Thermodynamics of Sodium Dodecyl Sulfate (SDS) Micellization: An Undergraduate Laboratory Experiment

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S *Supporting Information*

ABSTRACT: An undergraduate laboratory experiment is presented that allows a thermodynamic characterization of micelle formation of sodium dodecyl sulfate (SDS) in aqueous solutions. The critical micelle concentration (CMC) and the degree of micelle ionization (α) are obtained at different temperatures by conductimetry. The molar standard free energy ($\Delta_{mic}\bar{G}$), enthalpy ($\Delta_{mic}\bar{H}°$), and entropy ($\Delta_{mic}\bar{S}°$) for the micellization process are calculated using the CMC, α, and their temperature dependences within the framework of a simplified model, the closed association model, which assumes an equilibrium between free surfactant monomers and monodispersed micelles. On the basis of hydration phenomena of surfactant molecules, a physicochemical discussion of the results is also proposed.

C_T < CMC C_T > CMC

KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Aqueous Solution Chemistry, Conductivity, Micelles, Organosulfur Compounds, Thermodynamics
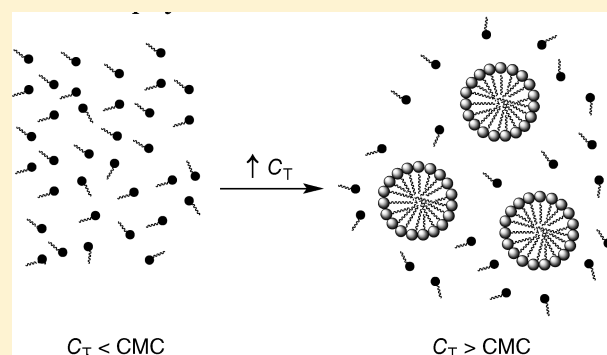
Surfactants (*surf*ace *act*ive *ag*ent) are amphiphilic compounds comprising a hydrophobic "tail" and a polar (ionic or nonionic) "head". They are present in a large number of commercial products that are widely used in daily life such as detergents, shampoos, and oils. Despite their growing importance, the study of micellar states is normally overlooked in most textbooks of general or experimental physical chemistry. As these systems represent a clear incumbency for chemists, their study constitutes an important area that should be included in undergraduate educative curricula.

It is well-known that as the surfactant concentration exceeds a critical value, normally referred to as the critical micelle concentration, CMC, the surfactant molecules in solution spontaneously arrange into self-organized micellar structures. Several experiments have been proposed in this *Journal* to familiarize undergraduate students with micellar systems[1,2] and the experimental techniques to determine CMC values.[3−7] However, those articles do not deal with the thermodynamic interpretation of such systems at an undergraduate level.

Electrical conductivity of ionic surfactant solutions, performed over a wide range of concentrations, can be used to determine the CMC and degree of micelle ionization, α. The method relies on the differences between the conductivity of free surfactant molecules in solution and those associated with molecules in micellar arrangements. Regardless of their extensive use, there are different approaches in the literature to describe the observed electrical conductivity data. Some authors consider that the conductivity of the surfactant monomer comprising the micelles should be the same as the one for free monomer in solution,[8−10]

whereas some other authors claim that this conductivity should be more conveniently expressed in terms of Stokes's law.[4,11−13] However, the CMC obtained from both approaches is the same, whereas α differs in a sensible fashion.

The CMC values, obtained at different temperatures, can be used for thermodynamic characterization of micelle formation. This requires the evaluation of the temperature dependence of the CMC in an explicit form, which can be obtained by fitting experimental data using different algebraic expressions. Instead of the widely used second-order[12,14,15] and third-order polynomial expressions,[9] Kim and Lim[16] recommended the use of a functional form of the type ln CMC = $A + BT + C/T$ citing that the former expressions are not theory based. Usually, calculations of thermodynamic magnitudes associated with micellar systems do not consider the dependence of α with the temperature,[10,17] which leads to non-negligible differences in the relevant thermodynamic information.[18]

Because of the diversity of approaches available in the literature of micellar systems and the need to incorporate fresh laboratory experiments in the undergraduate curricula a simple, robust, and inexpensive experiment is presented that extracts thermodynamic information associated with the micellization process of an ionic surfactant in aqueous solution. The current laboratory experiment is based on the determination of CMC of sodium dodecyl sulfate (SDS) by measuring electrical conductivities at different temperatures. Using the simple "closed

association model", the experiment involves the calculation of thermodynamic parameters of micellization and their physical interpretation based on concepts such as hydration phenomena of surfactant molecules.

CLOSED ASSOCIATION MODEL

The closed association model is employed to analyze the experimental data. This model assumes that free surfactant molecules in solution are in chemical equilibrium with monodisperse micelles, comprising a fixed number n of surfactant molecules at each temperature. Usually micellar solutions are not monodisperse;[19,20] however, it has been shown in literature[21,22] that this deviation does not significantly affect the validity of the model. To describe the micellization process of the SDS surfactant in salt-free aqueous solution, the following equilibrium is proposed

$$n S^- + (n - m)Na^+ \overset{K_{mic}}{\rightleftharpoons} (S_n Na_{n-m})^{m-}$$
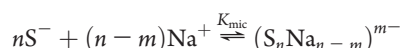
where S^- and Na^+ represent dodecyl sulfate anions and sodium cations, respectively, and the micelles, $(S_n Na_{n-m})^{m-}$, are charged moieties with net charge $-m$ containing n SDS molecules and $(n - m)$ sodium ions. The corresponding monomer−micelle equilibrium constant, K_{mic}, can be expressed as

$$K_{mic} = \frac{[(S_n Na_{n-m})^{m-}]}{[S^-]^n [Na^+]^{n-m}} \tag{1}$$

where the brackets represent molar concentrations. Normally, the CMC is sufficiently low so that ionic activity coefficients can be safely approximated by 1.

THERMODYNAMIC CALCULATIONS

The standard free energy of micelle formation, $\Delta_{mic}G°$, can be expressed in terms of K_{mic}:

$$\Delta_{mic}G° = -RT \ln K_{mic} \tag{2}$$

Combining eqs 1 and 2 and dividing by n, we obtain

$$\frac{\Delta_{mic}G°}{n} = \Delta_{mic}\overline{G}° = -\frac{RT}{n}\ln[(S_n Na_{n-m})^{m-}] + RT\ln[S^-]$$
$$+ (1 - \alpha)RT\ln[Na^+] \tag{3}$$

where $\alpha = m/n$ is the degree of micelle ionization. Considering that SDS micelles normally contain a large number of surfactant molecules in the micelle ($n > 50$), the first term of the right-hand side of eq 3 is negligible with respect to the other two terms. Moreover, when the surfactant concentration is close to the CMC, $[S^-] \approx [Na^+] \approx$ CMC. Under these circumstances, eq 3 can be rewritten as

$$\Delta_{mic}\overline{G}° \approx RT(2 - \alpha)\ln \text{CMC} \tag{4}$$

The above expression can be inserted in the classical Gibbs−Helmholtz equation

$$\frac{\partial(\Delta G/T)}{\partial T} = \frac{-\Delta H}{T^2}$$

yielding the following expression for the molar standard enthalpy for micelle formation, $\Delta_{mic}\overline{H}°$,

$$\Delta_{mic}\overline{H}° \approx -RT^2\left[(2 - \alpha)\left(\frac{\partial \ln \text{CMC}}{\partial T}\right) - \left(\frac{\partial \alpha}{\partial T}\right)\ln \text{CMC}\right] \tag{5}$$

Finally, the molar standard entropy for the micelle formation, $\Delta_{mic}\overline{S}°$, can be calculated using

$$\Delta_{mic}\overline{G}° = \Delta_{mic}\overline{H}° - T\Delta_{mic}\overline{S}° \tag{6}$$

DETERMINATION OF CMC AND α FROM CONDUCTIVITY MEASUREMENTS

The values of CMC and α that are necessary to perform thermodynamic calculations of micelle formation can be obtained by means of conductimetry. Conductivity measurements of ionic surfactants have been reported previously in this *Journal* by Bachofer.[4] The mathematical expressions describing the electrical conductivity of ionic surfactant solutions below or above the CMC are different. Below the CMC, the SDS molecules are considered to be a fully dissociated 1:1 strong electrolyte. Under this circumstances and assuming that ionic molar conductivities are independent of concentration, the electrical conductivity, κ, of the surfactant solution can be computed as

$$\kappa = (\lambda^{S^-} + \lambda^{Na^+})C_T = p_1 C_T \tag{7}$$

where λ^{S^-} and λ^{Na^+} are the ionic molar conductivities for the dodecyl sulfate anion and Na^+, respectively (expressed in mS M^{-1} cm^{-1}), C_T is the total molar surfactant concentration, and p_1 represents the slope of the linear fit of κ versus C_T plot below the CMC.

Above CMC, free SDS molecules coexist with micellar structures that are considered a weak electrolyte. An increase in the SDS concentration leads to an increase of the micellar concentration, whereas free surfactant concentration remains practically constant near the CMC value. In this case, the electrical conductivity for the SDS solution can be represented as

$$\kappa = \text{CMC}(\lambda^{S^-} + \lambda^{Na^+}) + \frac{C_T - \text{CMC}}{n}\lambda^{mic}$$
$$+ (C_T - \text{CMC})\alpha\lambda^{Na^+} \tag{8}$$

where λ^{mic} is the ionic conductivity of the micelle, and $(C_T - \text{CMC})/n$ is the molar concentration of micelles. In principle, the value of λ^{mic} is unknown but two different approaches can be used to make an estimation: (i) considering $\lambda^{mic} = n\alpha\lambda^{S^-}$ or (ii) employing Stokes's law, which establishes that the conductance of a spherical ion is proportional to the square of the charge divided by the ionic radius. Using the latter approach, thermodynamic quantities are obtained that agree well with the reported values of $\Delta_{mic}\overline{H}°$ in the literature.

Assuming that the radius of the micelle scales as $n^{1/3}$,[11] λ^{mic} can be approximated as

$$\lambda^{mic} \approx \frac{m^2}{n^{1/3}}\lambda^{S^-} \tag{9}$$

where, within the realm of the Stokes's law approximation, the value of λ^{mic} can be estimated from λ^{S^-}, that is, the conductivity of the singly charged ($m = -1$) SDS monomer ($n = 1$). Equation

8 can be rearranged to obtain

$$\frac{\kappa - CMC(\lambda^{S^-} + \lambda^{Na^+})}{C_T - CMC} = \frac{1}{n}\lambda^{mic} + \alpha\lambda^{Na^+} \qquad (10)$$

Placing eqs 7 and 9 into eq 10 and rearranging, the following expression is obtained

$$\frac{\kappa - CMC(\lambda^{S^-} + \lambda^{Na^+})}{C_T - CMC} = \frac{m^2}{n^{4/3}}(p_1 - \lambda^{Na^+}) + \alpha\lambda^{Na^+} \qquad (11)$$

The left-hand side of the eq 11 represents the slope of the linear fit of κ versus C_T plot above the CMC, p_2. Considering the definition of $\alpha = m/n$, this equation can be rewritten yielding the quadratic equation

$$n^{2/3}(p_1 - \lambda^{Na^+})\alpha^2 + \lambda^{Na^+}\alpha - p_2 = 0 \qquad (12)$$

To evaluate α from eq 12, additional assumptions are needed: (i) First, n is allowed to change with temperature. Values of $n = 72$ ($T = 284$ K), 69 ($T = 288$ K), 65 ($T = 293$ K), 62 ($T = 298$ K), 59 ($T = 303$ K), 56 ($T = 308$ K), 54 ($T = 313$ K), 50 ($T = 323$ K), and 47 ($T = 333$ K) were obtained by means of inter- and extrapolations of experimental data reported by Zana and co-workers[13] (see written directions for students included in the Supporting Information). (ii) Second, values of λ^{Na^+} were approximated by the value at infinitely diluted solutions, $\lambda_\infty^{Na^+}$. Values of $\lambda_\infty^{Na^+} = 34.7$ ($T = 284$ K), 39.3 ($T = 288$ K), 44.9 ($T = 293$ K), 50.6 ($T = 298$ K), 56.3 ($T = 303$ K), 62.0 ($T = 308$ K), 67.7 ($T = 313$ K), 79.0 ($T = 323$ K), and 90.3 ($T = 333$ K) were calculated by means of linear interpolation of experimental data reported by Benson and Gordon[23] (see written directions for students included in Supporting Information).

■ MATERIALS AND METHODS

Electrophoresis-grade SDS was provided by Sigma and used as received. Solutions of different concentrations were prepared using deionized water (10 MΩ cm) previously filtered in a commercial Millipore Milli-Q system equipped with a filter of 0.22 μm pore size (MQ water). To carry out the conductometric measurements, five SDS solutions of concentrations lower than 0.20% w/v (0.01, 0.05, 0.09, 0.12, and 0.18% w/v) and five higher than 0.30% w/v (0.30, 0.40, 0.50, 0.60, and 0.70% w/v) were prepared.

Glass bottles with SDS solutions of different concentrations were placed into a container with thermostatted water using a Julabo EM thermostat. Temperatures were adjusted with an accuracy of 0.2 °C. To determine the conductivity of the solutions, a digital benchtop conductivity meter model 162A was used. The digital conductivity meter was previously calibrated with two sodium chloride standard solutions of 692 ppm (1413 μS cm^{-1}) and 7230 ppm (12.9 mS cm^{-1}) to determinate the cell constant.

■ HAZARDS

Special care must be taken to prepare solutions of SDS from the solid reagent, as it can cause allergic reactions in the airways and skin. No other significant hazards are associated with this experiment.

■ RESULTS

Conductimetry measurements on the SDS solutions were performed at different temperatures. The results obtained in a standard laboratory experiment are shown in Figure 1. For each
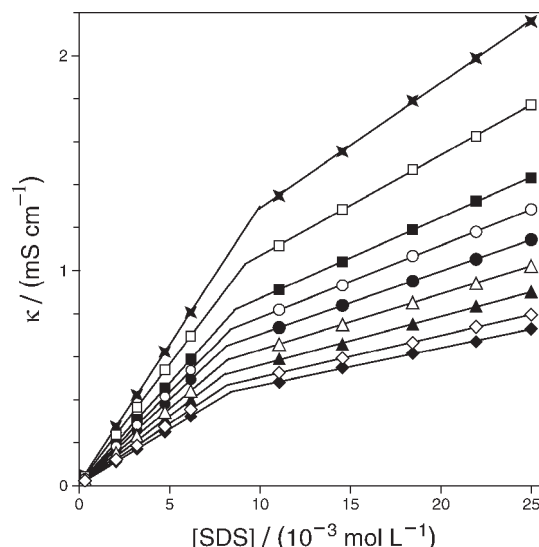

Figure 1. Electrical conductivity (κ) as a function of SDS concentration recorded at 11 °C (♦), 15 °C (◇), 20 °C (▲), 25 °C (△), 30 °C (●), 35 °C (○), 40 °C (■), 50 °C (□), and 60 °C (×).

temperature, as the SDS concentration is varied, an inflection point in the electrical conductivity is observed. These results are in good agreement with those observed by Goddard and Benson.[17]

A linear regression analysis of the conductivity data at each temperature was performed before and after the inflection point. In all cases, the linear fits were accurate and no significant deviations from linearity were observed within the concentration range used here. CMC values were determined at each temperature by using the "Williams method", which consists in the resolution of the corresponding pair of linear equations. Alternatively, one can resort to the "Phillips method" that approximates the second derivative of the conductimetry versus concentration curve by an inverted Gaussian. Within this procedure, the CMC would coincide with the minimum of the inverted Gaussian profile. However, Mosquera and co-workers[24] have shown for SDS that the Phillips method yields the same results as the method described by Williams. The results presented in Table 1 correspond to the Williams method.

The value of CMC at 25 °C, 8.2 mM, is in good agreement with literature values obtained using the same technique.[5,17,25] Uncertainties Δ(CMC) = ±0.1 mM, calculated from the average of five independent measurements using the same set of samples, are comparable to those previously reported.[4] The dependence of ln CMC with the temperature is shown in Figure 2, where a minimum is observed between 20 and 25 °C. For SDS, the presence of a similar minimum has been reported by different authors from conductometric,[17] acoustic,[26] and UV−vis spectroscopic[27] data. Results of a fit of the form ln CMC = $A + BT + C/T$, as recommended by Kim and Lim,[16] are shown in Figure 2. Special care should be taken in the use of the absolute temperature scale for the adjustment. By setting $A = -30$, $B = 0.0044$ K^{-1}, and $C = 3817$ K, a fit is obtained with $R^2 = 0.9998$. As such, the previous equation is suitable to compute $\partial \ln CMC/\partial T$.

At each temperature, α was calculated by means of eq 12. A linear dependence of α with temperature is observed over the entire range of temperature, showing a slope of 0.0013 K^{-1} (data not shown). At this point, the values of CMC, α, and their temperature dependences can be readily used to calculate $\Delta_{mic}\overline{H}°$ and $\Delta_{mic}\overline{S}°$ using eqs 5 and 6, respectively. Results for

Table 1. CMC, α, and Thermodynamic Parameters of SDS Micellization at Different Temperatures

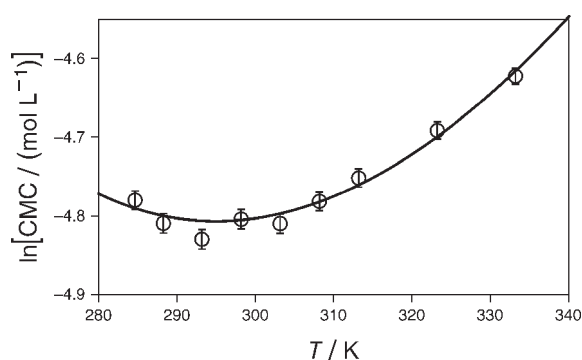| T/K	CMC/mM	α	$\Delta_{mi}\overline{G}°/(kJ\ mol^{-1})$	$\Delta_{mi}\overline{H}°/(kJ\ mol^{-1})$	$\Delta_{mi}\overline{S}°\ /(J\ K^{-1}\ mol^{-1})$
284	8.4	0.19	−20.4	−0.6	70
288	8.2	0.20	−20.7	−2.1	65
293	8.0	0.21	−21.1	−4.1	58
298	8.2	0.22	−21.2	−6.2	50
303	8.2	0.22	−21.6	−8.3	44
308	8.4	0.23	−21.7	−10.3	37
313	8.7	0.24	−21.8	−12.5	30
323	9.2	0.25	−22.1	−16.7	17
333	9.2	0.26	−22.3	−21.0	4

Figure 2. The ln CMC of SDS as a function of temperature. Solid line represents a functional form of the type ln CMC = $A + BT + C/T$. Error bars were calculated from the average of five independent measurements using the same set of samples.

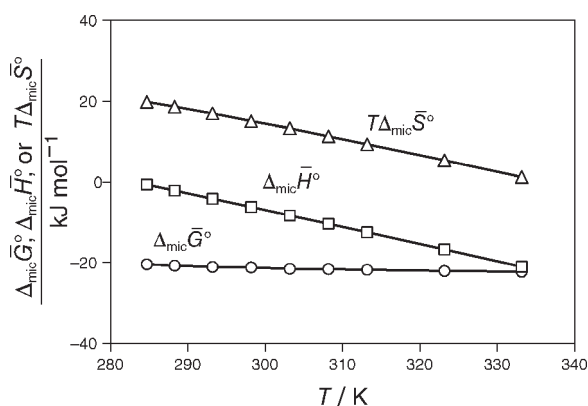**Figure 3.** The thermodynamic parameters, $\Delta_{mic}\overline{G}°$, $\Delta_{mic}\overline{H}°$, and $T\Delta_{mic}\overline{S}°$, as a function of temperature.

$\Delta_{mic}\overline{G}°$, $\Delta_{mic}\overline{H}°$, and $\Delta_{mic}\overline{S}°$ obtained at different temperatures are listed in Table 1 and depicted in Figure 3. Note that the value of $\Delta_{mic}\overline{G}°$ ($T = 298K$) = −21.2 kJ mol^{-1} is identical to the one obtained by Benrraou et al.[13] and also close to the one reported by Aniansson et al. (−22.6 kJ mol^{-1}).[19] $\Delta_{mic}\overline{H}°$ values are slightly lower than calorimetric values found in the literature.[14,28] Interestingly, $\Delta_{mic}\overline{G}°$ remains negative and relatively constant at all temperatures, confirming that micelle formation occurs spontaneously when concentration reaches the CMC value. Furthermore, the constancy in the $\Delta_{mic}\overline{G}°$ value reveals cancellation effects between $\Delta_{mic}\overline{H}°$ and $T\Delta_{mic}\overline{S}°$ at all temperatures.

DISCUSSION

The thermodynamic information obtained from these experiments may be useful to spark the students' interest in performing a critical evaluation of the raw data. Within this context, several relevant questions that might be asked by laboratory instructors are

- What reasons would explain why, at room temperature, $\Delta_{mic}\overline{S}°$ is positive, despite the fact that the surfactant adopts a more ordered configuration when is organized in micellar entities?
- What is the reason for the decrease of $\Delta_{mic}\overline{S}°$ as temperature increases?
- Is the micellization process an enthalpy driven or an entropy driven process?

As possible answers to these questions, the following physical arguments may be considered. Compared to monomer-like states in solution, surfactants aggregated into micellar states exhibit more ordered structures. Consequently, one might be tempted to conclude that the micellization should involve a decrease in the entropy of the system. However, this line of reasoning does not agree with the experimental evidence that reveals that $\Delta_{mic}\overline{S}°$ is positive at low temperatures. This apparent paradox can be rationalized by considering that the surfactant degrees of freedom alone provide an incomplete picture and that the reorganization of the structure of the surfactants involves concomitant modifications in the solvent structure as well. In fact, the water molecules surrounding the micelles exhibit a lower degree of organization when compared to those solvating individual SDS monomers. This effect would lead to a positive entropic contribution that overcompensates the entropy decrease arising from the loss of SDS degrees of freedom.

As temperature increases, a gradual decrease in the solvation structure of surfactant molecules is expected to occur. Evans and Wightman[18] showed that the solvation effect becomes negligible at temperatures higher than 116 °C for tetradecyltrimethylammonium bromide. Thus, $\Delta_{mic}\overline{S}°$ is expected to drop when temperature increases owing to the reduced contribution of water molecules in the process of micellization.

Large linear changes in $\Delta_{mic}\overline{H}°$ and $\Delta_{mic}\overline{S}°$ are observed with temperature. However, such changes compensate each other, leading to a value of $\Delta_{mic}\overline{G}°$ almost invariant along the temperature range of study. This phenomenon is known in literature as "compensation phenomena". According to this thermodynamic point of view, the SDS micellization is considered an entropy driven process at low temperatures and an enthalpy driven process at higher temperatures.

CONCLUSION

We have presented a new laboratory experiment that introduces basic thermodynamic concepts using micellar systems. The rationalization of the data can be cast in terms of the "closed association model" that establishes an equilibrium between monomeric and micellar states of the surfactants. We have shown that conductivity measurements of surfactant solutions performed at different temperatures can be a convenient route to evaluate two key elements that are presented in the theoretical approach: the CMC and the degree of micelle ionization, α. The experimental technique represents a nonhazardous, simple, robust, and reproducible laboratory experiment that can be conducted in an undergraduate-level laboratory class. The simple consideration of the temperature trends for the different thermodynamic quantities describing the micellization process can be used to undertake interesting discussions to rationalize the basic mechanisms that control this aggregation process in solution.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Instructor notes (including CAS number of SDS and safety warnings) and written directions for students. This material is available via the Internet at http://pubs.acs.org.

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