



Thermodynamics on the micellization of various pure and mixed surfactants: Effects of head- and tail-groups



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ABSTRACT

The values of critical micelle concentration (CMC) for the micellization of various pure and mixed surfactants are determined by the UV–Vis spectrophotometric method. And the effects of temperature on the CMC values have been measured and thermodynamic parameters' values are calculated to analyse the effects of head- and tail-groups on the micellization of surfactant molecules. The results show that the values of ΔG° are negative and those of ΔS° are positive for the micellization of all the surfactants within the measured temperature range. But the values of ΔH° are positive or negative, depending on the kinds of surfactants. All these thermodynamic parameters' values are decreasing together with the increase of temperature for all the surfactants. And these thermodynamic parameters' values are depending severely on the chain length of alkyl group also as much as on the head-groups of surfactant molecules.

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1. Introduction

Surfactant molecules, having a hydrophilic head-group and a hydrophobic tail-group in the same molecule simultaneously, make a micellar aggregation in an aqueous solution, which are constructed with the ionic surface and the hydrophobic core [1–5]. The surface of a micelle is made with the head-groups of surfactant molecules and an electric double layer is formed around the surface of the micelle. The core part is constructed with the tail-groups of surfactant molecules and can be divided into a palisade region that is near to the surface and an inner core region that water can't penetrate into at all. Normally, the organic and inorganic compounds are solubilized on the ionic surface, the polar palisade, and the hydrophobic core region of a micelle through an electrostatic interaction or a hydrophobic interaction between the solubilized compounds and the micelle [6,7]. The solubilized sites of those compounds in a micelle are dependent on the properties of compound and micelle, the kinds of interactions, and the strength of the interactions with a micelle.

Nowadays various experimental methods and theories have been developed and used in order to study the micellization of surfactants and the solubilization of compounds by the surfactant systems [6–10]. In this work, we want to study the micellization

of various surfactants, having the same hydrophobic alkyl-group but different head-groups, by using the UV–Vis spectrophotometric method. We used the solubilization phenomena of 4-chlorobenzoic acid by surfactant systems to measure the critical micelle concentration (CMC) of various surfactants. An atmosphere surrounding a solubilized 4-chlorobenzoic acid in a micelle state is very different from that in pure water so that the absorbance peak of 4-chlorobenzoic acid is moved to the shorter wave length due to their solubilization and the absorbance values of solutions at fixed wave length are changing with the concentration of surfactant (especially around the CMC of surfactant). Various pure and mixed surfactants with different head-groups such as cationic, non-ionic, and amphoteric surfactants were used. Cationic surfactants with the same head group such as DTAB (dodecyltrimethylammonium bromide), TTAB (tetradecyltrimethylammonium bromide, and CTAB (cetyltrimethylammonium bromide) were used. Non-ionic surfactants such as Tween-20 (polyoxyethylene(20) sorbitan monolaurate), Tween-40 (polyoxyethylene(20) sorbitan monooleate), and Tween-80 (polyoxyethylene(20) sorbitan monooleate) were used and LSB (lauryldimethyl(3-sulfopropyl) ammonium hydroxide) as an amphoteric surfactant was used to study the effects of head- and tail-groups on the micellization of surfactants. The mixed systems of LSB with cationic surfactants (DTAB, TTAB, and CTAB) and non-ionic surfactants (Tween-20, Tween-40, and Tween-80) were measured also to compare with those of pure surfactants.

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2. Experimental

2.1. Materials and making solutions

All the chemicals of surfactants, used in this study, were obtained from Aldrich Corp. The provenances and purities of the chemicals are listed in table 1 and they were used directly without further purification except for drying in a desiccator for 24 h. Distilled and deionized water, made by using a Millipore system, was used as a solvent to make the solutions. All the solutions were prepared by weighing methods as in the previous papers [6,7,11,12]. At first, the stock solutions of 4-chlorobenzoic acid (the concentration was less than $1 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$) were made and weighed as a solvent.

Next, pure surfactants in the solid or liquid state were weighed and dissolved into this stock solution to make another stock solution of surfactant. This stock solution of surfactant was diluted continuously with the same stock solution of 4-chlorobenzoic acid to make solutions having the same concentration of 4-chlorobenzoic acid but a different concentration of surfactant. The concentration of surfactant in each solution was changed from 0 to about three times of the CMC value and the overall mole fraction (α_{LSB}) of LSB for the mixed surfactant systems at every solution was fixed at 0.5 by diluting the same stock solution of surfactant continuously.

2.2. Apparatus and methods

Absorbance values of the solutions, having the same concentration of 4-chlorobenzoic acid but different concentrations of surfactant, were measured at the same wave length (250 nm) and they were plotted against the concentrations of surfactant to decide the CMC value [11,12]. The absorbance value of the solution was not changed almost until the concentration of surfactant was increased from zero to the CMC value. When the concentration of surfactant was reached to the CMC value, the absorbance value was changed abruptly by the solubilization of 4-chlorobenzoic acid into a micelle. Two straight lines can be drawn around the critical micelle concentration and from that cross point the CMC values of surfactants can be determined. The maximum absorbance peak of 4-chlorobenzoic acid was occurred at about 290 nm in pure water, but this peak was moved to the shorter wave length in the solution of surfactant by the solubilization of 4-chlorobenzoic acid [6,13]. The UV-Vis spectrophotometer of Scinco Corp. (model S-4100) was used for the measurement of absorbance values of solutions and temperature was changed from 284.15 K to 312.15 K for the thermodynamic study. To control the temperature accurately ($\pm 0.01 \text{ K}$), each solution was kept in a Fisher Scientific thermostat (model 9101) for 30 min before the measurement.

TABLE 1
Provenance and purity of reactants.

Chemical names	Source	Initial mass fraction purity	Purification method	Further treatments before use
DTAB	Aldrich	0.99	None	Drying in a desiccator
TTAB	Aldrich	0.99	None	at $T = 298.15 \text{ K}$ for
CTAB	Aldrich	0.95	None	more than 24 h
Tween-20	Aldrich		None	
Tween-40	Aldrich		None	
Tween-80	Aldrich		None	
LSB	Aldrich	0.98	None	

3. Results and discussion

3.1. Calculation of thermodynamic parameters

The CMC values of pure and mixed surfactants have been measured at various temperatures and the results were plotted against temperature for several surfactants in figure 1. The plot of the non-ionic surfactant (Tween-20) is decreased with the increase of temperature but those for other systems such as cationic (DTAB), amphoteric (LSB), and the mixed systems (LSB/DTAB and LSB/Tween-20) are all increased. All the plots in figure 1 are curved slightly so that the second order equation of temperature can be applied to all the surfactants as in equation (1) [14–17]. The parameters' values of a , b , c , and the RMSD (root mean square deviation) in equation (1) are calculated by applying the non-linear least square method to the micellization of every surfactant and the results are listed in table 2. And the minimum CMC values (CMC^*) and the temperatures (T^*) at that point are calculated and listed also in table 2 for every surfactant.

The Gibbs energy changes ΔG° for the micellization of surfactants, representing thermodynamic equilibrium between monomeric surfactant molecules and a micelle, can be also calculated from equation (2) by using the values of a , b , and c in table 2 for every surfactant. At this equation, the CMC value is using a mole fraction unit, obtained by dividing the measured CMC value in a molality unit with 55.5, and the B value in equation (2) represents the counter-ion binding constant of a micelle [18,19]. In this research, we used the same B values of 0.7 for the ionic surfactants and assumed that this value was not dependent on temperature severely to compare the micellization of each surfactant. The calculated ΔG° values by using equation (2) are listed in table 3 and are plotted against temperature for all the surfactants in figure 2.

$$\ln \text{CMC} = aT^2 + bT + c \quad (1)$$

$$\Delta G^\circ = (1 + B)RT \ln \text{CMC} \quad (2)$$

3.2. Effect of head-groups of surfactants

At every temperature, the ΔG° values for pure surfactants are decreasing in the order of $\text{LSB} < \text{DTAB} < \text{Tween-20}$. All the plots in

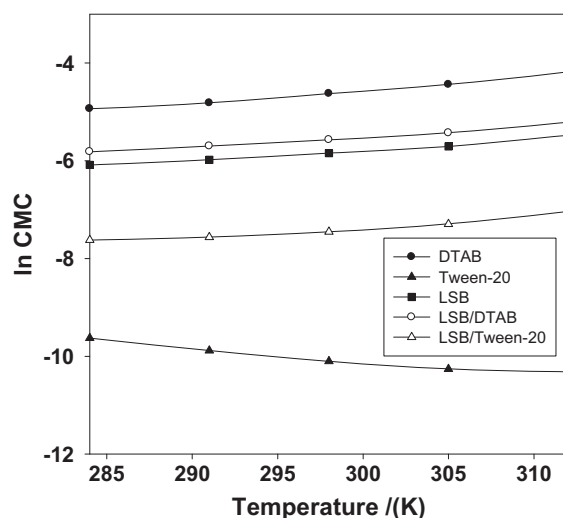


FIGURE 1. Plots of $\ln \text{CMC}$ against temperature for the micellizations of various pure and mixed surfactants. The solid lines represent the corresponding correlation by the non-linear least squares method. (●) DTAB; (▲) Tween-20; (■) LSB; (○) LSB/DTAB ($\alpha_{\text{LSB}} = 0.5$); (△) LSB/Tween-20 ($\alpha_{\text{LSB}} = 0.5$).

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