Preparation and Properties of Sodium Alkyl Sulfoacetates

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Abstract

The preparation and properties for a homologous series of sodium salts of alkyl sulfoacetates, containing 10, 12, 14 and 16 carbon atoms are described. The sodium salts of alkyl sulfoacetates were prepared from monochloroacetic acid, sodium sulfite and corresponding higher alcohol. The Krafft point, c.m.c. value, surface tension, solubilizing power, emulsifying power, foaming power, and calcium ion stability and resistance to acid hydrolysis were measured as the properties of these compounds. The c.m.c. values at 40 C obtained by electrical conductivity were related to the alkyl carbon number (N) of the compounds by log c.m.c. = 4.852 − 0.301 N. Solubilizing power, emulsifying power and foaming power increased with the number of carbon atoms of alkyl chain in the surfactant. But the calcium ion stability and resistance to the acid hydrolysis decreased with an increase in the length of the hydrophobic portion.

Introduction

The important surfactants of sulfomonocarboxylic acid type appear to be largely confined to those of sulfoacetic esters. Nacconol LAL, of the Allied Chemical and Dye Co., is the typical sodium alkyl sulfoacetic ester synthesized from coconut oil alcohol. Several methods for the preparation of the surfactant of sulfomonoacetic ester type have been disclosed in patents and reports (1,2). However, these reports were limited in scope and did not refer in detail to the exact data for surface and bulk properties of these surfactant solutions.

In this report, a series of sodium alkyl sulfoacetates prepared from sodium sulfite and alkyl chloroacetyl esters of octyl, decyl, dodecyl and myristyl alcohol were examined for surface active properties.

Experimental Procedures

Materials

Sodium alkyl sulfoacetate homologous series are prepared by the following reaction:

(a) $CH_2ClCOOH + SOCl_2 \longrightarrow CH_2ClCOCl + SO_2 + HCl$

(b) $CH_2ClCOCl + ROH \longrightarrow ROCOCH_2Cl + HCl$

(c) $ROCOCH_2Cl + Na_2SO_3 \longrightarrow ROCOCH_2SO_3Na + NaCl$

The octyl, decyl, dodecyl and myristyl alcohols used as starting material were purified by vacuum distillation from good commercial grade alcohols. The purity of each alcohol was confirmed to be above 98% by gas chromatography. Monochloroacetic acid and anhydrous sodium sulfite, used in this experiment were of guaranteed reagent; thinoyl chloride was of extra pure. The details of each reaction step are as follows: (a) A mixture of 1 mole of chloroacetic acid and 1.2 moles of thionyl chloride was heated and stirred for 1 hr at 40 C, then at 90 C for 1 hr. The product was distilled under reduced pressure. (b) Chloroacetyl chloride, 1 mole, was added dropwise for 20 min to 1 mole of higher alcohol. The mixture was first heated at 50 C for 2 hr then at 80 C for 6 hr. Distillation under reduced pressure resulted in the products. (c) Sodium alkyl sulfoacetate was prepared by sulfonation of 0.4 moles of alkyl chloroacetyl ester with 0.5 moles of sodium sulfite in water at 115 to 150 C for 25 hr. The water in the reaction mixture was then evaporated under reduced pressure.

After being extracted with petroleum ether for 75 hr and recrystallized three times from ethanol, the sodium alkyl sulfoacetate series were obtained as a white flake powder. The purity of the compounds was assessed by minimum absence in the surface tension, as opposed to the concentration curve of the aqueous solution.

Sodium dodecyl sulfate was prepared from dodecyl alcohol and chlorosulfonic acid by the method of Dreger et al. (3). The product was recrystallized twice from water and three times from ethanol, and then extracted with petroleum ether for 120 hr.

Krafft Points

It has been stated that the ionic surfactants can be soluble as micelle only above the definite temperature known as the Krafft point; above this temperature the solubility of surfactant increases rapidly. The Krafft point must be determined before the measurements of surface tension and electrical conductivity of the surfactant solution are taken from the micelle formation.

The Krafft point of these compounds was estimated from the temperature at which the abrupt change in conductivity occurred, as there was an increase in solubility of the surfactants when they were in a sedimented state (4).

The measurements of electrical conductivity for

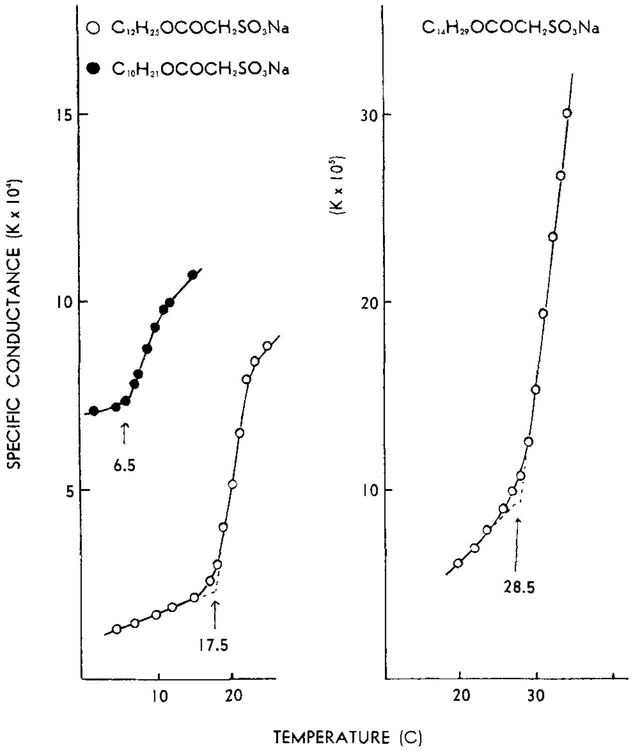

FIG. 1. Krafft point of the alkyl sulfoacetates. Specific conductivity of surfactant solution vs. temperature.

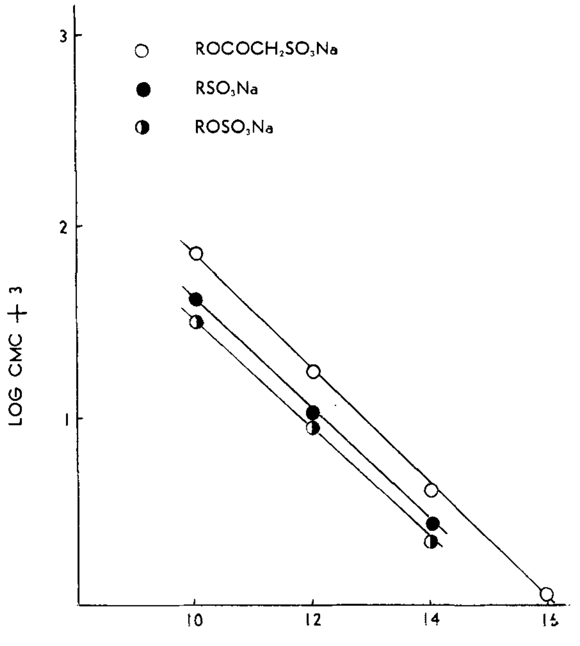

FIG. 2. Relationship of critical micelle concentration to chain length for sodium alkyl sulfoacetates, sodium alkyl sulfates (6) and sodium alkyl sulfonates (7).

determination of the Krafft point were made in a cell containing 50 ml of pure water and sufficient surfactant to give a sedimented phase.

A Yokokawa conductivity bridge was used to measure the conductivity of the solution. Before beginning the measurement, cell constants at 5 to 60 C were determined by the use of 0.01 mole KCl under gradual heating. Subsequently, the conductivity of the solution in the sedimented phase of surfactant was measured under the same gradual heating. Figure 1 shows the temperature vs. conductivity of the solution diagram.

Critical Micelle Concentration

The c.m.c. values of a series of sodium alkyl sulfoacetates were estimated from electrical conductivity and surface tension of these aqueous solutions. These values were determined from the break point in specific conductivity vs. concentration diagram at 40 C (5).

The surface tension of the aqueous solution of the compounds was measured by the drop weight method at 40 C. The first three drops were neglected and the mean of about ten successive drops was used to calculate the surface tension, using the correction factors of Harkins and Brown (6).

The c.m.c. values estimated by conductivity and surface tension are listed in Table II, in which the decrease of c.m.c. values with an increase in the length of the alkyl chain in a homologous series of the alkyl sulfoacetates are shown.

Figure 2 shows the relationship between the c.m.c. values (by the conductivity method) and the carbon atoms in the alkyl chain of sulfoacetates. The same relationships between the c.m.c. values and the carbon atoms of the sodium alkyl sulfate (6) and of the sodium alkyl sulfonate (7) were given in Figure 2 as a comparison.

TABLE I

C.M.C. Value of Sodium Alkyl Sulfoacetates[a]

	C.M.C., mmoles/liter, 40 C			
	Number of alkyl carbon atoms			
Methods	8	10	12	14
Conductivity	70.0	17.0	3.8	1.1
Surface tension	63.0	15.0	3.5	0.9

[a] C.M.C., mmoles per liter, 40 C.

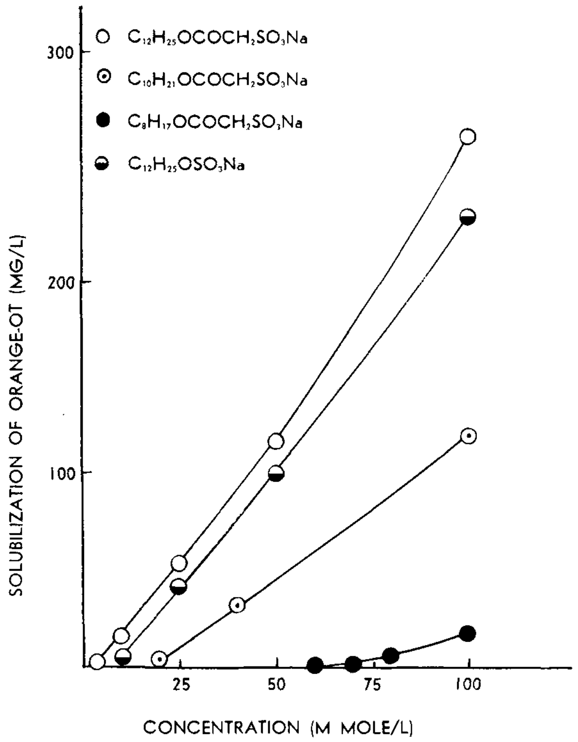

FIG. 3. Solubilization of Orange OT in aqueous solution of alkyl sulfoacetates and sodium dodecyl sulfate.

Klevens (9) found the following relationship between the c.m.c. values and the alkyl chain length: log c.m.c. = A − B·N, in which A and B are constants, and N is the number of carbon atoms in an alkyl chain length. The relationship between the number of carbon atoms in the alkyl chain of alkyl sulfoacetates and the c.m.c. values was expressed as log c.m.c. = 4.852 − 0.301·N.

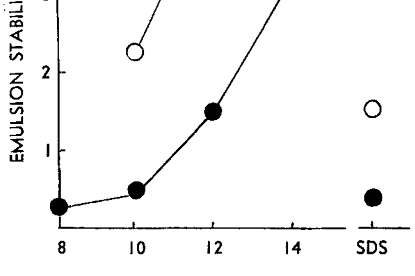

FIG. 4. Emulsion stability of alkyl sulfoacetate and dodecyl sulfate (SDS). The time required for a separation of 9 ml of aqueous volume vs. number of carbon atoms.

TABLE II

The Foam Formation and Foam Stability of Sodium Alkyl Sulfoacetates and Sodium Dodecyl Sulfate

Concentration of sample, mmoles/l., 40 C	Foam formation, mm					Foam stability, %				
	Number of alkyl carbon atoms of R				SDS	Number of alkyl carbon atoms				SDS
	8	10	12	14	12	8	10	12	14	12
1	1.0	2.5	138.0	153.0	8.0	100	100	15.2	6.5	62.5
5			227.0		181.0			2.6		7.7
10			232.0		221.0			5.2		18.6
20	6.0	178.0	226.0	230.0	205.0	100	8.4	6.0	20.9	17.0

Solubilization of Dye

A water insoluble dye such as Orange OT can be solubilized in the surfactant solution of the concentration above c.m.c. The solubility process was carried out as follows (10).

An excess of water insoluble dye Orange OT and 10 ml of surfactant aqueous solution was introduced into an L type test tube. The tubes were sealed off and agitated vigorously in a Monod-style thermostat for least 72 hr at 30 C. After the agitation was completed, excess dye was removed by filtration through a glass filter G-4. Then, the solution was diluted with an equal volume of ethanol for an estimation of the amount of dye solubilized by the optical method.

The amount of solubilized dye in the solution was determined by measuring the maximum absorbancy, 497 mμ. Every spectrum was taken with a Beckmann photoelectric colorimeter, using a 1 cm quartz cell.

The solubilization of Orange OT vs. surfactant concentration is shown in Figure 3. The amount of solubilized dye Orange OT was very slight or zero at below the c.m.c., but increased linearly according to the increasing concentration of surfactant above the c.m.c. The amount of Orange OT solubilized at the same surfactant concentration of 100 mmoles increased with the chain length in a homologous series. Solubilizing power of dodecyl sulfate is smaller than the power of dodecyl sulfoacetate.

Emulsifying Power

The emulsifying power of alkyl sulfoacetate and dodecyl sulfate was estimated with liquid paraffin and an aqueous solution of the surfactant. Each of 1 and 20 mmoles surfactant solutions, 10 ml, and 6 ml of liquid paraffin was held in water at 40 C. After complete separation of two phases of the liquid, the cylinder was shaken vigorously by hand for about 5 sec. After that, the cylinder was again held in the thermostat. The duration of emulsion time was measured by the time elapsed from the moment of cessation of the shaking to the separation of 9 ml of aqueous volume from the emulsion layer. Figure 4 shows the emulsion stability of alkyl sulfoacetates and dodecyl sulfate.

It is shown in Figure 4 that the stability of the emulsion with the alkyl sulfoacetate series was increased with the number of carbon atoms in the alkyl chain. Comparison of the stability with that of the emulsion made by dodecyl sulfate indicates that introduction of the ester group improves the emulsion stability.

TABLE III

Resistance of Sodium Alkyl Sulfoacetates and Sodium Dodecyl Sulfate to Acid Hydrolysis

H_2SO_4 normality	Time required for clouding 5 mmoles/liter concentration, 40 C, hr & min				
	Number of alkyl carbon atoms				SDS
	8	10	12	14	12
1	....	4:27	4:09	1:54	....
2	....	3:04	1:54	0:58	....
3	4:28	1:37	1:07	0:26	....
4	2:30	1:02	0:35	0: 9	23:00

Foaming Properties

The foam formation and foam stabilizing of the aqueous solution of the alkyl sulfoacetates series and dodecyl sulfate were carried out according to the method of Ross and Miles (11).

The test was run at 40 C; foam heights were recorded after 5 min (A) and 30 min (B). The foam formation was represented as (A) and the foam stability was represented by the following formula: (a) $\% = 100(A - B)/A$.

The results are noted in Table II. The foam formation and foam stability increased with the concentration below the c.m.c. of surfactant, and reached a plateau state at the concentration above the c.m.c. The foam formation of the alkyl sulfoacetate series became higher with the increasing number of carbon atoms in the chain, and reached constancy after the 12 carbons in the alkyl chain. The foam formation and foam stability of dodecyl sulfoacetate were better than those of dodecyl sulfate at various concentrations.

Hydrolysis

Since sodium alkyl sulfoacetates series have ester groups decompose by hydrolysis, the resistance of the alkyl sulfoacetates and dodecyl sulfate to acid hydrolysis was measured. Each of 1, 2, 3 and 4 normal H_2SO_4 and 0.005 mol aqueous solution of the alkyl sulfoacetate was mixed in a well stoppered test tube.

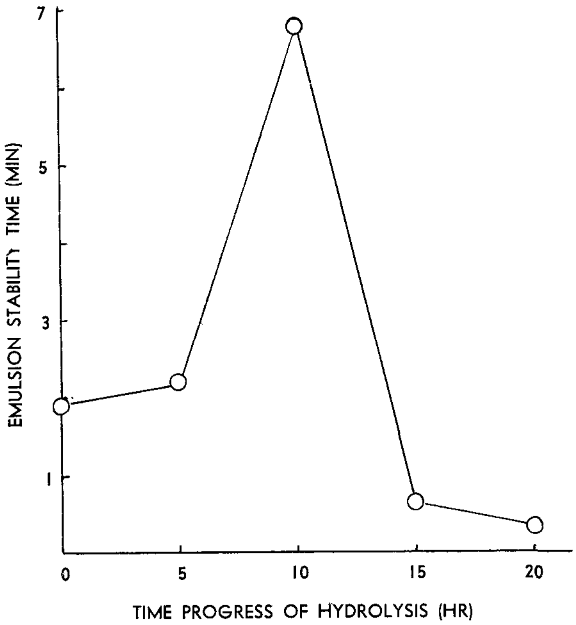

FIG. 5. Stability to hydrolysis of dodecyl sulfoacetate (by emulsion stability). The time required for a separation of 9 ml of aqueous phase vs. time progress of hydrolysis of the surfactant.

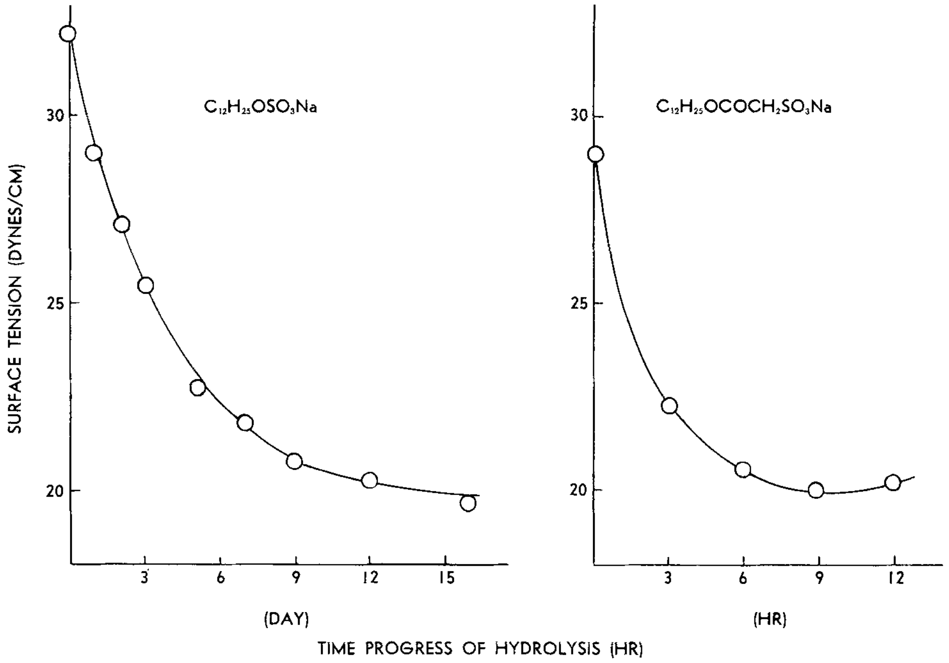

FIG. 6. Stability to hydrolysis of dodecyl sulfoacetate and dodecyl sulfate (by surface tension). Surface tension vs. time progress of hydrolysis of the surfactant.

Then, the tube was held in a thermostat at 40 C. The time required for a sample solution to be clouded as the result of hydrolysis was a measure of resistance of the surfactant to hydrolysis. Table III gives these values for alkyl sulfoacetates and dodecyl sulfate.

Resistance to acid hydrolysis was also examined by the measurement of emulsifying power and surface tension value of the dodecyl sulfoacetate and dodecyl sulfate solution at 0.01 mol concentration, after heating at 40 C with 0.1 normal H_2SO_4 in definite time intervals. The results, as shown in Figures 5 and 6, are the resistance of dodecyl sulfate to hydrolysis to compare with that of dodecyl sulfoacetates. The acid stability test of alkyl sulfoacetates series became less stable with the increasing number of carbon atoms in the alkyl chain and were more unstable than dodecyl sulfate. The surface tension of the dodecyl sulfoacetate solution changed with the progress of the hydrolysis of the surfactant. This phenomenon can be explained by the adsorption of dodecyl alcohol produced by hydrolysis on the water surface.

The hydrolysis of dodecyl sulfoacetate also improves the emulsifying power of the sample solution. This phenomenon is probably due to the formation of a mixed monolayer of dodecyl sulfoacetate anion and dodecyl alcohol molecules produced from hydrolysis at the interface emulsion droplet.

Calcium Stability

Calcium ion stability of alkyl sulfoacetates and dodecyl sulfate was measured by a modified Hart (12) method. The test procedure consisted of titrating 10 ml of 10 mmol aqueous solutions of the surfactant in a 300 ml conical beaker with a 0.1 nomal solution of $CaCl_2$. The end point of the titration was determined by observation of the fine cloudiness of the solution. Results are shown in Table IV.

TABLE IV
Calcium Ion Stability of Sodium Alkyl Sulfoacetates and Sodium Dodecyl Sulfate

Temperture, C	Converted into $CaCO_3$ p.p.m.				
	Number of alkyl carbon atoms				SDS
	8	10	12	14	12
25	>4500	>4500	2800	insoluble	170
30	>4500	>4500	3300	980	560
35	>4500	>4500	3850	1060	850
40	>4500	>4500	>4500	870	1400

The calcium ion stability of the surfactant increased markedly on increasing the temperature from 25 to 60 C, but the stability of myristyl sulfoacetate decreased with the increase. The stability of alkyl sulfoacetates to calcium ions was better than that of the dodecyl sulfate, except for sodium myristyl sulfoacetate.

Results and Discussion

The sodium salts alkyl sulfoacetate esters which are prepared from monochloroacetic acid and higher alcohol containing from 8 to 14 even carbon atoms are readily soluble in water because the introduction of ester groups to the alkyl chain decreases hydrophobic property of the hydrocarbon chain. This concept is confirmed by the higher critical micelle concentration, and the lower Krafft point of alkyl sulfoacetate than that of surfactant having the same number of carbon atoms in an alkyl chain, the like of SDS.

The existence of an ester group in the alkyl chain improves the surface tension, the emulsifying power and the other surface active properties, but is more susceptible to hydrolysis in acid solution.

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