Effect of Position of Ester Group and Temperature on Critical Micelle Concentration of Ester Containing Surfactants

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ABSTRACT

The critical micelle concentrations of sodium sulfoalkyl alkanoates, $C_nH_{2n+1}COO(CH_2)_mSO_3Na$ (n = 9, 10, and 11; m = 2, 3, and 4), in aqueous solution were measured by an electro conductivity method from 15 to 50 C. Plots of critical micelle concentrations versus temperature show a minimum for all of the surfactants. Increasing the number of methylene groups between the ester and sulfonate groups in the surfactant molecule lowered the temperature at which the minimum critical micelle concentration was observed. When the percentage deviation of critical micelle concentration values obtained at different temperatures from critical micelle concentration values at 30 C was plotted as a function of the temperature, deviation in the range below 30 C increased with length of the hydrocarbon chain in the fatty acid portion of the surfactant, and decreased with the increase in length of the hydrocarbon chain situated between ester and sulfonate groups. These phenomena suggest that the change of interaction between the ester group and water molecule with the temperature is largely dependent on the position of the ester group in the alkyl chain of the surfactant. On the other hand, deviation values above 30 C increased with length of the hydrocarbon chain in the fatty acid portion and of the hydrocarbon chain situated between ester and sulfonate groups. These results indicate that interaction between the ester group and water molecule decreases with rise in temperature. The enthalpies, free energies, and entropies of micelle formation were calculated from temperature variation of critical micelle concentrations, and are consistent with current theories of the role of solvent in micelle formation.

INTRODUCTION

Micelle formation of surfactants in aqueous solution depends on the solution's environment, including its temperature. Numerous reports regarding the effect of temperature on critical micelle concentration (CMC) of ionic and nonionic surfactants have appeared in the literature. However, the greater part of these reports have dealt with the dependence of CMC on such factors as the nature of the counterion, length of hydrophobic portion, length of hydrophilic portion, and addition of other substances (1-5).

In several earlier reports (6-9), we prepared surfactants that contained an ester group in the hydrocarbon chain, and found that the ester group had a significant effect upon micelle formation of surfactant in aqueous solution. Insertion of an ester group into the hydrocarbon chain raised the CMC value, and CMC of these surfactants increased regularly as the ester group was moved further away from the sulfate group. From these results it can be inferred that the ester group influenced the structure of water around the hydrocarbon chain of the surfactant.

In the present work, variation of CMC with temperature for these surfactants has been measured from 15 to 50 C by the electro conductivity method, and the relation between temperature and position of the ester group in surfactant molecules on the CMC value was investigated. Furthermore, the enthalpy, entropy, and free energy of micellization of the surfactant have been calculated from variation of CMC with temperature.

EXPERIMENTAL PROCEDURES

Materials

The following 7 surfactants were used in this experiment: sodium 2-sulfoethyl caprate (9C-2), 2-sulfoethyl laurate (11C-2), 3-sulfopropyl caprate (9C-3), 3-sulfopropyl undecylate (10C-3), 3-sulfopropyl laurate (11C-3), 4-sulfobutyl caprate (9C-4), and 4-sulfobutyl laurate (11C-4). These surfactants were prepared from corresponding pure fatty acids with sodium isethionate, propane sultone, or butane sultone by the method described previously (10). They were purified by recrystallization 3 times from methanol and ethanol, and then by extraction with petroleum ether in a Soxhlet extractor for 100 hr. Purity of the materials was checked by chemical analysis and by shapes of plots of surface tension versus concentration of the aqueous solution. Results of carbon and hydrogen analyses of compounds coincided with theoretical values for their composition within ± 0.3%. Surface tension versus concentration curves did not show a minimum near the CMC.

Water was purified by passage through a mixed bed ion exchange resin column, followed by distillation from alkaline potassium permanganate in Pyrex. Specific conductance of the water was 1.0-1.5 x 10^{-6} ohm^{-1} at 25 C.

Method

Electrical conductivity of surfactant was measured with a conductance bridge, CM-1DB, and a dipping cell fitted with platinized conductance electrodes, CG201PL (Towa Dempa Co.) in 25 ml solution in a special test tube. The apparatus was kept in a thermostat at various

TABLE I

Critical Micelle Concentration of Sodium Sulfoalkyl Alkanoates

Temperature	Critical micelle concentration (m mole/1)						
(C)	9C-2	9C-3	9C-4	10C-3	11C-2	11C-3	11C-4
15	26.8	19.6	12.2	9.1	7.0	5.0	3.25
20	25.8	19.1	12.1	8.85	6.6	4.8	3.2
30	24.9	18.9	12.1	8.7	6.2	4.7	3.2
40	25.3	19.5	12.7	9.1	6.5	5.0	3.35
50	26.5	20.7	13.7	9.85	7.1	5.5	3.8

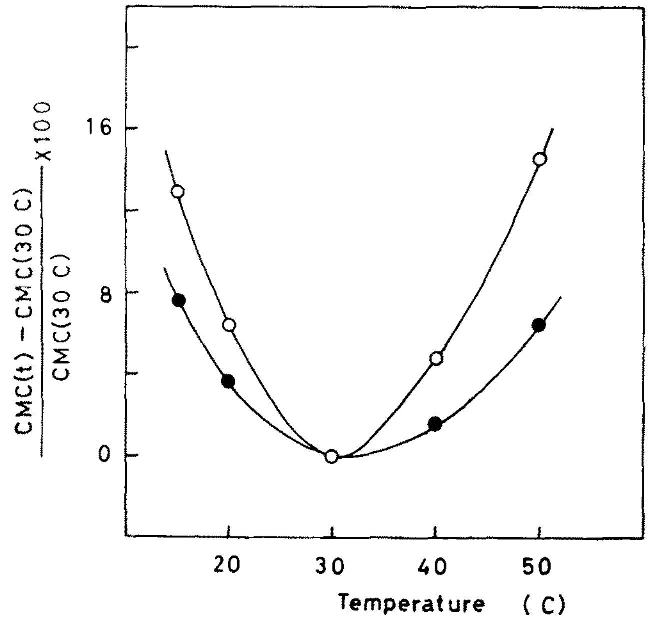

FIG. 1. Effect of temperature on critical micelle concentrations (CMC) of 9C-2 (●) and 11C-2 (○). Percentage deviations from CMC value at 30 C.

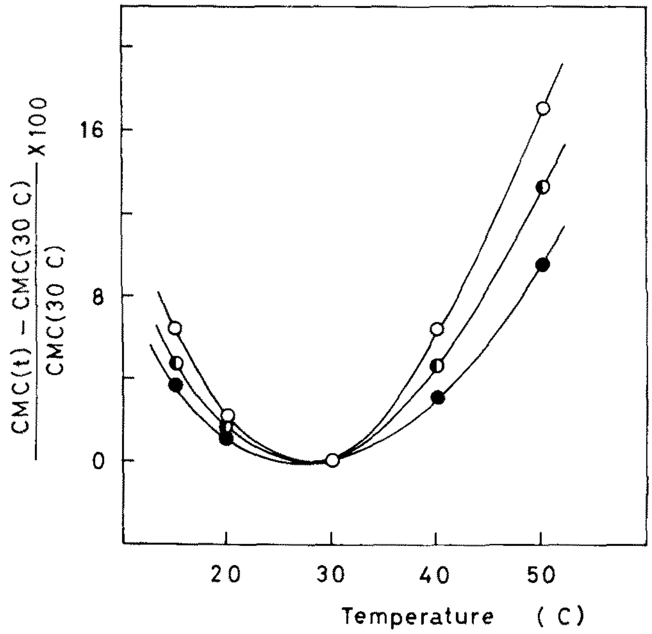

FIG. 2. Effect of temperature on critical micelle concentrations (CMC) of 9C-3 (●), 10C-3 (◐), and 11C-3 (○). Percentage deviations from CMC value at 30 C.

temperatures of 15-50 C. The temperature was controlled to within ± 0.05 C.

RESULTS

CMCs of 7 surfactants in aqueous solution have been determined as a function of temperature 15-50 C. CMC values were estimated from the intersection of 2 extrapolated straight line portions in the plots of equivalent conductance against the square root of concentration. Values are given in Table I.

To estimate the effect of temperature on CMC of each surfactant, percentage deviation of CMC at 30 C, [CMC(T)-CMC(30 C)] /CMC(30 C), has been adopted (1). Values of deviation for the sodium 2-sulfoethyl alkanoate derivatives are given as functions of temperature (Fig. 1); those of 3-sulfopropyl alkanoate derivatives are given in Figure 2; and those of 4-sulfobutyl alkanoate derivatives are given in Figure 3.

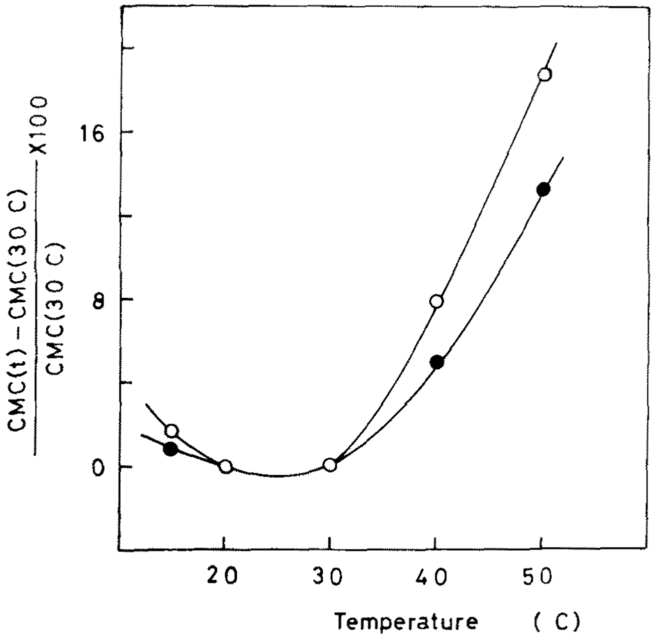

FIG. 3. Effect of temperature on critical micelle concentrations (CMC) of 9C-4 (●) and 11C-4 (○). Percentage deviations from CMC value at 30 C.

The figures show that there is a minimum in each of the curves, and that the position of the minimum is affected by the position of the ester group in the hydrocarbon chain of the surfactant. The minima shifted to lower temperature in the order: 2-sulfoethyl alkanoate derivatives > 3-sulfopropyl alkanoates derivatives > 4-sulfobutyl alkanoates derivatives. For the surfactants with same number of methylene groups inserted between the ester group and the sulfonate group, the position of minimum occurred at the same temperature, and the number of methylene groups in the fatty acid portion of the surfactant molecule did not affect the temperature at which the minimum occurred. In the temperature range below the minimum, the following became clear after investigation of the percentage deviation values of each surfactant. For 3 series with the same number of methylene groups between the ester and sulfonate groups, i.e., 9C-2 and 11C-2, 9C-3, 10C-3 and 11C-3, and 9C-4 and 11C-4, the deviation value increased with the number of methylene groups in the fatty acid portion. However, for 2 series with the same number of methylene groups in the fatty acid portion, i.e., 9C-2, 9C-3 and 9C-4, 11C-2, 11C-3 and 11C-4, the deviation value decreased with the increase in the number of methylene groups between the ester and sulfonate groups.

On the other hand, for each of 3 series with the same number of methylene groups between the ester and sulfonate groups, the deviation value in the temperature range above the minimum increased with the number of methylene groups in the fatty acid portion. Further, for each of 2 series with the same number of methylene groups in the fatty acid portion, the deviation value increased with the number of methylene groups between ester and sulfonate groups.

From the results described above, for a series with the same total number of methylene groups in the surfactant molecule, i.e., (9C-4, 10C-3, and 11C-2, changing the ester group away from the terminal position to a more central position in the alkyl chain decreased remarkably the deviation value in the temperature range below the minimum.

Whereas, in the temperature range above the minimum, the difference between deviation values for the 3 surfactants with the same total number of methylene groups becomes small, as Figure 4 shows.

On the assumption that micelle formation is a phase separation process (11,12) enthalpies of micelle formation, ΔHm, have been determined from temperature dependence of CMC, by using a Clausius-Clapeyron type of equation (13-15).

$$\Delta Hm = -RT^2[d\ln(CMC)/dT]_p \qquad (I)$$

The ΔHm values obtained for these surfactants over the temperature range are given in Table II. Then, free energy of micelle formation, ΔGm°, can be calculated from the following equation.

$$\Delta Gm^\circ = RT\ln\,(CMC) \qquad (II)$$

Values obtained are given in Table III. Entropies of micelle formation, ΔSm, are calculated readily from the ΔHm. These values are given in Table IV. The signs of ΔHm and ΔSm are reversed at a certain temperature range.

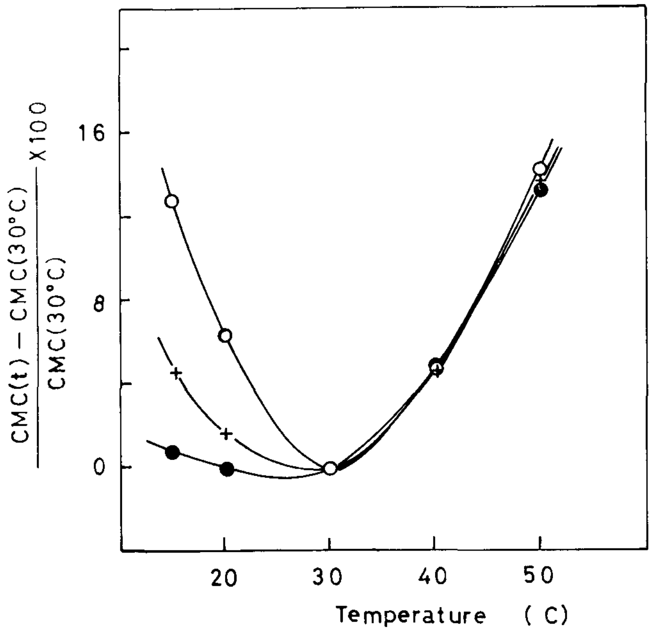

FIG. 4. Effect of temperature on critical micelle concentrations (CMC) of 9C-4 (●), 10C-3 (+), and 11C-2 (○). Percentage deviations from CMC value at 30 C.

DISCUSSION

Several papers that discuss CMC of surfactants in aqueous solution suggest that micelle formation is influenced by properties of water medium. Particularly, the effect of temperature on CMC can be explained mainly from the theory of hydrophobic interaction (1,15,16). In this experiment, it is considered that interaction between the ester group inserted in the hydrocarbon chain and water structure is an important factor in micelle formation.

CMC of each of the 7 surfactants showed a minimum, and then increased with a rise in temperature (1,2). Enthalpies of micelle formation, as determined from temperature variation of the CMC's, decreased with increasing temperature, and then changed for negative in higher temperature region. This change of sign of enthalpy is expected, because the strength of hydrophobic interactions should increase with a rise in temperature to a certain temperature and decrease at higher temperature (17,18). In effect, water molecules around the hydrocarbon chain of the single surfactant ions are considered to have a largely ordered ar-

TABLE II

Variation of ΔHm with Temperature

Temperature	ΔHm (Kcal/mole)						
(C)	9C-2	9C-3	9C-4	10C-3	11C-2	11C-3	11C-4
15	2.98	2.24	0.63	2.40	4.41	3.40	1.31
20	1.99	1.27	0.04	1.23	2.60	1.72	0.09
30	0.08	-0.40	-1.48	-1.06	-1.14	-1.49	-2.62
40	-1.49	-1.81	-2.99	-2.86	-4.01	-3.80	-4.04
50	-2.38	-2.83	-3.79	-3.50	-4.36	-4.32	-4.38

TABLE III

Variation of ΔGm° with Temperature

Temperature	ΔGm° (Kcal/mole)						
(C)	9C-2	9C-3	9C-4	10C-3	11C-2	11C-3	11C-4
15	-4.14	-4.50	-5.04	-5.38	-5.68	-6.06	-6.55
20	-4.26	-4.61	-5.14	-5.50	-5.84	-6.22	-2.69
30	-4.45	-4.78	-5.31	-5.71	-6.12	-6.45	-6.92
40	-4.57	-4.90	-5.43	-5.84	-6.26	-6.59	-7.05
50	-4.66	-4.98	-5.51	-5.93	-6.35	-6.68	-7.15

TABLE IV

Variation of ΔSm with Temperature

Temperature	ΔSm (cal/deg. mole)						
(C)	9C-2	9C-3	9C-4	10C-3	11C-2	11C-3	11C-4
15	10.3	7.8	2.2	10.0	15.3	11.8	4.6
20	6.8	4.3	0.1	4.2	8.8	5.9	0.3
30	0.3	-1.3	-4.9	-3.5	-3.8	-4.9	-8.6
40	-4.8	-5.8	-9.6	-9.1	-12.8	-12.2	-12.9
50	-7.4	-8.9	-11.7	-10.8	-13.5	-13.4	-13.6

rangement owing to the hydrophobic interaction of water and hydrocarbon chain at lower temperature (1,15,19). As the temperature is raised, there is a breakdown of water structure and, therefore, an increase in the energy of the single ion state. Consequently, the value of enthalpy falls and eventually becomes negative. These factors would cooperate to give an entropy change on micellization. As the temperature is raised, water structure progressively breaks down so that at higher temperatures the positive water contribution to the entropy change becomes small, and the negative entropy change associated with aggregation predominates (4,13,20).

As is evident from the figures, the difference among deviation values of the surfactants at lower temperature range is proof that the micelle formation is affected remarkably by the position of the ester group in the hydrocarbon chain (6,10,21,22). The cause of this phenomenon may be hydration of the ester group through interaction between the water molecule and the ester group (21). Moreover, the interaction between the water molecule and ester group becomes larger as the ester group is moved to a more central position in the hydrocarbon chain. In this case, the increase of interaction between the water and the ester group would prevent so much aggregation of the surfactant molecule (21). On the other hand, it is considered that interaction between the ester group and water molecule increases with the strength of the hydrophobic interaction. Accordingly, as seen in Figures 1-3, the order of rate of CMC decreasing in lower temperature range is: 2-sulfoethyl alkanoates > 3-sulfopropyl alkanoates > 4-sulfobutyl alkanoates.

For the series with the same number of methylene groups between ester and sulfonate groups, the deviation value of CMC in the lower temperature region becomes larger with the increase of the number of methylene groups in the fatty acid portion. The decrease in CMC with the rise in temperature can be attributed to an increase in the strength of hydrophobic interaction. This phenomenon suggests that the strength of hydrophobic interaction on the micelle formation becomes larger with the increasing length of hydrocarbon chain in the surfactant molecule.

In the range of temperature above the minimum CMC, deviation values increased with the rise in temperature and with the number of carbon atoms in the alkyl chain. The difference among deviation values of surfactants with the same total number of methylene groups, 9C-4, 10C-3, and 11C-2, was small. It is suggested that the effect of position of the ester group on deviation value is relatively small.

These phenomena are rationalized as follows. The degree of structural order of the water surrounding a hydrocarbon chain becomes less with the rise of temperature, and the effect of that reduction in order is more evident during micelle formation by a surfactant with a longer hydrocarbon chain. Accordingly, deviation value of CMC becomes larger with an increase in the number of methylene groups. On the other hand, the interaction between water molecules and the ester group decreases with hydrophobic interactions. Therefore, the effect of position of the ester group on deviation value of CMC is small in the higher temperature range.

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