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Synthetic Detergents from Animal Fats. VI. Polymerizable Esters of Alpha-Sulfonated Fatty Acids[1]

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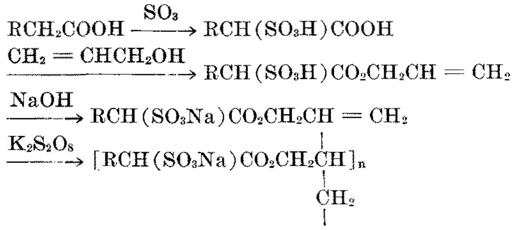
THE EASE of preparation of esters of α-sulfonated saturated fatty acids, such as sodium alkyl α-sulfopalmitates and stearates (4), or disodium 2-sulfoethyl α-sulfopalmitates and stearates (5), has suggested similar esterification with unsaturated alcohols to form polymerizable anionic surface-active agents and detergents. Allyl alcohol was the alcohol selected for this purpose.

Accordingly, sodium allyl α-sulfopalmitate, sodium allyl α-sulfostearate, and their respective polymers were prepared and examined for surface-active and detergent properties.

Reactions involved in the preparation of the monomers and polymers are as follows:



$$\mathrm{RCH_2COOH} \xrightarrow{\mathrm{SO_3}} \mathrm{RCH(SO_3H)COOH}$$
$$\xrightarrow{\mathrm{CH_2=CHCH_2OH}} \mathrm{RCH(SO_3H)CO_2CH_2CH=CH_2}$$
$$\xrightarrow{\mathrm{NaOH}} \mathrm{RCH(SO_3Na)CO_2CH_2CH=CH_2}$$
$$\xrightarrow{\mathrm{K_2S_2O_8}} \mathrm{[RCH(SO_3Na)CO_2CH_2\underset{\underset{\mid}{CH_2}}{\overset{\mid}{C}H}]_n}$$

where R is $C_{14}H_{29}$ or $C_{16}H_{33}$ and n is the degree of polymerization.

Sodium Allyl α-Sulfopalmitate

A solution of 0.357 mole (120 g.) of α-sulfopalmitic acid (5), N. E. 163.2 in 500 ml. of allyl alcohol was heated and stirred 6 hrs. at the reflux temperature, neutralized with a solution of sodium hydroxide in aqueous ethanol, and cooled to —25°. The yield of the precipitated ester was 85%. The purity at this point, also about 85%, is adequate for use in surface-active or detergent compositions, or for conversion to the polymer. Crystallization from water to remove unesterified α-sulfopalmitic acid as the sparingly soluble sodium salt, and further crystallization of the ester from methanol gave sodium allyl α-sulfopalmitate as a white solid, m. p. 92.2–93.4°, in a yield of 35%.

Analysis: Calculated for $C_{19}H_{35}NaO_5S$, 57.26% C, 8.88% H, 5.77% Na, 8.05% S, Iodine No. 63.7; found, 56.93, 8.85, 5.68, 8.12, 61.1, respectively.

Sodium Allyl α-Sulfostearate

In a similar manner α-sulfostearic acid (5), N. E. 179.9 was esterified with allyl alcohol, and the purified sodium allyl α-sulfostearate, m.p. 99.2–100.5°, was isolated.

Analysis:[3] Calculated for $C_{21}H_{39}NaO_5S$, 59.12% C, 9.21% H, 5.39% Na, 7.52% S, Iodine No. 59.5; found, 58.97, 9.14, 5.39, 7.40, 58.9, respectively.

Polymerization

The polymerization of sodium allyl α-sulfopalmitate or sodium allyl α-sulfostearate was carried out as follows.

A solution of 75 g. of the monomer and 3.5 g. of potassium persulfate in 700 ml. of water was heated 8 hrs. at 70°. The progress of polymerization was evident by an increase in viscosity; after about 3 hrs. the solutions were too viscous to stir effectively. The polymer was separated by adding 3 volumes of 95% ethanol to 1 volume of the aqueous solution. The precipitated amorphous solid was redissolved in water and again precipitated by the addition of 2 volumes of ethanol. This operation was twice repeated, and the final precipitate was dried in a vacuum oven. The purified polymer was obtained as a light, cream-colored solid in a yield of 70%. The Wijs Iodine No. of the polymer, about 2 to 4, somewhat inexact because of the limited solubility of the polymer in chloroform and glacial acetic acid, indicated a degree of polymerization of the magnitude of 10^1.

Solubility and Viscosity

The monomers are readily soluble and form aqueous solutions of about 20% concentration which may become viscous solutions or gels on standing at room temperature. The polymers form viscous solutions at a concentration of about 2%; and they are practically insoluble in the usual organic solvents.

The viscosity of a 2% aqueous solution of polymerized sodium allyl α-sulfostearate, which has thixotropic properties, was measured with a Brookfield synchroelectric viscometer, using a No. 3 spindle. At 25°, and at speeds of 6, 12, 30, and 60 r.p.m., the viscosity was 3680, 2380, 1430, and 1080 centipoises, respectively. The viscosity of the polymers indicates possible use as a thickening agent.

Different preparations of the same polymer were sometimes found to have quite different viscosities, perhaps because of minor impurities or slight differences in the method of polymerization.

Surface-Active Properties

Values for surface and interfacial tension, wetting and emulsifying properties and calcium stability are recorded in Table I for the monomers and polymers.

The monomers lower the surface tension of water, and the interfacial tension against petrolatum, in a manner similar to that found for sodium alkyl α-sul-

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[3] Microanalyses for C, H, and S performed by Dolores A. McClelland.

TABLE I
Surface-Active Properties

	Surface and Interfacial Tension,[a] dynes/cm.		Wetting Time,[a] seconds (3)	Emulsion Stability,[b] seconds (1)	Ca Stability, p.p.m. $CaCO_3$ (6)
	S.T.	I.T.			
Na Allyl α-Sulfopalmitate	36.5	7.8	18.1	160	1,540
Na Allyl α-Sulfostearate	34.8	5.9	31.0	320	735
Polymerized Na Allyl α-Sulfopalmitate	68.6	33.9	>1,800	11,600	500
Polymerized Na Allyl α-Sulfostearate	71.2	31.0	......	5,550	175

[a] 0.1 solutions, 25°.
[b] Time in seconds for 10 ml. of aqueous phase to separate from an emulsion of 40 ml. of petrolatum and 40 ml. of 0.1% aqueous solution.

fopalmitates and stearates. The polymers have very little effect on surface or interfacial tension.

Wetting properties were measured as the time in seconds required to sink a 9-in. length of suspended standard binding tape (3). The monomers had wetting properties similar to those found for the sodium alkyl α-sulfopalmitates and stearates. The polymers were not wetting agents.

Emulsions were prepared by a method of intermittent violent shaking (1). A stoppered 500-ml. Erlenmeyer flask, containing 40 ml. of light petrolatum and 40 ml. of an aqueous solution 0.1% with respect to the emulsifying agent, was manually shaken in 5 violent downward motions and allowed to stand 1 min. This operation was repeated 5 times. The time required for 10 ml. of the aqueous phase to separate from emulsions so prepared was taken as a measure of the effectiveness of the emulsifying agent. The monomers were about equal to some commercial surface-active agents. The greater stability of emulsions formed with the polymers suggests that polymers may be found to be effective emulsifying agents despite their slight effect on surface and interfacial tension.

The calcium stability (6) of the monomers was about equal to that of sodium alkyl α-sulfopalmitates and stearates. The polymers were less stable in hard water.

The monomers and polymers gave low values of from 10 to 60 mm. in the Ross-Miles foam height test (2) on 0.25% solutions in water of 300 p.p.m. at 60°.

Detergency

Detergency was measured in the Terg-O-Tometer, washing 10 swatches of A.C.H. No. 114[4] standard soiled cotton in 1 liter of detergent solution, in hard water of 300 p.p.m. (as $CaCO_3$), for 20 minutes at 60°, at 110 cycles per minute. Detergency was measured as △R, the increase in reflectance after washing.

From Table II it is apparent that the builder alone is able to remove considerable soil. At 0.1% concentration in hard water of 300 p.p.m. the monomers were not very effective detergents. The unbuilt ester disodium 2-sulfoethyl α-sulfostearate (5) was more effective. The polymer was a poor detergent. Sodium isopropyl α-sulfostearate (4), a representative alkyl ester of an α-sulfo acid, at 0.1% concentration in hard water was about equal to the monomers in detergency.

TABLE II
Detergency
[Terg-O-Tometer, 20 min. at 60°, 110 cycles/min., 10 swatches/l. of detergent solution in hard water of 300 p.p.m. (as $CaCO_3$)]

	Detergency, △R
0.1% Na Allyl α-Sulfopalmitate	22.3
0.1% Na Allyl α-Sulfopalmitate + .15% B[a]	36.6
0.1% Na Allyl α-Sulfostearate	16.9
0.1% Na Allyl α-Sulfostearate + .15% B	35.6
0.1% Polymerized Na Allyl α-Sulfopalmitate	10.4
0.1% Polymerized Na Allyl α-Sulfopalmitate + .15% B	29.9
0.1% Na Isopropyl α-Sulfostearate	19.7
0.1% Na Isopropyl α-Sulfostearate + .15% B	33.2
0.1% Na_2 2-Sulfoethyl α-Sulfostearate	26.8
0.1% Na_2 2-Sulfoethyl α-Sulfostearate + .15% B	36.8
0.1% Na Dodecyl Sulfate	18.4
0.1% Na Dodecyl Sulfate + .15% B	33.7
0.15% B	25.5
0.25% B	27.1

[a] Builder B: $Na_5P_3O_{10}$, 55%; Na_2SO_4, 24%; $Na_4P_2O_7$, 10%; Na Metasilicate, 10%, and CMC, 1%.

All of the esters were considerably improved in detergency by the presence of a builder. The built polymer however did not have a △R value much greater than that of the builder alone. The values for built and unbuilt sodium dodecyl sulfate are included for comparison.

Stability to Hydrolysis

The presence of an α-sulfo group in sodium alkyl α-sulfopalmitates and stearates (4) and disodium sulfoalkyl α-sulfopalmitates and stearates (5) has been shown to retard hydrolysis to a considerable extent. The data in Table III show that the monomers and polymers are likewise very resistant to hydrolysis and resemble the sodium alkyl α-sulfopalmitates and stearates in the value of their reaction rate constants. The polymers are more resistant to alkaline hydrolysis.

TABLE III
Rate of Hydrolysis at 100°

	Acid Hydrolysis in N/3 H_2SO_4, k_1	Alkaline Hydrolysis, k_2
Na Methyl α-Sulfopalmitate	0.0047	0.14
Na Allyl α-Sulfostearate	0.0033	0.11
Polymerized Na Allyl α-Sulfopalmitate	0.0063	0.033
Polymerized Na Allyl α-Sulfostearate	0.0057	0.026

k_1 = first order reaction rate constant
= 1/t ln a/a–x in reciprocal minutes.
k_2 = second order reaction rate constant
= 1/t x/a(a–x) in liters·moles^{-1}·minutes^{-1}.

Summary

Sodium allyl α-sulfopalmitate and sodium allyl α-sulfostearate, prepared by esterification of an α-sulfonated fatty acid with allyl alcohol, resemble sodium alkyl α-sulfopalmitates and stearates in surface-active and detergent properties and stability to hydrolysis.

The allyl esters are easily converted to a new type of water-soluble polymer. The polymers may be thickening and emulsifying agents and may have other uses yet to be discovered.

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[4] American Conditioning House Inc. Mention of a particular test cloth does not constitute recommendation by the U. S. Department of Agriculture over similar products not mentioned.