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Studies of Ester-Containing Surfactants. Preparation and Properties of Sodium Sulfoalkyl Alkanoates

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A series of sodium sulfoalkyl alkanoates, $RCOO(CH_2)_jSO_3Na$, were prepared by means of sodium isethionate, propane sultone, and butane sultone with normal primary fatty acid composed of 10, 11, and 12 carbon atoms respectively. The effects of the position of the ester group on the Krafft point, the critical micelle concentration (CMC), the surface tention, and the other surface and colloidal properties of these surfactants were investigated. For a given number of carbon atoms, moving the ester group from the ionic head to a more central position in the hydrocarbon chain increased the CMC value and the calcium ion stalbility, and decreased the emulsion stability and the stability to hydrolysis. However, the wetting time was not strongly influenced by the position of the ester group in these compounds. The Krafft point of these surfactants decreased as the ester group was moved to a more central position.

Many investigations have been published regarding the effect of the molecular structure on the surface and colloidal properties. For example, Stirton and his co-workers[1–4] studied the surface-active properties (the Krafft point, the critical micelle concentration, the surface tension, the detergency, the wetting time, the calcium-ion stability, *etc.*) of the sodium α-sulfo fatty ester series and observed that a good wetting agent was usually not a good detergent. Livingstone and Drogin[5] measured the CMC, the surface tension, and the detergency of alkyl thioalkyl and alkoxy alkyl sulfates. Finger and co-workers[6] measured the effect of the structure of the alkyl group in sulfate-type surfactants on the surface tension and the detergency. Previously, I have investigated the effect of the position of the ester group of alkyl sulfo acetate[7] and alkyl β-sulfo propionate[8] on the CMC, the Krafft point, and other bulk properties.

In this experiment, I prepared sodium 2-sulfoethyl alkanoates, $RCOO(CH_2)_2SO_3Na$, 3-sulfopropyl alkanoates, $RCOO(CH_2)_3SO_3Na$, and 4-sulfobutyl alkanoates, $RCOO(CH_2)_4SO_3Na$, and compared their surface-active properties in order to discuss in detail the relation between the position of the ester group and the surface activities.

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[2] A. J. Stirton, R. G. Bistline, Jr., J. K. Weil, W. C. Ault and E. W. Maurer, *ibid.*, **39**, 128 (1962).

[3] W. C. Ault, T. J. Micich, A. J. Stirton and R. G. Bistline, Jr., *ibid.*, **42**, 233 (1965).

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[7] T. Hikota and K. Meguro, *ibid.*, **46**, 579 (1969).

[8] T. Hikota and K. Meguro, *ibid.*, **47**, 158 (1970).

Experimental

Materials. The capric and lauric acids were kindly provided by the Nippon Oil & Fat Co. The purity of each fatty acid was confirmed to be above 99% by gas chromatography. Normal undecylic acid was prepared according to the following procedure. Decyl alcohol (more than 98% pure) was chlorinated with thionyl chloride; the decyl chloride was then reacted with sodium cyanide in dimethyl sulfoxide.[9] The hydrolysis of the 1-cyanodecane by refluxing it with an excess of 35% of hydrochloric acid gave an undecylic acid. After the removal of the solvent, the residue was purified by distillation; bp 182—185°C/31 mmHg. The sodium isethionate was of a reagent grade. Propane sultone manufactured by the Shell Chemical Co. was further purified by distillation; bp 130°C/3 mmHg. The butane sultone was prepared in the following way. Acetyl chloride was gradually added to tetrahydrofuran according to the method of Cloke and Pilgrim.[10] The reaction mixture was then washed with water, and the oily layer was separated. After the esterification, the solution of δ-chlorobutyl acetate was refluxed and stirred with an aqueous solution of sodium sulfite; then most of the water was removed under reduced pressure. The residue was stirred and refluxed with the excess methanol, and hydrogen chloride was passed into the solution. The reaction mixture was cooled and filtered. The distillation of the filtrate gave a transparent, colorless, and viscous liquid; bp 146°C/17 mmHg.

Preparation of Sodium 2-Sulfoethyl Caprate. A mixture of one mole of capric acid and 1.5 mol of thionyl chloride was heated and stirred at 30°C for one hour, and then at 90°C for one hour. The reaction product, capryl chloride, was distilled under reduced pressure. After the addition of 0.35 mol of sodium isethionate to 0.4 mol of the capryl chloride, the mixture was heated a 90°C for two hours. The crude product thus obtained was recrystallized three times from methanol. Then it was extracted for 100 hr with petroleum ether in order to remove all traces of the unchanged fatty acid. The pure sodium 2-sulfoethyl caprate was obtained as a white flaky powder.

Found: C, 47.45; 4H, 7.44%. Calcd for $C_9H_{19}COO(CH_2)_2SO_3Na$: C, 47.67; H, 7.67%.

Preparation of Sodium 2-Sulfoethyl Laurate. A procedure similar to that used with sodium 2-sulfoethyl caprate was used in the preparation of sodium 2-sulfoethyl laurate from lauric acid and sodium isethionate. The salt was a white, flaky powder.

Found: C, 51.01; H, 8.15%. Calcd for $C_{11}H_{23}COO(CH_2)_2SO_3Na$: C, 50.89; H, 8.24%.

Preparation of Sodium 3-Sulfopropyl Caprate. Sodium 3-sulfopropyl alkanoates was prepared as has been described by Hirai *et al.*[11] A mixture of 0.3 mol of sodium caprate (the sodium alkanoates used in this experiment had been prepared by neutralizing fatty acid with sodium methylate in the toluene), 0.3 mol of propane sultone, and 300 m*l* of toluene was refluxed for 10 hr under stirring. The reaction mixture was then cooled and diluted with 500 m*l* of acetone. The precipitated salt was filtered and recrystallized three times from methanol. Then it was extracted for 100 hr with petroleum ether in order to remove all traces of the unchanged fatty acid. The salt was a white powder.

Found: C, 48.75; H, 7.27%. Calcd for $C_9H_{19}COO(CH_2)_3SO_3Na$: C, 49.35; H, 7.65%.

Preparation of Sodium 3-Sulfopropyl Undecylate and Laurate. The esterification of undecylic and lauric acids with propane sultone was performed in a manner similar to that used with sodium 3-sulfopropyl caprate.

Found: C, 50.90; H, 8.43%. Calcd for $C_{10}H_{21}COO(CH_2)_3SO_3Na$: C, 50.89; H, 8.24%. Found: C, 51.19; H, 8.04%. Calcd for $C_{11}H_{23}COO(CH_2)_3SO_3Na$: C, 51.19; H, 8.49%.

Preparation of Sodium 4-Sulfobutyl Caprate. Sodium 4-sulfobutyl caprate was prepared by the same procedure and with the quantities as in the preparation of the sodium 3-sulfopropyl caprate, but with the propane sultone replaced by butane sultone. The product was recrystallized three times from methanol; then it was extracted for 100 hr with petroleum ether to yield a white, flaky powder.

Found: C, 50.66; H, 8.24%. Calcd for $C_9H_{19}COO(CH_2)_4SO_3Na$: C, 50.89; H, 8.24%.

Preparation of Sodium 4-Sulfobutyl Laurate. The esterification of lauric acid with butane sultone was performed in a similar manner.

Found: C, 53.45; H, 8.89%. Calcd for $C_{11}H_{23}COO(CH_2)_4SO_3Na$: C, 53.61; H, 8.72%.

Measurements. *Krafft Point.* The Krafft point was measured by the electro conductivity method,[12] which corresponds to the estimation of the Krafft point by measuring the change in solubility with the temperature. A rapid increase in solubility at the Krafft point accompanied the rapid increase in electrical conductivity. Thus, the measurement of the change in the conductivity of the surfactant solution with the temperature in a surfactant sufficent to give a solid phase made it possible to estimate the Krafft point. The conductivity measurements were made using a Leeds and Northrup Co., No. 4197, conductivity cell and a 4866 conductivity-resistivity indicator.

Critical Micelle Concentration. The critical micelle concentration (CMC) of the aqueous solution was determined by the conductivity method at 40°C. The conductivity of the water used was about 1×10^{-6} reciprocal ohm.

Surface Tension. The surface tension of the surfactants was measured by the Wilhelmy-plate (Shimadzu Instr. Co.) method at 30°C.

Emulsion Stability. The emulsion was prepared from 10 m*l* of a 20 mmol aqueous solution of the surfactant and 5 m*l* of toluene at 40°C. The emulsifying property was determined by the time (in minutes) it took for an aqueous volume separating from the emulsion layer to reach 9 m*l*, counting from the moment of the cessation of its shaking.

Wetting Property. The wetting property was measured by using a felt 20 mm in diameter and 1 mm thick at 40°C.[13] A solution of 75 m*l* of the 20 mmol surfactant

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TABLE 1. THE KRAFFT POINT TEMPERATURE AND CMC OF SURFACTANT

Derivatives	Abbreviation	Krafft point °C	CMC mol/*l* Conductivity 40°C	 Surface tension 30°C
$C_9H_{19}COO(CH_2)_2SO_3Na$	9C-2	nearly 0	0.0248	0.025
$C_{11}H_{23}COO(CH_2)_2SO_3Na$	11C-2	14.5	0.0064	0.0062
$C_9H_{19}COO(CH_2)_3SO_3Na$	9C-3	below 0	0.0192	0.0019
$C_{10}H_{21}COO(CH_2)_3SO_3Na$	10C-3	4.6	0.009	0.009
$C_{11}H_{23}COO(CH_2)_3SO_3Na$	11C-3	9.0	0.0047	0.0043
$C_9H_{19}COO(CH_2)_4SO_3Na$	9C-4	below 0	0.0126	0.013
$C_{11}H_{23}COO(CH_2)_4SO_3Na$	11C-4	below 0	0.0033	0.0025

to be tested was placed in a 150 m*l* beaker, and then the felt disk was put into the solution in such a position that the disk could run parallel to the surface of the solution. The wetting time was shown by the seconds from the moment the disk was put into the solution until the moment it stated going down.

Stability to Hydrolisys. A mixture of 10 m*l* of the 10 mmol surfactant and 10 m*l* of 2N sulfuric acid was placed in a thermostat at 40°C. The time it takes for a sample solution to be clouded as the result of hydrolysis shows the stability of the surfactant to hydrolysis.

Calcium Stability. The calcium-ion stability of a 10 mmol aqueous solution was measured by the modifide Hart method[14] using 0.1N calcium chloride.

Results and Discussion

The Krafft points of the sulfoalkyl alkanoates given in Table 1 are lower than that of surfactant with the same number of methylene groups in an alkyl chain, just as with sodium alkyl sulfate and alkyl sulfonate. This behavior suggests that the ester group introduced into the alkyl chain decreases the hydrophobic property of the hydrocarbon chain. For one series of 3-propane ester salts, 9C-3, 10C-3, and 11C-3, the Krafft point increased with the number of carbon atoms in the fatty acid chain. However, for two series with the same number of carbon atoms in the fatty acid portion, that is, 11C-2, 11C-3, and 11C-4, and 9C-2, 9C-3, and 9C-4, the Krafft point decreased with the increase in the number of methylene groups inserted between the ester group and the ionic head. For a series with the same number of carbon atoms in the surfactants, 9C-4, 10C-3, and 11C-2, the Krafft point decreased in the order of the decrease in the melting point of the corresponding fatty ester, as the ester group in the compounds was moved to a more central position. For instance, butyl caprate has a melting point of −20°C, compared with that of −10°C for the ethyl laurate of the same carbon atoms.

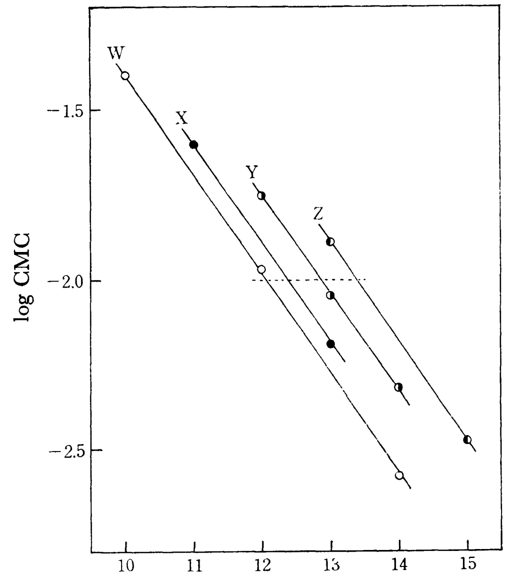

Fig. 1. Relation between log CMC and total number of mthylene groups in the chain.
RSO_3Na (○), $RCOO(CH_2)_2SO_3Na$ (●), $RCOO(CH_2)_3SO_3Na$ (◑), $RCOO(CH_2)_4SO_3Na$ (◐)

The CMC values of the surfactants, determined as the break points in the equivalent conductance againest the concentration curves, are given in Table 1. Furthermore, the logarithm of the CMC has been plotted against the total number of methylene groups for each of the sulfoalkyl alkanoate series. For comparision, the CMC value of sodium alkyl sulfonate[15] is also presented. Figure 1, which gives examples of the plots, shows that the slopes of all of the curves (W, X, Y and Z) are parallel, following the $\log \mathrm{CMC} = A - B \cdot N$ relationship. By measuring the horizontal distance between the curves (dotted line), one can compare the effects of the alkyl chain and of the position of the ester group on the CMC. The value of the horizontal distance was found to be 0.22 methylene groups for $\overline{WX}$ (the horizontal distance between

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[15] K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, "Colloidal Surfactants," Academic Press, N. Y. (1963), p. 43.

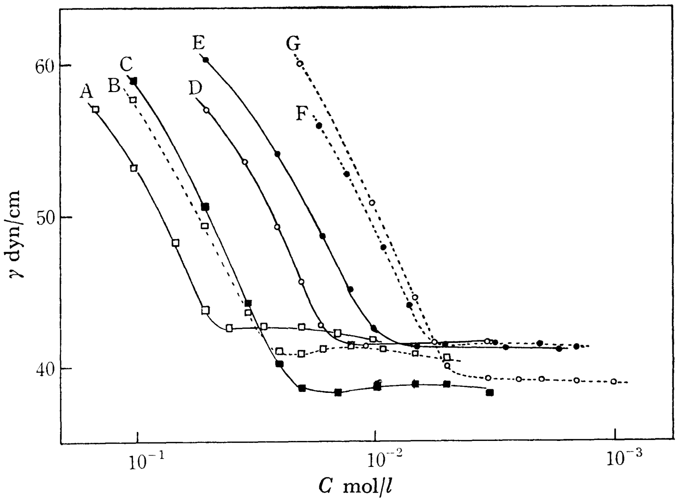

Fig. 2. Surface tension *vs.* concentration curves 11C-4 (A), 11C-3 (B), 11C-2 (C), 10C-3 (D), 9C-4 (E), 9C-3 (F) and 9C-2 (G).

the curve W and the curve X), 0.72 methylene groups for $\overline{\text{WY}}$, and 1.22 methylene groups for $\overline{\text{WZ}}$. This means that the isethionate, propane sultone, and butane sultone derivatives decrease the hydrophobic property of the hydrocarbon chain by 0.22, 0.72, and 1.22 units of the methylene group respectively with regard to the CMC value. Hence, the CMC of these surfactants increases regularly as the ester group is moved to a more central position in the chain.

The surface tension *vs.* the log concentration curve of the surfactants is shown in Fig. 2. The curve was inflected at the point which corresponds to the CMC. The CMC value estimated by means of the surface tension was in good agreement with that determined by means of the electro conductivity method, as is shown in Tables 1 and 2. The surface tension of the isethionate derivative above the CMC was about 39 dyn/cm, a little lower than that of the corresponding propane sultone and butane sultone derivatives. However, the surface tensions of these surfactants below the CMC are lower in this order: ethyl ester<propyl ester<butyl ester at the same concentration.

TABLE 2. PROPERTIES AND STABILITY OF SURFACTANT

Derivatives	Surface tension γ at CMC dyn/cm	Emulsion stability sec	Wetting time sec	Stability to hydrolysis min & sec
9C-2	39.10	12	3.3	43 : 51
11C-2	38.80	297	3.7	20 : 53
9C-3	41.24	146	3.8	39 : 45
10C-3	41.20	245	3.6	25 : 27
11C-3	40.40	378	4.0	18 : 39
9C-4	41.10	188	4.0	30 : 06
11C-4	42.30	442	3.5	16 : 26

The emulsion stability of the surfactants is shown in Table 2. As may be seen in the table, the emulsion stability increased with the number of the methylene group of the alkyl chain in the surfactant. For a series with the same number of methylene groups, 9C-4, 10C-3, and 11C-2, the emulsion stability increased as the ester group, was moved toward the center of the chain.

TABLE 3. CALCIUM STABILITY AND TEMPERATURE

Derivative	Converted into $CaCO_3$ Temperature °C					
	10	20	30	40	50	60
9C-2	>4500	>4500	>4500	>4500	>4500	>4500
11C-2	insoluble	insoluble	260	500	1930	2380
9C-3	900	>4500	>4500	>4500	>4500	>4500
10C-3	100	700	3800	>4500	>4500	>4500
11C-3	insoluble	insoluble	100	150	700	2210
9C-4	670	>4500	>4500	>4500	>4500	>4500
11C-4	insoluble	insoluble	580	1090	2930	>4500

The wetting properties of the surfactants are shown in Table 2. These surfactants were very effective wetting agents in a distilled water solution.

The relation between the stability to hydrolysis and the chain length in the surfactant is shown in Table 2. The stability to hydrolysis decreased with the increase in the number of carbon atoms in the surfactant. The data indicates, therefore, that at the same number of the methylene group in the surfactant the relative order of stability to hydrolysis is: ethyl ester>propyl ester>butyl ester. That indicates that the sulfo group protects the ester linkage through steric hindrance.

The calcium-ion stability of the surfactants (in relation to the temperature) is shown in Table 3. It is apparent that the stability increases markedly with an increase in the temperature, but decreases with an increase in the number of methylene group in the alkyl chain length under conditions of a constant temperature. For a given number of the methylene group, moving the ester group from the terminal to a more central position in the alkyl chain increases the calcium stability. This means that the hydrophilic property of the surfactant increases with the movement of the ester group toward the the center of the chain.

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