Energitics of micellizaion of sodium *n*-dodecyl sulfate at physiological conditions using isothermal titration calorimetry

Asghar Taheri-Kafrani · Abdol-Khalegh Bordbar

Abstract The micellization characteristics of sodium *n*-dodecyl sulfate (SDS) have been investigated by microcalorimetric technique at conditions close to the physiological ones. The thermodynamics of micellization were studied at 20, 25, 30, 35 and 40 °C in 50 mM HEPES buffer, pH 7.4 and 160 mM NaCl using isothermal titration calorimetric (ITC) technique. The calorimeter can operate in a stepwise addition mode, providing an excellent method of determination of critical micelle concentration (CMC) and enthalpy of demicellization (and hence micellization). It can as well distinguish between aggregating and non-aggregating amphiphiles (solutes) in solution. The dilution enthalpy (ΔH_{dil}) was calculated and graphed versus concentration in order to determine the micellization enthalpy (ΔH_{mic}) and CMC. In addition to the CMC and ΔH_{mic}, the effective micellar charge fraction (α) of the ionic surfactant micellization process can also be determined from ITC curves. The Gibbs free energy of the micellization (ΔG_{mic}), entropy of the micellization (ΔS_{mic}), and specific heat capacity of the micellization ($\Delta C_{P,mic}$) process have been evaluated by the direct calorimetric method (mass-action model) as well as by the indirect method of van't Hoff by processing the CMC and α results of microcalorimetry at different temperatures. The differences of the results obtained by these two procedures have been discussed. The presence of NaCl (160 mM) in the solutions decreased the CMC of SDS. The enthalpy changes associated with micelle dissociation were temperature-dependent, indicating the importance of hydrophobic interactions. The ΔG_{mic} was found to be negative, implying, as expected, that micellization occurs spontaneously once the CMC has been reached. The values of ΔG_{mic} were found to become more negative with increasing temperature and the ΔS_{mic} was found to decrease with increasing temperature in both models.

Keywords Critical micelle concentration · Isothermal titration calorimetry · Micellization thermodynamics · Sodium *n*-dodecyl sulfate · van't Hoff enthalpy

Introduction

In an aqueous medium, both pure and mixed surfactants form micelles after reaching a concentration called the critical micelle concentration (CMC), whose determination has considerable practical importance normally to understand the self-organizing behaviors of surfactants in exact and detailed ways. The self-organization (micelle formation) of surfactants in solution is an important and amply studied thermodynamically favorable physicochemical phenomenon [1–5]. From the viewpoint of usability, self-organization of a surfactant at a lower concentration is preferable. These make scope for synthesizing new surfactants as well as modifying head groups of existing surfactants and studying their solution properties with reference to micelle formation. Many studies have been also devoted to the elucidation of micellar structures under different conditions [6–10]. The micellization process of surfactants has been extensively studied since the time McBain first described surfactant

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aggregates in solution [11]. The determination of CMC and energetics of the micellization process is normally done by tensiometric, conductometric, spectrophotometric, NMR, calorimetric, and other methods. Among all these methods, calorimetry has a distinction for it can estimate both CMC and enthalpy of micellization from a single run, which is not possible by any other method. The thermometric titration method for the determination of CMC and enthalpy of micellization (ΔH_{mic}) was elaborately introduced by Kresheck and Hergraves [12] and pursued by others [13–27]. When the surfactant concentration in the titration cell is lower than the CMC, the observed enthalpy contains the heats from surfactant demicellization and dilution effect. At surfactant concentrations much higher than CMC, only the dilution enthalpy of surfactant micelle is measured. If ΔH_{mic} and ΔH_{diss} refers to the enthalpy change when surfactant monomers cooperatively aggregate into micelles or cooperatively demicellize into surfactant monomers at CMC, respectively, then $\Delta H_{\mathrm{mic}} = -\Delta H_{\mathrm{diss}}$.

The surfactant, sodium *n*-dodecyl sulfate (SDS), is a very commonly used amphiphile; the basics of its micellization and related behaviors have been essentially studied via calorimetric method [12, 14, 20, 21, 28–31]. Paula et al. [28] have demonstrated how a high sensitivity titration microcalorimeter having a provision for multistage addition and working in demicellization mode can help to determine the CMC and enthalpy of micellization by selecting four surfactants, sodium dodecyl sulfate, octyl glucoside, sodium cholate, and sodium deoxycholate. Similar microcalorimetric procedures for the study of self-aggregating and interacting systems have been demonstrated by Johnson et al. [29] and Blandamer et al. [32]. It is, therefore, worthwhile to reassess the basics of micellization with the help of this unique microcalorimetric method.

As can be seen in these literatures, values for these fundamental thermodynamic properties vary significantly and also there is no report of CMC and corresponding thermodynamic parameters of SDS in physiological conditions. So, there has been a trend to research further to determine the CMC and thermodynamic values in such medium. In the present study, investigation of the thermodynamic properties of micellization is conducted using calorimetric method. The anionic surfactant, SDS in HEPES buffer, pH 7.4 and 160 mM NaCl is used and the CMCs and the thermodynamic parameters were quantified at different temperatures. Scaling relationships between the thermodynamic properties at various temperatures were developed. ΔH_{mic}, ΔS_{mic} and $\Delta C_{P,\mathrm{mic}}$ values of SDS obtained from direct calorimetry and van't Hoff treatment and results have been compared with each other.

Experimental

Materials

The anionic surfactant, SDS, was purchased from Sigma Chemical Co. Sodium chloride and *N*-(2-hydroxyethyl) piperazine-*N'*-(2-ethanesulfonic acid) (HEPES) buffer were obtained from Merck Chemical Co. All the used reagents were of highest degree of purity. All of the solutions were prepared using double distilled water. The 50 mM HEPES pH 7.4, 160 mM NaCl was used as buffer. All solutions were used freshly after preparation.

Methods

Isothermal titration calorimetry experiments

The calorimetric measurements were carried out using MCS-ITC (MicroCal Inc., Northampton, MA, USA) isothermal titration calorimeter. This calorimeter was used to measure enthalpies of dilution at 20.0, 25.0, 30.0, 35.0, and 40.0 °C. Two hundred micro liter aliquots of SDS solution (60 mM) were injected sequentially by a computer-controlled syringe (5 μL in each injection) into a 1.46 mL reaction cell containing buffer solution. Each injection lasted 5 s and there was an interval of 180 s between every successive injection. The solution in the reaction cell was stirred at a speed of 315 rpm throughout the experiments. After each injection, the computer records the heating rate required to maintain a constant temperature difference between the sample cell and a reference cell filled with purified water. The integration of the rate of heating yields a plot of heat required to maintain the temperature difference after each injection, q_{inj}, versus the increasing concentration of surfactant in the sample cell, C_{cell} [33]. The enthalpy change of dilution, ΔH_{dil}, is found by dividing q_{inj} by the number of moles of surfactant injected in each 5 μL aliquot.

Thermodynamics of micellization

A graph of ΔH_{dil} versus concentration exhibits two plateaus. The first plateau, found at low concentrations, represents the dilution of a micellar solution into a monomeric solution. The second plateau is representative of a micellar solution being injected into another micellar solution and is far less endothermic than the first plateau. The enthalpy of micellization, ΔH_{mic}, is found by subtracting the plateau value at low surfactant concentrations from the plateau at high surfactant concentrations. This plot of ΔH_{dil} versus C_{cell} not only provides a value for ΔH_{mic}, but also the CMC of the surfactant can be evaluated by finding the inflection point between the high-concentration plateau and the

low-concentration plateau [17]. Once ΔH_{mic} and the CMC at the five temperatures have been determined, the mass-action (MA) model is used to find ΔG_{mic} and ΔS_{mic} by direct calorimetry [34]. Then we can use the calorimetric CMC values to compare ΔH_{mic}, ΔS_{mic} and $\Delta C_{P,mic}$ obtained by the van't Hoff method of calculation and by the direct processing of the calorimetric results.

Results and discussion

Micellization of SDS in physiological condition at different temperatures

When micellar surfactant solution is titrated into buffer solution, ITC records the differential enthalpy changes related with the demicellization and the dilution of surfactant molecules. Both CMC and ΔH_{mic} can be directly obtained from one ITC experiment [35, 36]. A typical illustration of the heat flow, enthalpy of dilution, and the corresponding differential plot against the SDS concentration at 30 °C is presented in Fig. 1. The enthalpy of micellization (ΔH_{mic}) has been obtained by subtracting the initial enthalpy from the final enthalpy indicated by the vertical arrow in this figure. The estimation of the enthalpy of micellization (ΔH_{mic}) here is sharp and accurate.

At the beginning of the experiment the SDS concentration in the injector was well above the CMC, whereas there was no SDS in the reaction cell. Hence, the large endothermic peak observed at low surfactant concentrations could be attributed to the dissociation of surfactant micelles when they were titrated into the reaction cell, because the exposure of non-polar surfactant tails to the surrounding aqueous phase is endothermic [4, 29, 37–39]. Once the total surfactant concentration in the reaction cell exceeded the CMC of the surfactant, micelle dissociation no longer occurred, and the endothermic enthalpy change decreased appreciably. At surfactant concentrations greatly exceeding the CMC, the enthalpy changes are primarily due to micelle dilution effects [40]. The CMC corresponds to the onset of micellization. Above the CMC, addition of more surfactant monomers produces more surfactant micelles rather than increasing the size or the aggregation number of surfactant micelles [18]. The dependence of the enthalpy change on the surfactant concentration can be used to determine the CMC of the surfactant, that is, from the inflection point in the ΔH_{dil} versus surfactant concentration curve [41]. The CMC point is indicated in the differential plot in Fig. 1. The similar trends were observed at other studied temperatures. The enthalpies of dilution versus the concentrations of SDS plots at different temperatures are also presented in Fig. 2. It is evident that the temperature does not alter the shape of the titration curves
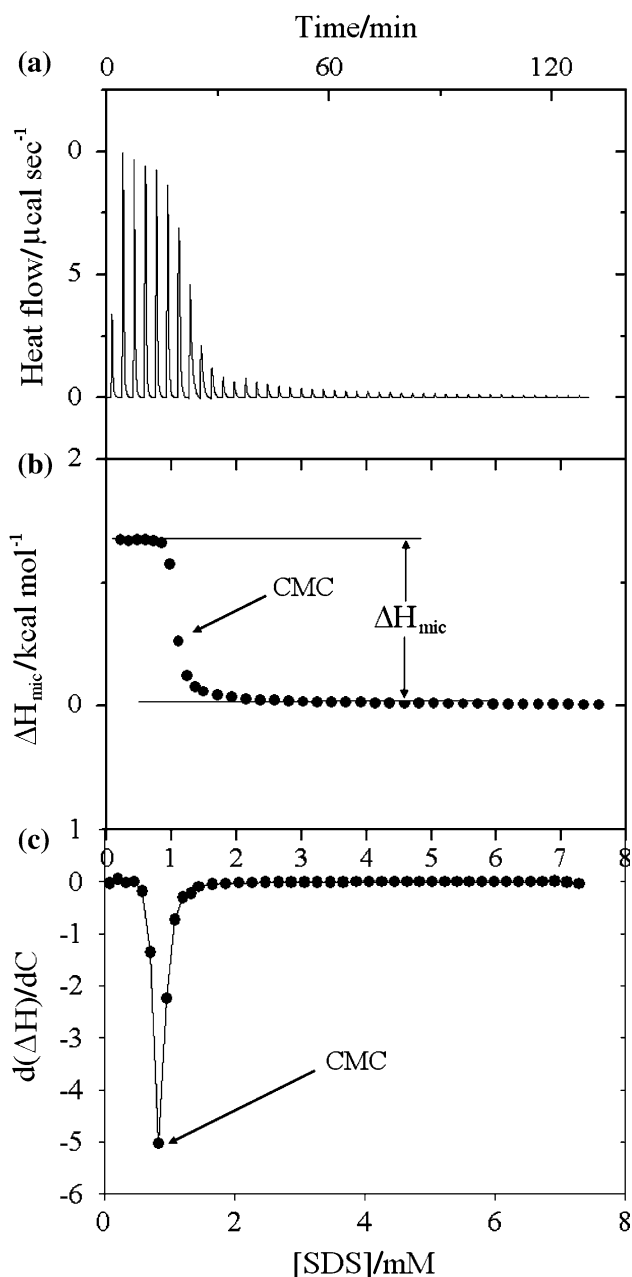

Fig. 1 Titration of 200 μL aliquots of SDS micelles (60 mM) into 1.46 mL of 50 mM HEPES buffer pH 7.4 and 160 mM NaCl at 30 °C. **a** Calorimetric traces (heat flow against time). **b** Process enthalpy versus SDS concentration in the cell. The ΔH_{mic} is represented by the length of the arrow. **c** First derivative of curve B calculated from the interpolated values. The similar curves were obtained at other temperatures

but the difference in the titration curves is mainly attributed to the temperature dependence of the SDS micellization process. The CMC and the ΔH_{mic} values derived following the procedure described with reference to Fig. 1 are also presented in Table 1. As can be seen from this table, all ΔH_{mic} were exothermic for the SDS and will be more negative with increasing temperature. It is interesting to
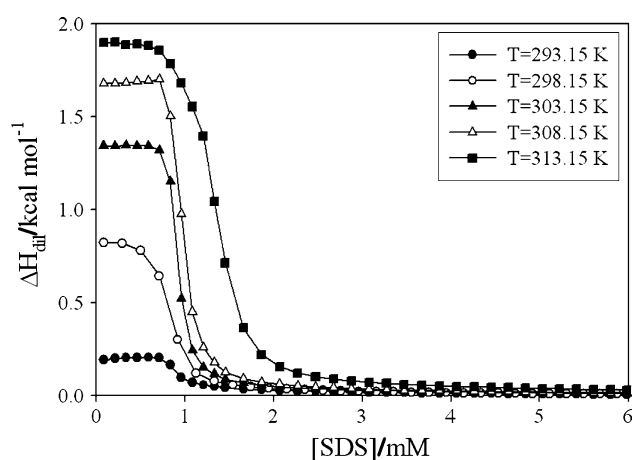
Fig. 2 Microcalorimetric determination of ΔH_{mic} of SDS at 20, 25, 30, 35 and 40 °C: titration of 200 μL aliquots of SDS solution (60 mM) into 1.46 mL of 50 mM HEPES buffer pH 7.4 and 160 mM NaCl

note that the plateau in obtained enthalpograms at all studied temperatures does not stay flat. The CMC for this surfactant also tends to increase with increasing temperature but it is different from other reported CMC in water. It is manifest that salts suppress the CMC of ionic surfactants [42]. The influence of NaCl on the CMC of the SDS was investigated by Thongngam and McClements. They show that there is a steep decrease in the CMC with increasing salt concentration from 0 to 50 mM NaCl, followed by a more gradual decrease at higher salt concentrations. The maximum enthalpy change associated with micelle dissociation was also relatively independent of salt concentration [27]. Fuguet et al. showed that the CMC values in phosphate–SDS buffer are lower than the CMC values in water–SDS [43]. In our study the CMC's of SDS appreciably decrease in the presence of NaCl (160 mM) and 50 mM HEPES buffer, pH 7.4 that is in good conformity with latest consequences [27, 43].

Thermodynamics of micellization

As described previously, the dilution enthalpies for both surfactant monomers and surfactant micelles are negligible for anionic surfactants compared to the enthalpy of the surfactant demicellization process, a step transition for the enthalpy at the CMC can be observed from the ITC curves. The enthalpy change per mole of injectant (SDS) versus [SDS] plot of the present study is illustrated in Fig. 3; the ΔH_{mic} values are distinctly documented on it. Similar curves were obtained at other temperatures. The typical S-shape isothermal titration curve commonly observed for non-ionic surfactant solution was not evident. The determination of ΔH_{mic} from the SDS, ITC curve is illustrated in the figure, where $\Delta H_{\mathrm{dil,1}}$, $\Delta H_{\mathrm{dil,2}}$, and ΔH_{mic} represent the dilution enthalpies of surfactant monomers and surfactant micelles and the micellization enthalpy, respectively. The dilution enthalpies of both surfactant monomers and surfactant micelles $\Delta H_{\mathrm{dil,1}}$ and $\Delta H_{\mathrm{dil,2}}$ cannot be ignored for ionic surfactants, which is related to the non-ideal properties of ionic surfactant systems.

Once ΔH_{mic} and the CMC at all studied temperatures have been determined, the MA model is used to find ΔG_{mic} and ΔS_{mic}. This model, takes into account the fraction of counter-ions bound to the micelle [34]. Equations 1 and 2 can be used to determine ΔG_{mic} and ΔH_{mic} from the temperature dependence of the CMC [2, 44–47].

$$\Delta G_{\mathrm{mic}} = \left(1 + \frac{m}{n}\right) RT \ln X_{\mathrm{cmc}} \qquad (1)$$

$$\Delta H_{\mathrm{mic}} = -(1 + \alpha) RT^2 \left(\frac{\partial (\ln X_{\mathrm{cmc}})}{\partial T}\right)_P - RT^2 \ln X_{\mathrm{cmc}} \left(\frac{\partial \alpha}{\partial T}\right)_P \qquad (2)$$

In these equations, R is the ideal gas constant, T is the absolute temperature, ΔX_{cmc} is the mole fraction of surfactant at the CMC, m is the number of counter-ions bound per micelle and n is the aggregation number. The parameter α defined as m/n is called the effective micellar charge fraction. For SDS, the α value ranges from 0.46 to 0.86, depending on the experimental techniques employed [5]. Once these values are obtained, ΔS_{mic} can be evaluated by the Gibbs equation (Eq. 3).

$$\Delta S_{\mathrm{mic}} = \frac{\Delta H_{\mathrm{mic}} - \Delta G_{\mathrm{mic}}}{T} \qquad (3)$$

As mentioned previously, the $\Delta H_{\mathrm{dil,1}}$ and the $\Delta H_{\mathrm{dil,2}}$ cannot be neglected for SDS in aqueous solutions. At

Table 1 Temperature dependence of the SDS dilution in 50 mM HEPES buffer pH 7.4 and 160 mM NaCl as observed from ITC studies at 1 atm

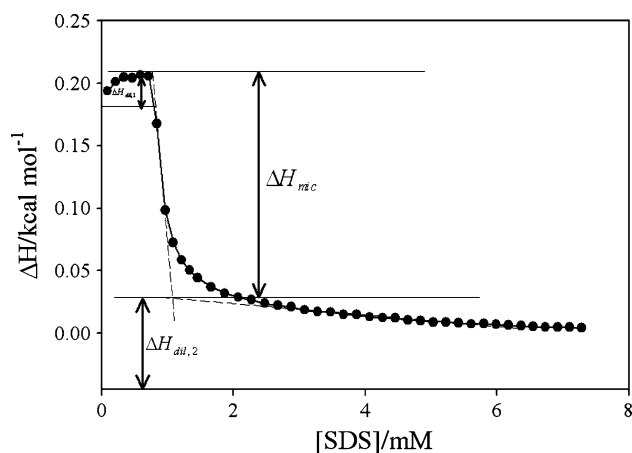| Temperature (K)	$\Delta H_{\mathrm{d,1}}$ (cal mol^{-1})	ΔH_{mic} (cal mol^{-1})	$\Delta H_{\mathrm{d,2}}$ (cal mol^{-1})	CMC (mM)	K_1	K_2	α
293.15	−12.246	−0.186	32.103	0.891	0.131	−0.043	0.654
298.15	−11.324	−0.788	58.631	0.914	0.128	−0.041	0.651
303.15	−10.947	−1.184	116.719	0.961	0.123	−0.043	0.647
308.15	−10.626	−1.378	258.971	0.985	0.119	−0.043	0.645
313.15	−10.031	−1.940	365.289	1.347	0.112	−0.041	0.637

Fig. 3 ITC curve of 60 mM SDS into 1.46 mL of 50 mM HEPES buffer pH 7.4 and 160 mM NaCl at 20 °C and 1 atm. The determination of CMC and thermodynamic parameters is indicated in this curve. The similar trends were observed at other temperatures

$$\Delta C_{P,\text{mic}} = \left(\frac{\partial \Delta H_{\text{mic}}}{\partial T}\right)_P \qquad (4)$$

Like other self-organizing systems (micelles and micro-emulsions), the ΔH_{mic} and ΔS_{mic} nicely compensate between them. Such a phenomenon is possible owing to the small variation of ΔG_{mic} in the studied temperature range of 20 °C: the major part of the associated heat is manifested in the form of disorder or the positive entropy change during the process. The slopes for the linear fittings of monomeric and micellar SDS at different concentration ranges as well as the calculated α values at different temperatures are also summarized in Table 1. The thermodynamic parameters of micellization of SDS (ΔH_{mic}, ΔG_{mic}, ΔS_{mic}, and $\Delta C_{P,\text{mic}}$) at different temperatures obtained by microcalorimetry in physiological condition with limits of their errors are also presented in Table 2. The ΔG_{mic} becomes more negative with increasing temperature, indicating a more favorable micellization process. The increase in temperature causes a decrease in entropy of micellization and also ΔH_{mic} becomes more negative with increasing temperature. This is due to the decrease in the amount of water that is ordered due to its nearness to the hydrophobic alkane chains and the amount of water bound to the SDS head groups [48]. While the decrease in ΔS_{mic} and ΔH_{mic} will be more negative with increasing temperature have opposite effects on the Gibbs free energy, it is seen that ΔG_{mic} also becomes more negative with temperature increasing, meaning that the change in ΔS_{mic} has more of an effect on ΔG_{mic} than the ΔH_{mic}. The data suggest that the large negative values of the free energy are primarily due to entropic contributions; however, the percentage of the free energy change that is due to the enthalpic term increases with increasing temperature range.

For the formation of surfactant micelles, the Gibbs energy of micellization is comprised of several components [49],

$C < \text{CMC}$, identical amounts of sodium (Na$^+$) and dodecyl sulfate (SD$^-$) ions are present in solution. $\Delta H_{\text{dil},1}$ is proportional to SDS concentration in solution, and the slope $d\Delta H_{\text{dil},1}/dC$ (denoted by k_1) remains constant. As $C > \text{CMC}$, surfactant micelles containing *n* monomers and *m* counter-ions coexist with $(n - m)$ free counter-ions in solution. $\Delta H_{\text{dil},2}$ is proportional to SDS concentrations, and the slope $d\Delta H_{\text{dil},2}/dC$ (denoted by k_2) is constant. Since the size of SD$^-$ and SDS surfactant micelles are much larger than that of Na$^+$, the absolute value of $(d\Delta H_{\text{dil},2}/dC)/(d\Delta H_{\text{dil},1}/dC)$, that is, $|k_2/k_1|$, is approximately equal to $(1 - \alpha)$. A similar approximation was adopted for studying the counter-ions binding from SDS conductivity titration curves, where $(1 - \alpha)$ was determined from the ratio of slopes before and after the CMC [47].

Based on the following relationship, the thermal heat capacity of micellization $\Delta C_{P,\text{mic}}$ could be evaluated.

Table 2 Thermodynamic parameters for the micellization of SDS at different temperatures in 50 mM HEPES buffer pH 7.4 and 160 mM NaCl as determined by the ITC method

Temperature (K)	ΔG_{mic} (cal mol^{-1})	ΔH_{mic} (cal mol^{-1})		ΔS_{mic} (cal mol^{-1} K^{-1})		$\Delta C_{P,\text{mic}}$ (cal mol^{-1} K^{-1})	
		van't Hoff	cal	van't Hoff	cal	van't Hoff	cal
293.15	−12.093	−7.149	−0.186	16.866	40.617	−234.218	−98.494
298.15	−12.272	−8.319	−0.788	13.255	38.517	−244.336	−90.443
303.15	−12.421	−9.558	−1.184	9.438	37.066	−254.454	−82.393
308.15	−12.597	−10.898	−1.378	5.514	36.407	−264.572	−74.344
313.15	−12.718	−12.197	−1.940	1.664	34.418	−274.690	−66.293

The error limits are $\Delta G_{\text{mic}} = 4\%$, ΔH_{mic}(van't Hoff) = 6%, ΔH_{mic}(cal) = 3%, ΔS_{mic}(van't Hoff) = 9%, ΔS_{mic}(cal) = 4%, $\Delta C_{P,\text{mic}}$(van't Hoff) = 17%, and $\Delta C_{P,\text{mic}}$(cal) = 9%

$$\Delta G_{\mathrm{mic}} = \Delta G(\mathrm{HP}) + \Delta G(\mathrm{contact}) + \Delta G(\mathrm{packing})$$
$$+ \Delta G(\mathrm{HG}) \tag{5}$$

where $\Delta G(\mathrm{HP})$ is the Gibbs energy derived from the dehydration of hydrophobic segment from the water phase into the hydrophobic micellar core, which contributes to the negative energy to the total Gibbs energy. $\Delta G(\mathrm{contact})$ is attributed to the solvent hydrocarbon contact in the micelles, which yields a positive contribution to the total micellization Gibbs energy. When a surfactant monomer enters a micelle, its head group will be located at the micellar surface, which restricts the conformational freedom of the hydrocarbon segments. This packing effect also gives rise to the positive Gibbs energy contribution of $\Delta G(\mathrm{packing})$. In addition, the interactions between the surfactant head groups also contribute positively to the micellization Gibbs energy $\Delta G(\mathrm{HG})$. The variation in ΔG_{mic} values is attributed to the change in the degree of non-polarity of micellar core and the change in the polarity of hydrophilic head. In addition, ΔS_{mic} values also increase with decreasing temperatures, which may be due to the fact that the amounts of water bound by the hydrophilic segments of surfactant monomer increase with low temperatures. The negative values of $\Delta C_{P,\mathrm{mic}}$ are normally observed for self-association of amphiphiles leading to micelle formation (Table 2). This is in line with the transfer of amphiphiles from their hydrophobically hydrated states in aqueous solution to more labile solvent free micellar interior [28, 47, 50]. Hence, the decrease of ΔH_{mic} with increasing temperature is caused by the disruption of water cages by hydrophobic groups and the amounts of water bound the surfactant monomers decrease with increasing temperatures [48]. Generally, it can be concluded that increasing the temperature will lead to a decrease in ΔH_{mic}.

We have used the calorimetric CMC values for the thermodynamic analysis. Our purpose is to compare the enthalpy, entropy, and specific heat parameters obtained by the van't Hoff method of calculation and by the direct processing of the calorimetric results. Very frequently, they do not agree [12, 47, 50–52]. For the evaluation of ΔH_{mic} by the van't Hoff method, $d\ln X_{\mathrm{cmc}}/dT$ and $d\alpha/dT$ values are required. Both $\ln X_{\mathrm{cmc}}$ and α are found to be nonlinear with respect to temperature so that polynomial equations relating $\ln X_{\mathrm{cmc}}$ and α with temperature (T) have been used for their evaluation [28, 47, 50, 53, 54]. Thus,

$$\ln X_{\mathrm{cmc}} = a + bT + cT^2 \tag{6}$$

and

$$\alpha = a' + b'T + c'T^2 \tag{7}$$

where a, b, c and a', b', c' are the respective fitting constants for Eqs. 6 and 7. The values of the fitting constants a,

b, and c obtained from the second-degree polynomial fitting of the $\ln X_{\mathrm{cmc}}$ (calorimetric CMC) versus T plot are -4.919, -0.054 and 2.374×10^{-4}, respectively. The values of the fitting constants a', b' and c' obtained from the second-degree polynomial fitting of the α versus T plot are -1.210, 0.015, -1.223×10^{-5}, respectively.

The $\ln X_{\mathrm{cmc}}$ and α values of SDS versus temperature plots fitted to a second-degree polynomial equation (Eqs. 6 and 7) are illustrated in Fig. 4. The measurements were taken in the temperature range of 293–313 K at 5 °C intervals which were reasonably close to derive reliable information on the involved process. As shown in Fig. 4, the dependence of α on temperature has a convex pattern for SDS although the limit of variation of α in the studied temperature range is of comparable magnitudes. Also the dependence of $\ln X_{\mathrm{cmc}}$ on temperature has a concave pattern. The fits of $\ln X_{\mathrm{cmc}}$ and α versus temperature plots for calorimetry is reasonably good. The calorimetric curves tend to rise appreciably after showing a tendency of a very shallow minimum toward the lower temperature. Minima in CMC in the lower range of temperature are normally obtained for ionic surfactants [28, 47, 55]. For the studied surfactant, SDS, the distinct presence of the minima in CMC is not observed up to the lower studied temperature
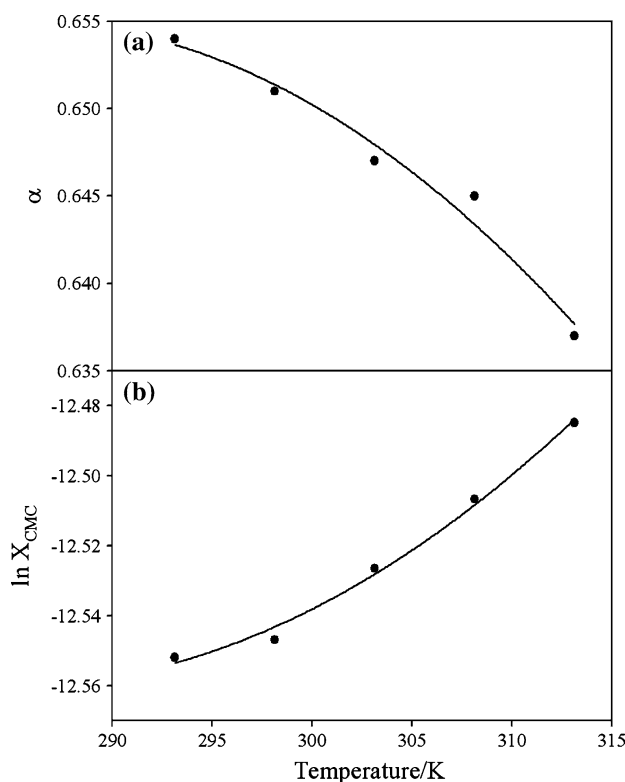

Fig. 4 Temperature-dependent of **a** α and **b** $\ln X_{\mathrm{cmc}}$ values for SDS in 50 mM HEPES buffer pH 7.4 and 160 mM NaCl by calorimetric methods fitted according to a second-degree polynomial equation

of 293 K. The counter-ion binding extents of SDS is nearly equal; it ranges between 65.4% and 63.7% in the temperature range of 20 °C.

From Eqs. 6 and 7, we have

$$\frac{d \ln X_{cmc}}{dT} = b + 2cT \tag{8}$$

and

$$\frac{d\alpha}{dT} = b' + 2c'T \tag{9}$$

These are used in Eq. 2 to evaluate ΔH_{mic} according to the final relation

$$\Delta H_{mic} = -RT^2[(1 + \alpha)(b + 2cT) + (b' + 2c'T)(\ln X_{cmc})] \tag{10}$$

The fitting Eq. 11 has been used to relate ΔH_{mic} with T

$$\Delta H_{mic} = A + BT + CT^2 \tag{11}$$

where A, B, and C are the fitting constants. The values of the fitting constants A, B, and C obtained from the second-degree polynomial fitting of the ΔH_{mic} versus T plot are -25.714, 0.359 and 1.012×10^{-3} (for van't Hoff) and 97.756, -0.571 and 8.054×10^{-4} (for calorimetry), respectively.

The differential form of Eq. 10 has been used to obtain $\Delta C_{P,mic}$ according to Eq. 4. Thus,

$$\Delta C_{P,mic} = B + 2CT \tag{12}$$

All polynomial fittings have been processed in a computer using the Microcal Origin software. The set of Eqs. 6–12 described above has, therefore, been used in deriving the thermodynamic information.

In Table 2, the differences of ΔH_{mic}, ΔS_{mic}, and $\Delta C_{P,mic}$ of SDS at different temperatures realized from microcalorimetric measurements and van't Hoff method are presented. It is evident that the calculated values do not agree with the experimental data determined directly from ITC experiment. The inequality between the two is, therefore, not unexpected [12, 47, 50–52]. ΔH_{mic} is dependent on the aggregation number, micelle shapes, and counter-ion binding, and these effects are not considered in the van't Hoff analysis. For ΔH_{mic} determined from ITC, the consequence of these effects and others, such as the heats of solvation–desolvation of surfactants, ionization, molecular rearrangement, and mixing, are included in the calorimetric measurements.

The method of calorimetry measures the integral enthalpy, whereas the van't Hoff procedure deals with the differential enthalpy [14, 51, 52]. The quantification of the observed difference, however, remains to be understood. Along with association of surfactant monomer (micelle formation), there can arise interaction of solute components with the solvent and nonspecific interactions in the system. The enthalpy change measured in a calorimeter thus corresponds to the sum total of all the involved heats, and hence it is called the integral heat of the process. The enthalpy change obtained from the van't Hoff rationale refers only to the concerned equilibrium process ($n(S^+$ or S^- or $S) \leftrightarrow (S_n^+$ or S_n^- or $S_n)$, where S^+ or S^- or S are surfactant monomer, S_n^+ or S_n^- or S_n are micelle, and n is the aggregation number), and this is termed as the differential enthalpy change. Franks [51] has thoroughly discussed the reasons for the discrepancy between the van't Hoff and calorimetric enthalpy changes and has made a statement that "calorimetry yields integral heat, the van't Hoff method gives rise to differential heat." He has also stated that for agreement with calorimetry, there should not be any cooperative effect involved in the expression of ln K in the van't Hoff model. The process of micellization often shows cooperativity [47, 52].

The change in the aggregation number and α as well as the shape of the micelles with temperature may have contributions on the energetics of the process. The first has remained virtually invariant with temperature, and the second has been used in the calculation. We consider minor changes in the shape of the SDS micelles with temperature. The ΔH_{mic} of SDS obtained by the van't Hoff rationale has a wide range of variation as well as ΔS_{mic} values. The range of the ΔH_{mic} values derived by the van't Hoff method from the calorimetric results using Eq. 2 (in reality Eq. 10) has a wide range of variation. As shown in Table 2, the ΔS_{mic} values obtained by combining the ΔG_{mic} (obtained from Eq. 1) with these ΔH_{mic} values using Eq. 3 likewise have fair agreement in this two methods. The same discrepancy also prevails with $\Delta C_{P,mic}$ (Table 2). The $\Delta C_{P,mic}$ values obtained for SDS by the van't Hoff treatment are more negative than the calorimetric values

Conclusions

The purpose of this study was to investigate the thermodynamics of the micellization process and how temperature affects these thermodynamic quantities. The use of ITC provides an accurate method to measure the thermodynamic quantities to provide some insight into the mechanism behind the processes of micellization. The ITC technique is unique in determining the CMC and ΔH_{mic}. It can differentiate between aggregating and non-aggregating solutes in solution. The anionic surfactant, SDS, was studied by ITC technique at five temperatures, 20, 25, 30, 35, and 40 °C, and at physiological conditions to determine the CMC and enthalpy of micellization. The change in enthalpy due to micellization was determined from the plots of the heat of dilution versus surfactant concentration.

As has been widely reported in the literature, ΔH_{mic} was found to be more negative with increasing temperature for SDS. The enthalpy changes associated with micelle breakup were temperature dependent, indicating the importance of hydrophobic interactions. The change in Gibbs free energy was found using Eq. 1 with the CMC determined experimentally from ITC. The Gibbs free energy change was found to be negative, implying, as expected, that micellization occurs spontaneously once the CMC has been reached. The values of ΔG_{mic} were found to become more negative with increasing temperature. The change in entropy was found to decrease with increasing temperature. Although the ΔH_{mic} values of the SDS obtained from calorimetry is of comparable magnitudes, the values obtained following the van't Hoff rationale significantly differ. The ΔS_{mic} values obtained by the van't Hoff method also appreciably differ. Similar is the observation for $\Delta C_{P,mic}$. The extent of counter-ions binding by SDS falls in the range of 63.7–65.4% in the studied temperature range of 293–313 K.

The procedure changes of the enthalpy, Gibbs free energy, and entropy of micellization matched literature values previously published, but the values of these parameters are differ from literature values previously published that is due to presence of NaCl and buffer medium in solution. As described previously, the salt NaCl has shown CMC decreasing effect for SDS.

The negative value of ΔG_{mic} and ΔH_{mic} indicate that the micellization of SDS surfactant is both enthalpy and entropy driven process.

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