Preparation and Properties of Sodium Alkyl ℬ-Sulfopropionates

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Abstract

A series of sodium alkyl β-sulfopropionates containing 11 to 17 carbon atoms was prepared from β-bromopropionic acid, sodium sulfite and even-numbered straight chain alcohols of 8 to 14 carbon atoms. The Krafft point, critical micelle concentration (cmc), emulsifying power, calcium ion stability and resistance to acid hydrolysis were determined. Sodium alkyl β-sulfopropionates, in which the ester linkage (hydrophilic group) is moved toward a more central position in the alkyl chain, have higher cmc values and lower Krafft points than the corresponding sodium alkyl sulfoacetates. The sodium alkyl β-sulfopropionates were less stable toward hydrolysis than the sodium alkyl sulfoacetates because the adjacent sulfo group in the sulfoacetates protects the ester linkage through steric hindrance. The emulsifying power increases, but the calcium ion stability decreases, with increasing alkyl chain length for a series of sodium alkyl β-sulfopropionates.

Introduction

The sodium sulfoalkyl esters derived from the higher alcohols have interesting surface active properties because of the ester linkage in the molecule. In a previous report (Hikota and Meguro, submitted for publication) it has been shown that sodium alkyl sulfoacetates have higher critical micelle concentration (cmc), lower Krafft point, greater emulsifying power and better calcium ion stability than the corresponding sodium alkyl sulfates. In the present type of surfactant, the surface activities will be altered through change in the length of the methylene group in the hydrophilic portion $-OCO(CH_2)_nSO_3Na$. The present report concerns the preparation of a series of sodium alkyl β-sulfopropionates $ROCO(CH_2)_2SO_3Na$ of 11 to 17 carbon atoms and an investigation of surface active properties and stability to hydrolysis.

TABLE I
Krafft Point and CMC Values of Sodium Alkyl Sulfopropionates

Alkyl	Critical micelle concentration (mmole/l.) Conductivity	Critical micelle concentration (mmole/l.) Surface tension	Krafft point (C)
Octyl	48.7	48.5	......
Decyl	13.1	10.2	12.5
Dodecyl	2.8	2.5	26.5
Tetradecyl	0.7	0.6	39.0

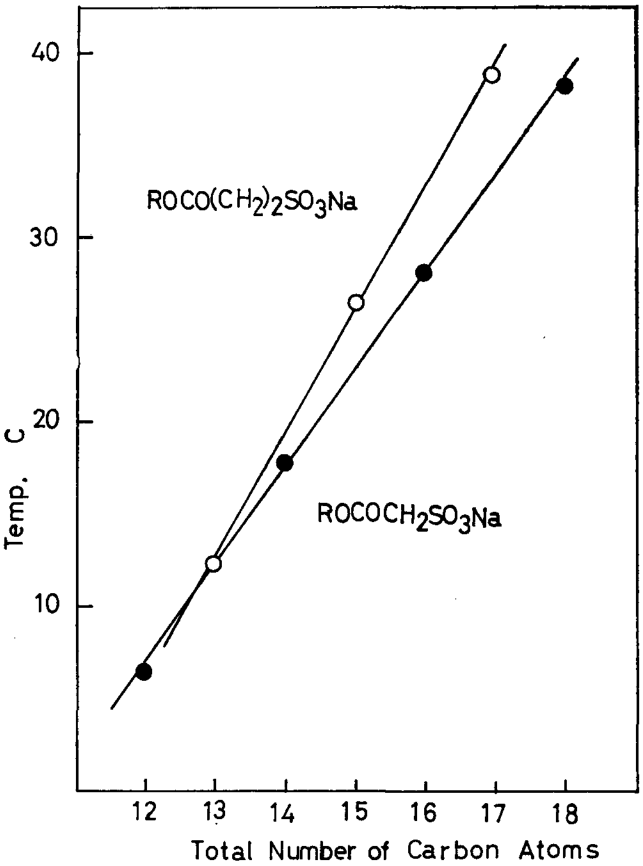

FIG. 1. Relation between Krafft point and the total number of carbon atoms in the alkyl chain of sodium alkyl β-sulfopropionates and alkyl sulfoacetates.

Materials

The preparation of sodium alkyl β-sulfopropionate is represented in the following chemical equations.

$$HOCH_2CH_2CN + HBr + H_2O \longrightarrow BrCH_2CH_2COOH \quad [1]$$

$$ROH + BrCH_2CH_2COOH \longrightarrow ROCOCH_2CH_2Br \quad [2]$$

$$ROCOCH_2CH_2Br + Na_2SO_3 \longrightarrow ROCOCH_2CH_2SO_3Na \quad [3]$$

Commercially pure octyl, decyl, dodecyl and tetradecyl alcohols used in this experiment were further purified by vacuum distillation. Gas chromatography showed that each of the higher alcohols was more than 98% pure. Carbon tetrachloride, sodium sulfite, 47%

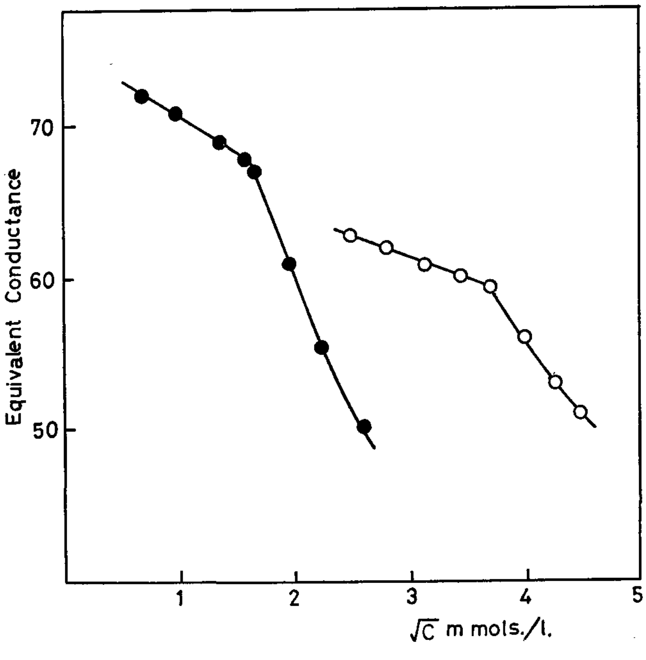

FIG. 2. Equivalent conductivity of sodium decyl (○) and dodecyl (●) β-sulfopropionate.

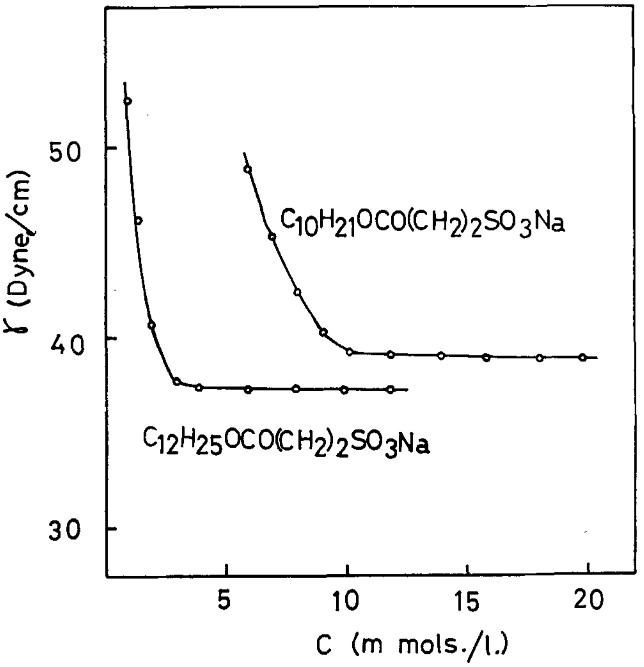

FIG. 3. Surface tension vs. concentration curves of sodium decyl and dodecyl β-sulfopropionate.

hydrobromic acid and ethylene cyanohydrin were reagent grade. The reaction steps were carried out as follows.

1. β-Bromopropionic acid: β-bromopropionic acid was prepared by the method of Kendall and McKenzie (1). Ethylene cyanohydrin, 1.5 mole, was brominated in the usual way by 5 moles of 47% hydrobromic acid. The product was extracted with carbon tetrachloride, the removal of which gave 1.2 moles of solid β-bromopropionic acid.

2. Esterification: A mixture of 0.3 mole of higher alcohol, 0.3 mole of β-bromopropionic acid, and 3 ml of concentrated hydrochloric acid in 200 ml of toluene was heated and stirred at reflux temperature for 15 hr with azeotropic removal of water.

3. Sulfonation: The sulfonation procedure was essentially that described previously for the preparation of sodium alkyl sulfoacetates (Hikota and Meguro, submitted for publication). A mixture of 0.3 mole of alkyl β-bromopropionate and 0.5 mole of sodium sulfite in 200 ml of water was stirred and refluxed for 40 hr. After cooling, the reaction mixture was obtained as a cream colored emulsion. Water was removed under reduced pressure.

The crude material was purified by three recrystallizations from ethyl alcohol followed by extraction with petroleum ether for 100 hr. The product was dried at room temperature under reduced pressure to give the purified sodium alkyl β-sulfopropionate as a white flaky powder.

These compounds showed no definite melting point because of decomposition above 170 C. Purity of the compounds was confirmed by infrared spectrum and elemental analysis. Analyses of these compounds for carbon and hydrogen gave the calculated values for their composition within ±0.3%.

Methods

Kraftt Point

It is well known that the solubility of an ionic surfactant increases rapidly a few degrees above a certain temperature called the Krafft point. Krafft points of the sodium alkyl β-sulfopropionates were determined by a conductivity method (2) using a Leeds and Northrup conductivity bridge No. 4866.

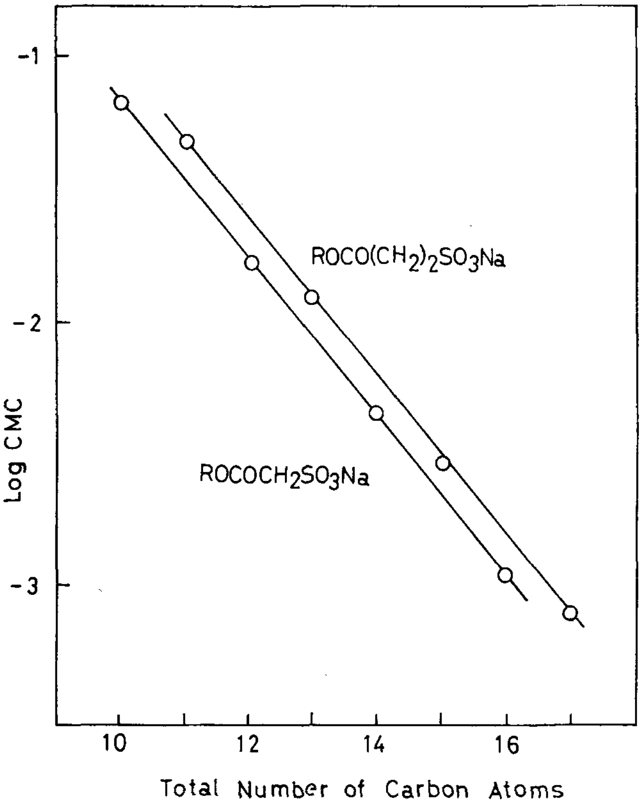

FIG. 4. Relation between log cmc and the total number of carbon atoms in the alkyl chain of sodium alkyl β-sulfopropionates and sulfoacetates.

The rapid increase of solubility at the Krafft point accompanied the rapid increase in electrical con-

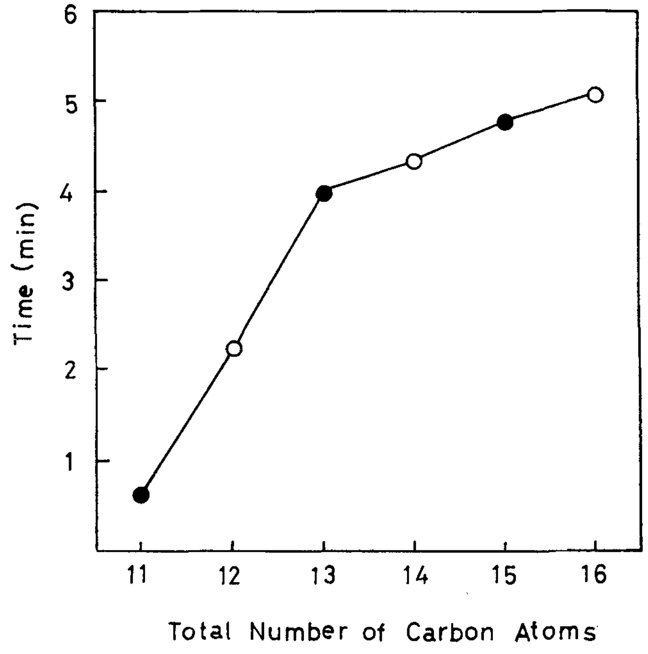

FIG. 5. Emulsion stability of sodium alkyl β-sulfopropionates (●) and alkyl sulfoacetates (○). The time required for a separation of 9 ml of aqueous phase vs. total number of carbon atoms.

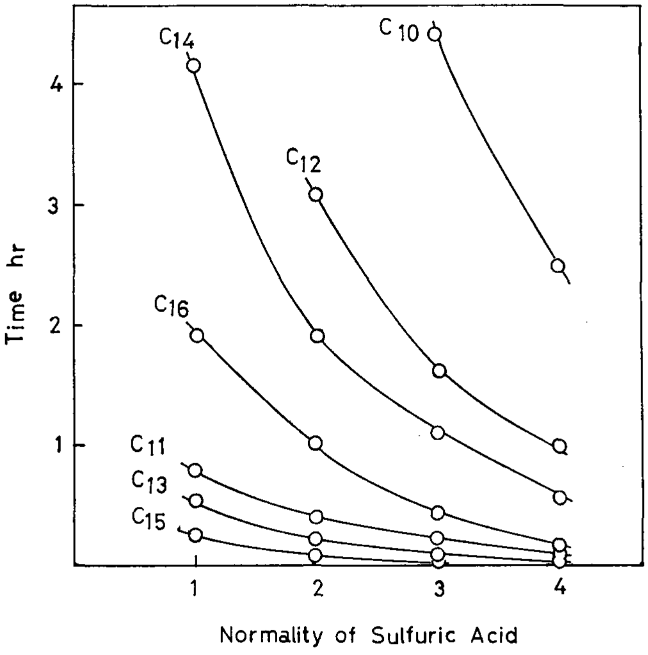

FIG. 6. Resistance of sodium alkyl β-sulfopropionates (C_{11}, C_{13} and C_{15}) and sodium alkyl sulfoacetates (C_{10}, C_{12}, C_{14} and C_{16}) to acid hydrolysis at 40 C.

ductivity. Thus the measurement of the change in the conductivity of the surfactant solution with temperature in the presence of the solid surfactant made it possible to estimate the Krafft point. Table I gives the Krafft point of the surfactant measured in this way.

The change in the Krafft point of sodium alkyl β-sulfopropionates and sulfoacetates with chain length of the alkyl group is represented in Figure 1. Increase in the Krafft point with the number of carbon atoms in the alkyl chain of sodium alkyl β-sulfopropionates was higher than for sodium alkyl sulfoacetates.

Critical Micelle Concentration

The micelle of the surfactant is formed at the critical micelle concentration (cmc). The cmc values of the aqueous solution of sodium alkyl β-sulfopropionates were determined by the electroconductivity (3) and surface tension methods at 40 C. The cmc values by the conductivity method were obtained from the intersection of two extrapolated straight line portions of the plot of the equivalent conductance against the square root of concentration. Typical conductance curves of decyl and dodecyl β-sulfopropionates are shown in Figure 2.

The surface tension of aqueous solutions of alkyl β-sulfopropionates was measured by the drop weight method. The correction factor of Harkins and Brown (5) was applied in all measurements. A typical plot of the surface tension for the decyl and dodecyl β-sulfopropionates against molar concentration is shown in Figure 3. The curve of surface tension against concentration shown an abrupt inflection at the point which corresponds to the cmc. The cmc values determined by the surface tension were in good agreement with those of the electroconductivity method as shown in Table I.

A plot of the cmc values decreases logarithmically with the increasing number of carbon atoms. The values lie closely on the straight line given by

$$\log \text{cmc} = 1.630 - 0.294 \cdot \text{N}$$

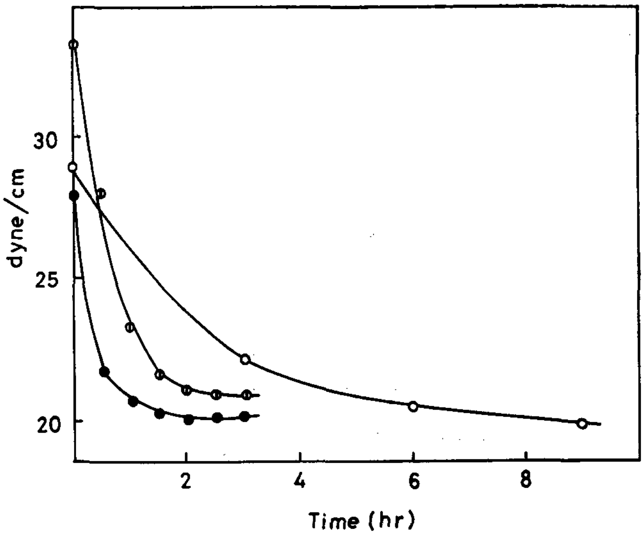

FIG. 7. Stability to hydrolysis of decyl β-sulfopropionate (⦶), dodecyl β-sulfopropionate (●) and dodecyl sulfoacetate (○) (by surface tension). Surface tension vs. time progress of hydrolysis of the surfactant.

where N is the total number of methylene groups.

The relation of cmc to alkyl chain length for alkyl β-sulfopropionates and sulfoacetates is shown in Figure 4. The cmc values of alkyl β-sulfopropionates were higher than those of alkyl sulfoacetates. For a given number of carbon atoms in the alkyl chain, the cmc became higher as a result of moving the hydrophilic group (ester group) from the terminal position to a more central position in the chain. This increase seems to be in agreement with the work of Klevens (5) and of Dreger et al. (6), and the cmc values of sodium alkyl β-sulfopropionates are about equal to those for alkyl sulfoacetates of one less carbon atom.

Emulsion Stability

The test emulsion was prepared from 6 ml of liquid paraffin and 10 ml of a 20 mmole solution of the alkyl β-sulfopropionate by an up and down manual shaking for 15 times for about 5 sec at 40 C. The volume of aqueous phase which separated was measured at different time intervals after completion of the shaking period. The time in seconds for 9 ml of the aqueous phase to separate is recorded in Figure 5. The data for the emulsifying power of alkyl sulfoacetates, given in Figure 5 for comparison, show that the two types of esters have similar emulsifying power.

The stability of emulsions with alkyl β-sulfopropionate increased with the number of carbon atoms in the alkyl chain.

Resistance to Hydrolysis

The acid catalyzed hydrolysis of the alkyl β-sulfopropionate was measured by the method previously described (Hikota and Meguro, submitted for publication). The surfactant solutions, 0.005 mole, containing different amounts of sulfuric acid were held in a thermostat at 40 C. The resistance to hydrolysis was defined as the time in minutes required to cause the solution to become turbid. The results are shown in Figure 6, where comparison is made with the alkyl sulfoacetate. The alkyl β-sulfopropionates become less stable with increasing number of carbon atoms in the alkyl chain and with increasing concentration of sulfuric acid.

TABLE II

Calcium Ion Stability of Sodium Alkyl Sulfopropionates and Sodium Alkyl Sulfoacetates

(Expressed as ppm $CaCO_3$)

Temperature C	Total number of carbon atoms						
	$ROCO(CH_2)_2SO_3Na$				$ROCOCH_2SO_3Na$		
	11	13	15	17	12	14	16
25	above 4,500	1,170	insoluble	insoluble	above 4,500	2,800	insoluble
30	above 4,500	2,440	310	insoluble	above 4,500	3,300	980
35	above 4,500	3,170	350	insoluble	above 4,500	3,850	1,060
40	above 4,500	3,680	750	insoluble	above 4,500	above 4,500	870
45	above 4,500	3,940	1,000	160	above 4,500	above 4,500	....
50	above 4,500	2,470	850	120	above 4,500	above 4,500	....

The resistance to acid hydrolysis of sodium decyl and dodecyl β-sulfopropionates was also determined by measuring the surface tension of a 0.01 molar solution, after heating at 40 C with 0.1 normal sulfuric acid for definite time periods. The results are shown in Figure 6, in which the resistance to acid hydrolysis of dodecyl sulfoacetate is presented for comparison. The change in surface tension with the progress of hydrolysis illustrated in Figure 7 may be due to adsorption onto the air-water interface of the higher alcohol produced by hydrolysis.

Sodium dodecyl sulfoacetate is more resistant to hydrolysis than sodium decyl and dodecyl β-sulfopropionates because the adjacent sulfo group in the sulfoacetate protects the ester linkage through steric hindrance (7).

Calcium Stability

The calcium ion stability of alkyl β-sulfopropionates was measured by a modified Hart method (8). The surfactant solution, 10 ml of 10 m mole, was titrated with 0.1 normal calcium chloride solution. The end point was determined by visual observation of the cloudiness of the surfactant solution. The experimental data in Table II are the results obtained at different temperatures. All of the compounds have excellent calcium stability except sodium tetradecyl β-sulfopropionate.

The calcium ion stabilities of both alkyl β-sulfopropionates and alkyl sulfoacetates increased markedly on increasing the temperature from 25 to 50 C, but decreased with increasing number of carbon atoms in the alkyl chain.

A comparison of the calcium ion stabilities of alkyl β-sulfopropionates with those of the alkyl sulfoacetates shows that the sulfoacetates are slightly less stable than sulfopropionates having the same alkyl group.

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