The Effect of Position of Ester Group on Critical Micelle Concentration of Ester-Linked Sulfonates

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Abstract

The critical micelle concentration (CMC) of sodium alkyl sulfoacetates and β-sulfopropionates, and sodium salt of 2-sulfo ethyl ester, 3-sulfo propyl ester and 4-sulfo butyl ester of fatty acids have been determined by the electrical conductance of each aqueous solution. The relation between CMC value and number of total methylene groups (N) for the $C_{n^*}H_{2n^*+1}COO(CH_2)_3SO_3Na$ and $C_9H_{19}COO(CH_2)_{n^{**}}SO_3Na$ ($n^* = 9$, 10 and 11. $n^{**} = 2$, 3 and 4) can be formulated as follows.

$$\log \mathrm{CMC} = -0.293\,N + 1.778$$
for $C_{n^*}H_{2n^*+1}COO(CH_2)_3SO_3Na$
$$\log \mathrm{CMC} = -0.147\,N + 0.011$$
for $C_9H_{19}COO(CH_2)_{n^{**}}SO_3Na$

From these equations it was determined that the methylene unit situated between ester and sulfonate groups is equivalent to 0.5 methylene groups in its effect on CMC. For a given number of carbon atoms in the alkyl chain, the log CMC value increased regularly with a change in the ester group away from the terminal position to more central positions in the hydrocarbon chain. The two different types of ester-linkages (RCOO– and ROCO–) have no apparent effect on the CMC value.

Introduction

There have been many reports on the effect of chain length, structure of hydrophobic portion and the position of hydrophilic group in surfactant molecules on their critical micelle concentration (CMC). For instance, Klevens (1) reported that the CMC value of the normal hydrocarbon chain of one homologous series decreased logarithmically with the increase in the number of carbon atoms of the molecule. Dreger et al. (2) reported that the position of a sulfate group has influence on the CMC value, and moving the sulfate group from the terminal position to more central positions increases the CMC value of the surfactant.

On the other hand, few reports on the effect of the position of the polar group inserted in the hydrocarbon chain have been published. Livingston and Drogin (3) reported that the CMC value of alkoxyalkyl sulfates increases as the oxygen atom is moved further away from the terminal sulfate group. Stirton et al. (4,5) obtained similar results for long chain ether alcohol sulfates.

We have reported the estimation of the Krafft point, CMC value and other surface active and colloidal properties of the series of sodium alkyl sulfoacetates and sodium alkyl β-sulfopropionates (6; also, Hikota and Meguro, submitted for publication). In this report, the effect of position of the ester group in surfactant molecules on the CMC value will be investigated in detail.

The surfactants containing ester group used for this experiment are of two fundamental types: (a) those in which the hydrophobic group is derived from the higher alcohol; (b) those in which the hydrophobic group is derived from the higher fatty acid. Surfactants of the first type are sodium salts of alkyl sulfoacetates $ROCOCH_2SO_3Na$ and sodium alkyl β-sulfopropionates $ROCO(CH_2)_2SO_3Na$, and the second type are the sodium salts of 2-sulfo ethyl ester of fatty acids $RCOO(CH_2)_2SO_3Na$, 3-sulfo propyl ester of fatty acids $RCOO(CH_2)_3SO_3Na$ and 4-sulfo butyl ester of fatty acids $RCOO(CH_2)_4SO_3Na$.

Experimental Procedures

Materials

Sodium alkyl sulfoacetates series $ROCOCH_2SO_3Na$ were prepared from 98% pure fatty alcohols (octyl, decyl, dodecyl and tetradecyl) obtained by fractional distillation of commercial grade and monochloro acetic acid. The series of sodium alkyl β-sulfopropionates $ROCO(CH_2)_2SO_3Na$ were prepared from corresponding 98% pure fatty alcohols and β-bromopropionic acid as previously described. The series of sodium salt of 2-sulfo ethyl ester, 3-sulfo propyl ester and 4-sulfo butyl ester of fatty acids (capric, undecanoic and lauric acids) $RCOO(CH_2)_2SO_3Na$, $RCOO(CH_2)_3SO_3Na$ and $RCOO(CH_2)_4SO_3Na$ were prepared from 99% pure corresponding fatty acids with sodium isethionate, propane sultone and butane sultone (7,8). The crude products were purified by recrystallization three times from methanol or ethanol, and by extraction with petroleum ether in a Soxhlet extractor for 100 hr. Each pure material was obtained as a white flake powder.

The purity of the surfactant prepared was confirmed by elementary analysis and surface tension measurement. The results of the chemical analysis of the carbon and hydrogen of the compounds (except 3-sulfo propyl caprate) coincide with the theoretical values for their composition within ±0.3%. The carbon content of sodium 3-sulfo propyl caprate was 0.4% above the theoretical values. The surface tension vs. concentration curve of aqueous solution of the compounds did not show a minimum.

Method

The CMC values of the aqueous solution of the surfactants were determined by the conductivity method (9) using No. 4866 conductivity indicator of Leeds and Northrup conductivity bridge. The cell constant was determined from a conductance measurement with 0.001 mole potassium chloride solution. The water used in all the experiments was prepared by passage through an ion exchange resin column and then by distilling from alkaline potassium permanganate in a Pyrex glass vessel. The specific conductance of the water so prepared was always below 1.7×10^{-6} ohm^{-1} at 25 C. The conductance measurements were carried out in the double thermostat at a temperature of 40 ± 0.1 C.

Results and Discussion

The CMC values determined from the plots of

TABLE I
The Critical Micelle Concentration of Various Surfactants

	Total number of methylene groups (mmole/liter)							
	9	10	11	12	13	14	15	16
$ROCOCH_2SO_3Na$	70		17		3.8		1.1	
$ROCO(CH_2)_2SO_3Na$		49		13.4		2.9		0.8
$RCOO(CH_2)_2SO_3Na$			24.8		6.5			
$RCOO(CH_2)_3SO_3Na$				18	9	4.7		
$RCOO(CH_2)_4SO_3Na$					12.6		3.3	

equivalent conductance vs. concentration diagram are shown in Table I.

The CMC of ordinary normal paraffin chain salts is known to depend on the chain length in such a way that the logarithm of the CMC is a linear function of the number of methylene groups in the salt. The CMC values were plotted as a function of the number of methylene groups in Figure 1 for $C_9H_{19}COO(CH_2)_{n^{**}}SO_3Na$, $C_{11}H_{23}COO(CH_2)_{n^{**}}SO_3Na$ and $C_{n^*}H_{2n^*+1}COO(CH_2)_3SO_3Na$ ($n^{**} = 2$, 3 and 4. $n^* = 9$, 10 and 11). The values lie closely on the straight line given by:

$$\log \text{CMC} = -0.293\text{ N} + 1.778 \quad \text{for } C_{n^*}H_{2n^*+1}COO(CH_2)_3SO_3Na \qquad [1]$$

$$\log \text{CMC} = -0.147\text{ N} + 0.011 \quad \text{for } C_9H_{19}COO(CH_2)_{n^{**}}SO_3Na \qquad [2]$$

$$\log \text{CMC} = -0.147\text{ N} - 0.577 \quad \text{for } C_{11}H_{23}COO(CH_2)_{n^{**}}SO_3Na \qquad [3]$$

Where N is the total number of methylene groups.

Equation 1 is for the compound in which the methylene groups inserted between the sulfonate group and the ester group have the same number, but the methylene groups of the fatty acid portion change from 9 to 11 in number. Equations 2 and 3 are for the compounds whose methylene groups between the sulfonate and ester groups change from two to four in number, but the lengths of fatty acid portion were constant. In Equation 1, the change of carbon number (N) is due to the change of the methylene group number of the fatty acid portion. Then the slope of Equation 1 can be represented as follows:

$$\delta\log \text{CMC}/\delta n^* = -0.293 \qquad [4]$$

δn^* means the infinitesimal change of the methylene group number of the fatty acid portion.

The changes of carbon number in Equations 2 and 3 depend on the change of methylene group number in the methylene chain inserted between the sulfonate and ester group. Therefore, the slope of Equations 2 and 3 are represented as follows:

$$\delta\log \text{CMC}/\delta n^{**} = -0.147 \qquad [5]$$

δn^{**} means the infinitesimal change of methylene group number inserted between the sulfonate group and ester group. The gradient in Equations 2 and 3 coincide with each other owing to the fact that the gradient of both equations show the change of log CMC with one methylene unit inserted between sulfonate group and ester group.

Equation 5 divided by Equation 4 expresses the ratio of the changing power of the methylene unit inserted between the sulfonate and ester groups to the power of the methylene unit in the fatty acid portion on the value of log CMC.

$$\frac{\delta\log \text{CMC}/\delta n^{**}}{\delta\log \text{CMC}/\delta n^*} = 0.5$$

The result of this ratio shows that the CMC decreasing power of the methylene unit situated between the sulfonate and ester groups is equivalent to half of that in the fatty acid portion in its effect on the log CMC.

Furthermore, Figure 2 shows that for a given number of methylene groups, changing the ester group away from the terminal position to more central positions in the chain regularly increases the log CMC value. The value of −0.147 is obtained for the slope of this line, which is in good agreement with the slope obtained for Equations 2 and 3. This result proved that the decreasing power of the

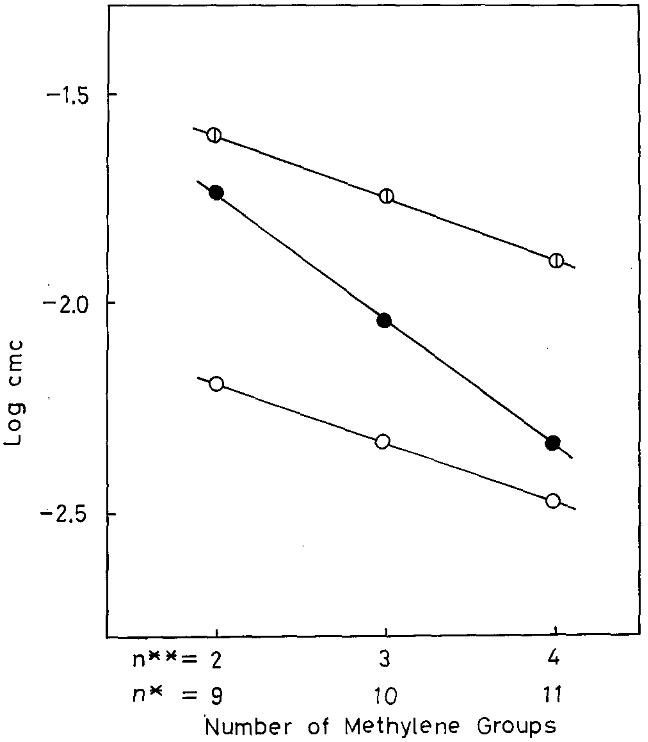

FIG. 1. Relation between log CMC and number of methylene groups for $C_9H_{19}COO(CH_2)_{n^{**}}SO_3Na$ (◐), $C_{11}H_3COO(CH_2)_{n^{**}}SO_3Na$ (○) and $C_{n^*}H_{2n^*+1}COO(CH_2)_3SO_3Na$ (●) ($n^{**} = 2$, 3 and 4. $n^* = 9$, 10 and 11).

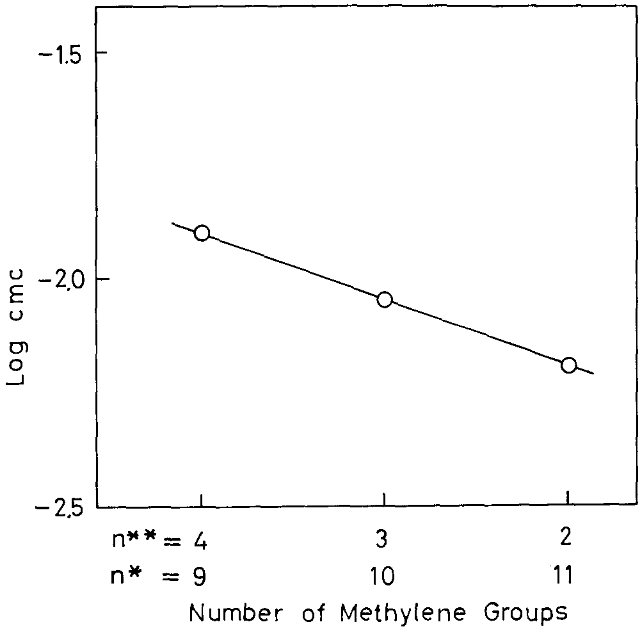

FIG. 2. Relation between log CMC and number of methylene groups for $C_{n^*}H_{2n^*+1}COO(CH_2)_{n^{**}}SO_3Na$ ($n^* + n^{**}$ = constant = 13).

methylene unit situated between sulfonate and ester groups is equivalent to half of that in the fatty acid portion. This conclusion can lead to the general equation for the dependency of log CMC on the total number of methylene groups as follows:

$$\log \mathrm{CMC} = -0.293(n^* + 0.5n^{**}) + 1.314 \qquad [6]$$

n^* the number of methylene groups in fatty acid portion. n^{**} the number of methylene groups situated between sulfonate and ester group.

The confirmation of this equation's validity is given in Figure 3 in which all of the log CMC values of each compound in this report lie on the one straight line where log CMC values were plotted as functions of $n^* + 0.5n^{**}$.

For a given number of total methylene groups (N) in the alkyl chain, the effect of position of ester group on CMC was calculated by the following equation.

$$N = n^* + n^{**} = \text{constant} \qquad [7]$$

when Equation 7 is inserted into 6

$$\begin{aligned}\log \mathrm{CMC} &= -0.293(N - n^{**} + 0.5n^{**}) + 1.314\\ &= -0.293(N - 0.5n^{**}) + 1.314\\ &= 0.147n^{**} - 0.293N + 1.314\end{aligned}$$

The movement of ester group from terminal to center of the molecule coincides with the increase of n^{**}. Therefore, the differential coefficient of log CMC with n^{**} means the effect movement of ester group from terminal to center.

$$\delta \log \mathrm{CMC}/\delta n^{**} = 0.147$$

The calculated result is supported by Figure 4.

Figure 4 shows the relation between log CMC and the total number of methylene groups in the various surfactants. The value of the slope of each line prepared is −0.29, which is in good agreement with the value of −0.30 obtained for the sodium alkyl sulfonate. As is evident from Figure 4, the CMC values of 3-sulfo propyl ester of fatty acid are equal to those for 2-sulfo ethyl ester of fatty acid of one less methylene group, and equal to those for 4-sulfo butyl ester of fatty acid of one more methylene group. Similarly, the CMC values of alkyl β-sulfopropionate are equal to those for alkyl sulfoacetate of one less methylene group. Furthermore, those of 2-sulfo ethyl ester of fatty acid are equal to those for alkyl β-sulfopropionate of the same number of methylene groups.

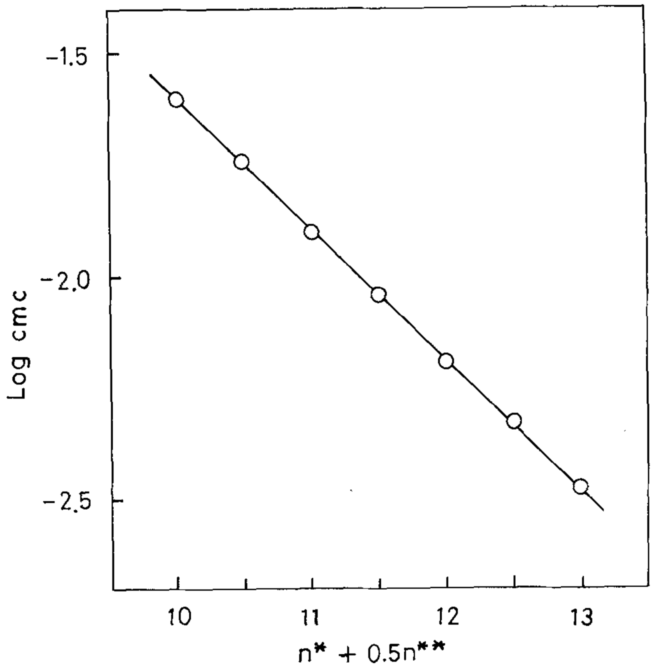

FIG. 3. Plot of log CMC against ($n^* + 0.5n^{**}$) for the seven sodium sulfoalkyl alkanoates.

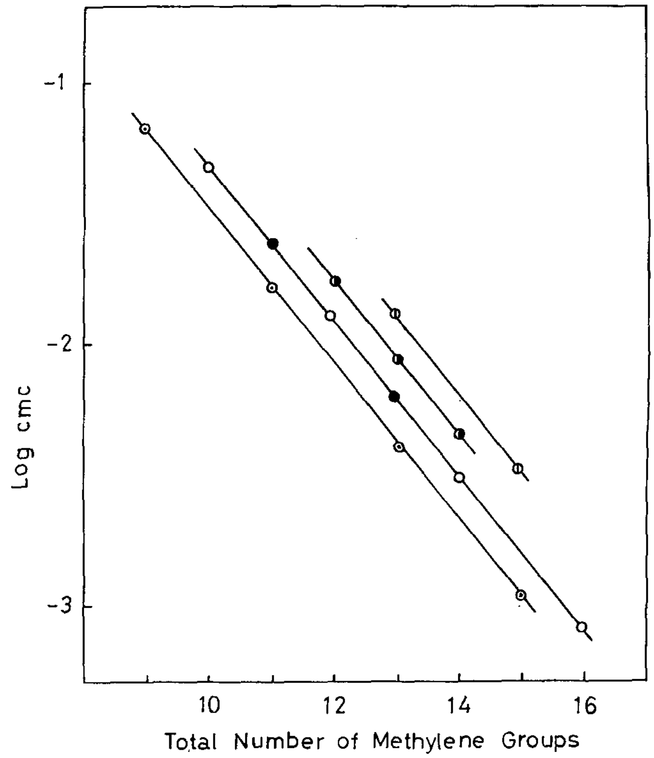

FIG. 4. Relation between log CMC and total number of methylene groups for $ROCOCH_2SO_3Na$ (⊙), $ROCO(CH_2)_2SO_3Na$ (○), $RCOO(CH_2)_2SO_3Na$ (●), $RCOO(CH_2)_3SO_3Na$ (◑), $RCOO(CH_2)_4SO_3Na$ (⦶).

The results, within the limits of this experiment, indicate that the effect of ester group on CMC value is almost independent of the two different types of ester-linked sulfonates (RCOO– and ROCO–) and is largely dependent on the position of the ester group in the alkyl chain.

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