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The Properties of Aqueous Solutions of Sodium 2-Sulfoethyl Alkanoates and Sodium Alkyl β-Sulfopropionates

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A series of sodium 2-sulfoethyl alkanoates $RCOO(CH_2)_2SO_3Na$ was prepared from sodium isethionate and fatty acids containing 9, 11, 13, and 15 carbon atoms. The Krafft point, the critical micelle concentration (CMC), the surface tension, the emulsifying power, the wetting time, the resistance to acid hydrolysis, and the calcium-ion stability of this series of surfactants were examined, and the results were compared with those of the corresponding sodium alkyl β-sulfopropionates $ROCO(CH_2)_2SO_3Na$, which have another structure of ester-linkage. The CMC values of sodium 2-sulfoethyl alkanoates almost coincide with those value of the sodium alkyl β-sulfopropionates with the same number of carbon atoms. However, the Krafft point and surface tension at the CMC of sodium 2-sulfoethyl alkanoates were lower than those of the sodium alkyl β-sulfopropionates with the same number of carbon atoms. Sodium 2-sulfoethyl alkanoates are more stable than sodium alkyl β-sulfopropionates in their resistance to hydrolysis and to the calcium-ion.

In the last few years, several authors have studied the relation between the molecular structure and the properties of surfactants containing an ester group.[1-3] However, ester linkage may be classified into two fundamental types: (a) those in which the hydrophobic group is derived from the higher fatty acid, and (b) those in which the hydrophobic group is derived from the higher alcohol. The object of this report is to clarify how this difference in ester linkage affects the surface and colloidal properties, such as the Krafft point, the CMC value, the surface tension, the emulsifying power, the wetting property, the resistance to acid hydrolysis, and the calcium-ion stability. The surfactants of the first type used for this experiment were sodium 2-sulfoethyl alkanotes, while the surfactants of later type were sodium alkyl β-sulfopropionates.

Experimental

Material. The preparation of sodium 2-sulfoethyl alkanoate and sodium alkyl β-sulfopropionate may be represented by the following equation:

$$\text{(a)}\quad RCOOH + HO(CH_2)_2SO_3Na \rightarrow RCOO(CH_2)_2SO_3Na + H_2O$$

$$\text{(b)}\quad ROH + Br(CH_2)_2COOH \rightarrow ROCO(CH_2)_2Br + H_2O$$

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[1] T. Hikota and K. Meguro, *J. Am. Oil Chemists' Soc.*, **46**, 579 (1969).

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

[3] T. Hikota, This Bulletin, **43**, 2236 (1970).

Table 1. Elementary analysis of the surfactants

Derivative	Abbreviation	C		H	
		Found	Calcd	Found	Calcd
$C_8H_{17}COO(CH_2)_2SO_3Na$	SEA-8	45.34	45.82	7.00	7.34
$C_{10}H_{21}COO(CH_2)_2SO_3Na$	SEA-10	49.05	49.35	7.73	7.96
$C_{12}H_{25}COO(CH_2)_2SO_3Na$	SEA-12	52.20	52.31	8.28	8.49
$C_{14}H_{29}COO(CH_2)_2SO_3Na$	SEA-14	54.64	54.82	8.63	8.93
$C_8H_{17}OCO(CH_2)_2SO_3Na$	SAP-8	46.01	45.82	7.15	7.34
$C_{10}H_{21}OCO(CH_2)_2SO_3Na$	SAP-10	49.76	49.35	7.73	7.96
$C_{12}H_{25}OCO(CH_2)_2SO_3Na$	SAP-12	52.32	52.31	8.61	8.49
$C_{14}H_{29}OCO(CH_2)_2SO_3Na$	SAP-14	55.00	54.82	8.78	8.93

$$ROCO(CH_2)_2Br + Na_2SO_3 \rightarrow ROCO(CH_2)_2SO_3Na + NaBr$$

Preparation of Odd-chain Fatty Acid. The odd-chain fatty acid used in the preparation of the (a)-type surfactant was synthesized from the even fatty alcohol with one less carbon atom.[4] The odd-chain fatty acid thus obtained was washed several times with water, dried, and then distilled under reduced pressure. The purity of the odd-chain fatty acids was confirmed by elementary analysis and by a study of the melting points (pelargonic acid, 11.7—12.5°C; undecylic acid, 28.3—29.2°C; tridecylic acid, 39.6—40.8°C; and pentadecylic acid, 50.8—51.9°C). The results of the chemical analyses of the carbon and hydrogen of the compounds gave the calculated values for their composition within $\pm 0.3\%$. The octyl, decyl, dodecyl, and myristyl alcohols used as starting materials were purified by vaccum distillation from good commercial-grade alcohols, and were confirmed to be more than 98% pure by gas chromatographic analysis.

Preparation of Sodium 2-sulfoethyl Alkanoate. Sodium 2-sulfoethyl alkanoate was prepared by the following reaction. A solution of 0.32 mol of odd-chain fatty acid and 0.3 mol of sodium isethionate in 100 m*l* of toluene was stirred and then heated at the reflux temperature for 10 hr. The water of esterification was removed by azeotropic distillation using a Barrett trap. The reaction mixture was then cooled, and the precipitate, sodium 2-sulfoethyl alkanoate, were separated by filtration. The crude material was recrystallized three times from methanol, and then extracted with petroleum ether for 120 hr. The residue was dried at room temperature under reduced pressure to give the purified sodium 2-sulfoethyl alkanoate as a white flaky powder.

Preparation of Sodium Alkyl β-Sulfopropionate. The sodium alkyl β-sulfopropionates were prepared from β-bromopropionic acid, sodium sulfite, and higher alcohol containing from 8 to 14 even carbon atoms by a previously described method.[2] The crude material was recrystallized three times from ethanol, and then extracted with petroleum ether for 120 hr.

The results of the elementary analysis of these surfactants for carbon and hydrogen are summarized in Table 1.

Measurements. The Krafft point was taken as the temperature at which there was a rapid increase of the solubility of the surfactant in water upon gradual heating. The rapid increase in solubility at the Krafft point accompanied the rapid increase in electrical conductivity.[5] Therefore, the measurement of the rapid increase in the conductivity of the surfactant solution with the temperature in the presence of the solid surfactant made it possible to estimate the Krafft point. The values of conductivity were measured by means of a Towa Denpa Co. electro-conductivity bridge.

The CMC value of the surfactant was estimated by means of the electro-conductivity method[6] at 40°C. These CMC values were determined from the break point in the diagram of equivalent conductivity *vs.* the root of the concentration.

The surface-tension of an aqueous solution of the surfactant was measured by the Wilhelmy plate method at 30°C.

The emulsion was prepared from 5 m*l* of toluene and 10 m*l* of a 20-mmol aqueous solution of the surfactant by hand shaking at 40°C. The duration of the emulsion time was measured by the time elapsed from the moment of the cessation of the shaking to the separation of 9 m*l* of an aqueous volume from the emulsion layer.

The wetting power of the surfactant was measured by the disk-sinking method,[7] in which the wetting time of a felt disk in the surfactant solution become the scale for the wetting. The practical procedure was as follows: 75 m*l* of the 20-mmol surfactant solution to be tested was placed in a 150-m*l* beaker; then the disk (20 mm in diameter and 1 mm thick) was immersed in horizontal position. The time (in seconds) required for the disk to sink was recorded as the wetting time.

The experiment to measure the stability to hydrolysis was carried out by heating a 10-mmol equivalent of the surfactant solution in 20 m*l* of 2N sulfuric acid at 40°C.

The calcium-ion stability of the surfactant solution (10 mmol, 10 m*l*) was measured by a modified Hart method,[8] using 0.1N calcium chloride.

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[4] R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960).

[5] T. Ino, *Nippon Kagaku Zasshi*, **80**, 456 (1959).

[6] O. Yoda, K. Meguro, T. Kondo and T. Ino, *ibid.*, **77**, 905 (1956).

[7] W. Yano, T. Isaji and W. Kimura, *Yukagaku*, **11**, 183 (1962).

[8] B. G. Wilkes and J. N. Wickert, *Ind. Eng. Chem.*, **29**, 1234 (1937).

Table 2. Surface active properties of surfactants

Derivative	Krafft point °C	CMC mmol/l		Surface tension (30°C)			Emulsifying power min : sec	Wetting time sec	Stability to hydrolysis min : sec	Calcium stability ppm
		Conductivity 40°C	Surface tension 30°C	γ at CMC dyn/cm	$\Gamma \times 10^{10}$ mol/cm^2	Å area/molec.				
SEA-8	0	47.5	46.0	39.0	3.18	52.3	: 53	8.8	47 : 33	4,500
SEA-10	8.1	13.2	10.5	38.7	3.21	51.8	6 : 07	3.6	39 : 43	1,790
SEA-12	24.2	3.4	2.2	38.5	2.86	58.1	6 : 43	3.5	24 : 06	210
SEA-14	36.2	0.9	—	—	—	—	3 : 20	4.3	10 : 32	55
SAP-8	0	48.7	48.0	41.4	2.90	57.4	1 : 06	7.5	49 : 16	4,500
SAP-10	12.5	13.1	11.0	40.7	2.81	59.2	5 : 25	3.3	32 : 40	650
SAP-12	26.5	3.0	2.2	40.0	2.56	65.0	5 : 40	3.8	15 : 36	160
SAP-14	39.0	0.9	—	—	—	—	3 : 48	3.3	4 : 52	40

Results and Discussion

Krafft Point. It has been stated that the ionic surfactant can be as soluble as the micelle only above the Krafft point. Therefore, the value of the Krafft point must be determined before the measurement of the CMC by means of electroconductivity and other surface active properties. The Krafft points of the sodium 2-sulfoethyl alkanoates and sodium alkyl β-sulfopropionates series are given in Table 2, and they are plotted against the alkyl chain length in Fig. 1. These plots become two nearly parallel straight lines for each series of surfactants. The Krafft points of the sodium 2-sulfoethyl alkanoates are lower than those of the corresponding sodium alkyl β-sulfopropionates.

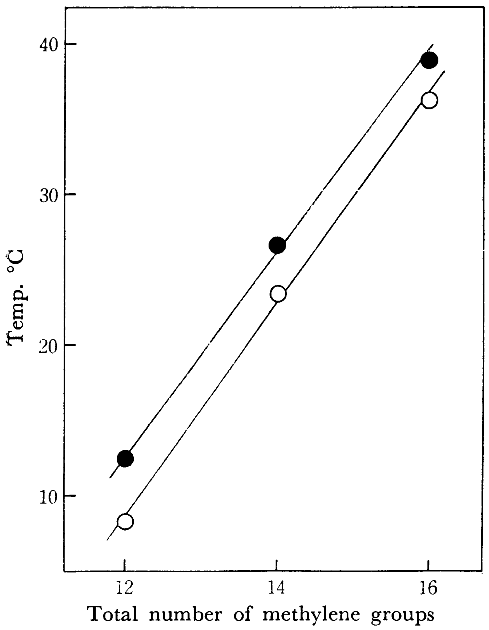

Fig. 1. Relation between Krafft point and total number of methylene groups in the chain. $RCOO(CH_2)_2SO_3Na$ (●), $ROCO(CH_2)_2SO_3Na$ (○).

Critical Micelle Concentration. The CMC values of two series of sodium 2-sulfoethyl alkanoates and sodium alkyl β-sulfopropionates, as estimated by conductivity method, are given in Table 2. The CMC value decreased with the increase in the length of the hydrocarbon chain, and the relation between the logarithm CMC and the alkyl chain length in the each surfactant series can be shown by the following equation:

$$\log \mathrm{CMC} = 1.6 - 0.29N$$

where N is the number of the methylene group in the alkyl chain.

As is shown in Fig. 2, the CMC values of sodium 2-sulfoethyl alkanoates fell on the same line as the CMC values of the sodium alkyl β-sulfopro-

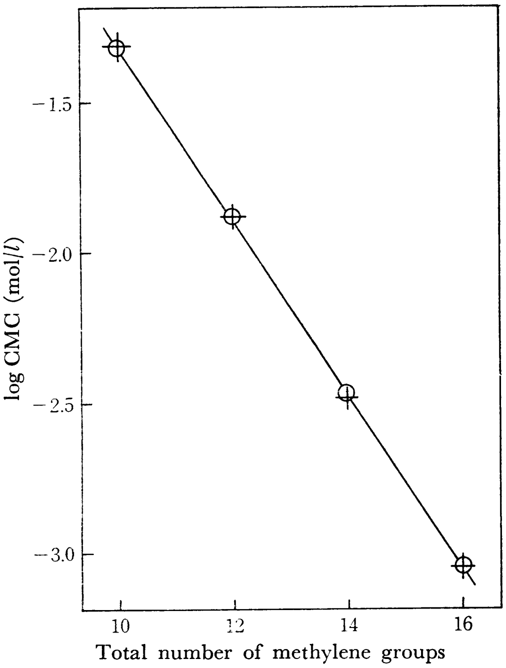

Fig. 2. Relation between log CMC and total number of methylene groups in the chain. $RCOO(CH_2)_2SO_3Na$ (○), $ROCO(CH_2)_2SO_3Na$ (+).

pionates. This indicates that the effect of the ester group on the CMC value is almost independent of the two different types of ester linkage (RCOO– and ROCO–), in sulfonate.[9]

Surface Tension. The values of the surface tension of aqueous solutions of the six surfactants (sodium 2-sulfoethyl pentadecanoate and sodium tetradecyl *β*-sulfopropionate are not shown) at 30°C are shown in Fig. 3.

The break point in the surface tension diagram coincides with the CMC values obtained by the electroconductivity method. The CMC values thus obtained from Fig. 3 are given in Table 2. As is shown in Fig. 4, the surface tension values at CMC lower with an increase in the alkyl chain length. The sodium 2-sulfoethyl alkanoates have a lower surface tension than the sodium alkyl *β*-sulfopropionates with the same carbon chain.

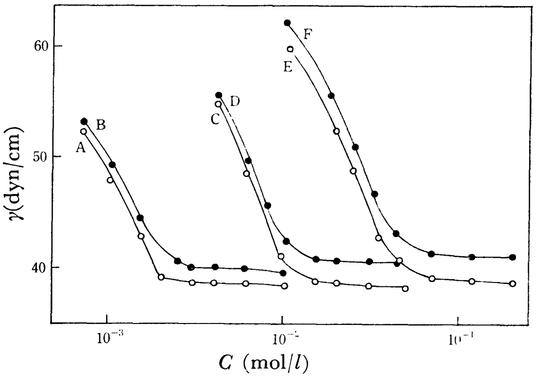

Fig. 3. Surface tension *vs.* concentration curves. SEA-12 (A), SAP-12 (B), SEA-10 (C), SAP-10 (D), SEA-8 (E), and SAP-8 (F).

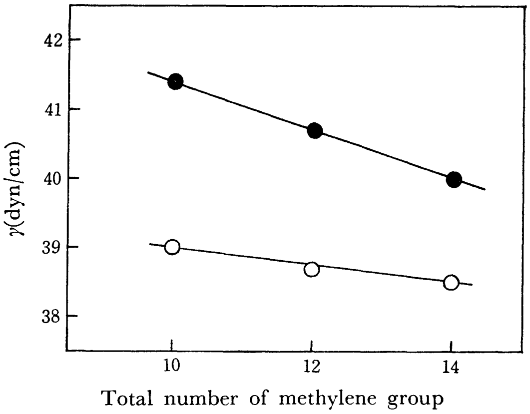

Fig. 4. Surface tension at CMC *vs.* total number of methylene groups. $RCOO(CH_2)SO_3Na$ (○), $ROCO(CH_2)_2SO_3Na$ (●).

According to the Gibbs adsorption isotherm equation, the inclination of the curves of the surface tension *vs.* the concentration gives the amount of surfactant adsorbed, Γ:

$$\Gamma = -\frac{1}{2RT} \times \frac{d\gamma}{d\ln C}$$

where γ is the surface tension and where C is the molar concentration. The area, A, occupied per surfactant molecule is calculated by the equation: $A = 1/N\Gamma$ from the amount of surfactant adsorbed; here, N is the Avogadro number. The values of the adsorption, the surface area, and the surface tension at the CMC of sodium 2-sulfoethyl alkanoates are compared with those of sodium alkyl *β*-sulfopropionates in Table 2.

Emulsion Stability. It is of interest to invesigate the effect of the difference in the ester linkage on the emulsifyng power of the surfactant. The emulsion stabilities of the surfactants are given in Table 2. The emulsions of all these surfactants with the exceptions of sodium 2-sulfoethyl pelargonate and sodium octyl *β*-sulfopropionate were more stable than that of sodium dodecyl sulfate. A comparison of sodium alkyl *β*-sulfopropionate and sodium 2-sulfoethyl alkanoate shows the later to be somewhat the better emulsifying agent.

Wetting Power. The wetting properties of the two different types of surfactants of the homologous series are shown in Table 2. It was difficult to find a certain relationship between the wetting properties and the alkyl chain length in the two series, sodium 2-sulfoethyl alkanoates and sodium alkyl *β*-sulfopropionates.

Stability to Hydrolysis and Calcium-ion Stability. The data obtained for stability to hydrolysis and the calcium-ion stability are shown in Table 2. The stability to hydrolysis of the sodium 2-sulfoethyl alkanoates is more stable than that of the corresponding sodium alkyl *β*-sulfopropionates, except for sodium 2-sulfoethyl pelargonate and sodium octyl *β*-sulfopropionate.

The calcium-ion stability of the surfactant decreases with an increase in the number of carbon atoms. This also shows that the calcium-ion stability of the sodium 2-sulfoethyl alkanoates is better than that of the sodium alkyl *β*-sulfopropionates.

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[9] T. Hikota and K. Meguro, *J. Am. Oil Chemists' Soc.*, **47**, 197 (1970).