ correspond to the enthalpies of solution of SDS in the monomer phase and micellar phase, respectively.

data show large variation. Table 2 shows that values range from a maximum of 2.51 to a minimum of -13.30 kJ mol^{-1}. Part of the variation in these data arises from the use of van't Hoff methods to calculate the enthalpy of micellar formation. As can be seen in Fig. 1, from Goddard and Benson [19] the CMC over the temperature range 10–55°C shows a deep minimum. Therefore, for van't Hoff experiments performed at $T > 35$°C the change in enthalpy of micellization is apparently exothermic, and for $T < 15$°C the apparent enthalpy change is endothermic. The literature also shows that data derived from calorimetry for the micellization of SDS at 298 K are all close to zero.

The experimental measurements of the enthalpies of micelle formation ($\Delta_f H_{mic}^{\ominus}$) in water and in salt were based on the enthalpies of solution of the SDS in the monomer phase ($\Delta_{sln} H_{mon}^{\ominus}$) and micellar phase ($\Delta_{sln} H_{mic}^{\ominus}$) in water. Fig. 2 shows the scheme used to calculate the enthalpy of micellization.

This procedure was also followed for the enthalpies of micelle formation of SDS in electrolyte solution (NaCl, 0.01–0.5 mol dm^{-3}). The results are shown in Table 1.

All the experimental results show that the dissolution of SDS in both the monomer and micellar phases is endothermic. We obtained a negative value for the enthalpy of SDS micelle formation in water (-1.42 ± 0.30 kJ mol^{-1}). Other values for the micellization of SDS in water were found in the literature and are also presented in Table 2, where it can be seen that negative values predominate for the enthalpy of micelle formation, although very different values are found, including some from authors who have found positive values.

Table 2
Enthalpies of micelle formation of SDS in water at 298 K

| Reference	Method	K	$\Delta_f H_{mic}^{\ominus}$/kJ mol^{-1}
Goddard and Pethica [26]	Calorimetric	298	-1.04
Flockhart and Ubbelohde [27]	Temperature	298	2.51
Goddard and Benson [28]	Calorimetric	298	0.42
Goddard and Benson [19]	Temperature	298	-0.042
Matijevic and Pethica [24]	Temperature	293–313	-1.67
Flockhart [29]	Temperature	293	1.67
Benjamin [25]	Calorimetric	298	-1.26
Pilcher et al. [30]	Calorimetric	298	0.36
Eatough and Rehfeld [31]	Calorimetric	298	2.20
Kresheck [32]	Calorimetric	298	-0.60
Kresheck and Hargraves [33]	Calorimetric	298	-2.13
Moroi et al. [34]	Temperature	298	0.10
Paredes et al. [35]	Calorimetric	298	0.68
Singh et al. [23]	Temperature	298	-13.30
Woolley and Burchfield [36]	Calorimetric	298	-0.75
Bergström and Olofsson [37]	Calorimetric	298	0.10
Johnson and Olofsson [38]	Calorimetric	298	-0.20
Sharma et al. [39]	Calorimetric	298	0.47
This work	Calorimetric	298	-1.42 ± 0.30
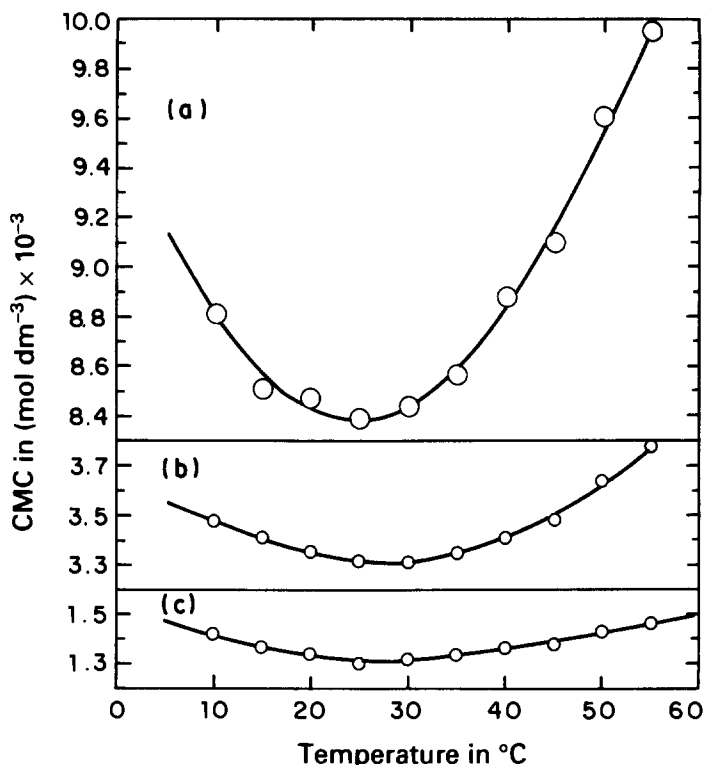
Fig. 1. Variation of the CMC with temperature: (a) sodium dodecylsulphate; (b) sodium decylsulphate; and (c) sodium octylsulphate.
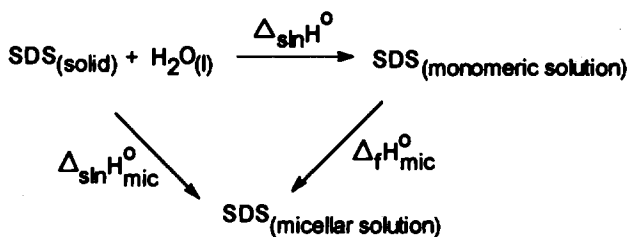

Fig. 2. Scheme for the calculation of the enthalpy of micelle formation.

The small enthalpy of micelle formation ($\Delta_f H^{\ominus}_{mic}$) can be explained in terms of the contribution effect of the structure of water, as in the model discussed by Frank and Evans [5].

Mazer and Olofsson [20], using a calorimetric system similar to that used here, obtained values for the enthalpies of solution of SDS in water and in electrolyte solution of the monomer and micelle, in the range 27–40 kJ mol^{-1} at 298 K, in

agreement with the results obtained in the present work (Table 1). The values of free energy change for micelle formation of SDS in water and in salt solutions contained in Table 1 were calculated using Eq. (4). The CMC of SDS in water and in salt solutions were obtained from Chiu et al. [21] and assumed the same degree of ionization, $\alpha = 0.38$ [22].

From the data in Table 1, it is possible to see that the enthalpies of solution of SDS in pure water in the monomer phase and in the micellar phase are close, whilst those in electrolyte solution have rather different enthalpies of micellization. Electrolyte solutions are usually utilized in thermodynamic studies to stabilize organized systems (micelles, liposomes, membrane). In the case of micelles, this stabilization occurs through electrostatic interaction of the electrolytes with the surfactant ions in the Stern layer and with unbound counterions in the Gouy–Chapman diffuse double layer.

Prediction of the effect of added salt is problematic but the experimental results obtained in this work show that increasing the added salt concentration increases the exothermicity of micellization.

The enthapy of micellization of SDS in 0.5 mol dm^{-3} NaCl solution reported in this work for a temperature of 298 K is -8.9 ± 0.15 kJ mol^{-1} and is consistent with that of Mazer and Olofsson [20].

If the interaction of counterions with micelles is exothermic and if more counterions are bound at higher concentrations, micellization should become more exothermic as the added salt concentration increases. The enthalpy of micellization obtained in this work in water and in salt solution contained in Table 1 confirms that micellization becomes more exothermic as the concentrations of salts increase. This may also be a consequence of the smaller energy required to break down the water-structured region or "iceberg" around the hydrocarbon chain. The relative stability of the micelles with added salt is clearly seen in the values of $\Delta_f G^{\ominus}_{mic}$ in Table 1: increasing the salt concentration lowers the CMC [21] and $\Delta_f G^{\ominus}_{mic}$ becomes more negative, indicating stable micelles. This is also in agreement with the entropy values calculated and contained in Table 1.

From the values of $\Delta_f H^{\ominus}_{mic}$ of SDS in water found in the literature and contained in Table 2, it can be shown that the average of the positive values is 0.94 kJ mol^{-1} and of the negative values -0.96 kJ mol^{-1}, excluding the value of -13.30 kJ mol^{-1} from Singh et al. [23].

On the basis of our data and of the literature data, the enthalpy of micellization of SDS in water is exothermic and the best value is selected to be -1.42 ± 0.30 kJ mol^{-1}, in good agreement with the values obtained by Matijevic and pethica [24] and Benjamin [25].

Acknowledgements

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