

Soap-Based Detergent Formulations: III. Surface Activity of Fatty Derivatives of 3-Hydroxypropanesulfonic Acid¹

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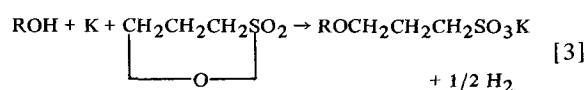
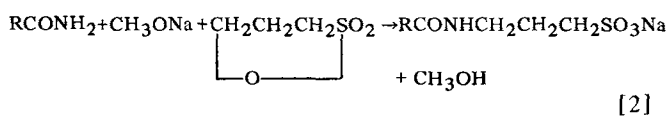
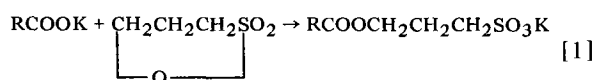
ABSTRACT

Pure 3-sulfopropylesters, ethers and amides were prepared from fatty acids, alcohols and amides by reaction with 1,3-propanesultone. Their solution properties, including Krafft point, critical micelle concentration, lime soap dispersing power and detergency, were compared with those of the analogous 2-sulfoethyl esters. The N-3-sulfopropylamides exhibited superior lime soap dispersing power as well as detergency in soap-based formulations at 300 ppm water hardness. The sulfopropyl ethers and amides displayed excellent stability to acid and alkaline hydrolysis. The sulfopropyl esters were much more stable to alkaline hydrolysis than the sulfoethyl esters, but only slightly more stable to acid hydrolysis.

INTRODUCTION

The sodium salts of fatty acid esters of 2-hydroxyethanesulfonic acid have frequently been proposed as additives to soap because of their good lime soap dispersing power and good detergency when combined with soap. A recent paper by Bistline and coworkers (1) reported a new method of synthesis of this type of compound and described the surface active properties of the esters derived from a number of different fatty acids. The principal deterrent to the use of these compounds in built detergents or soap combinations is their poor hydrolytic stability, particularly in the presence of alkali.

The synthesis of the 3-sulfopropyl esters and their solubility properties have been reported previously (2,3); however their surface active properties, particularly in combination with soap, have not been investigated. As part of a broad program to study the effects of different surfactant structures in combinations with soap, we have prepared 3-sulfopropyl esters and amides of various fatty acids and 3-sulfopropyl ethers of different fatty alcohols for comparison with 2-sulfoethyl esters. The syntheses were carried out according to the following schemes:



EXPERIMENTAL PROCEDURES

Materials

Potassium soaps of lauric, palmitic, stearic and oleic

acids were prepared from the corresponding fatty acids, which had been purified by standard distillation and crystallization procedures. The methyl esters of the purified fatty acids were found to have a purity in excess of 99% by gas liquid chromatography (GLC). The sodium soap of tallow fatty acids was prepared from hydrogenated tallow fatty acids, obtained from Wilson Martin Co. and composed of stearic 64.6%, oleic 1.3%, palmitic 29.7%, myristic 4.0% and lauric 0.2% acids.

Dodecanol, hexadecanol, octadecanol and *cis*-9-octadecen-1-ol were purified in a manner similar to that for the fatty acids and also found to have a purity in excess of 99% by GLC.

The amides of lauric, palmitic, stearic and oleic acids were prepared by amidation of the respective fatty acid chlorides. All the fatty amides had melting points within 2 C of the literature value. 1,3-Propanesultone, obtained from Shell Chemical Co., was fractionally distilled (bp 103-104 C/0.9 mm, $n_D^{40} = 1.4515$, freezing point 31 C).

3-Sulfopropyl Esters of Fatty Acids

The preparation of potassium 3-sulfopropyl laurate serves as a typical example of the ester synthesis. In a flask equipped with mechanical stirring, 21.1 g (0.173 mole) 1,3-propanesultone was added to 41.2 g (0.173 mole) potassium laurate which was dissolved in 500 ml *t*-butanol at reflux. The reaction was complete in 40 min, indicated by the absence of carboxylate absorbance (1560 cm^{-1}) from the IR spectrum. The product was recrystallized once from 1600 ml absolute methanol yielding 89.6% pure product, which had the following elemental analysis: Calculated for $\text{C}_{15}\text{H}_{29}\text{SO}_5\text{K}$: C, 49.97; H, 8.11; S, 8.90. Found: C, 50.16; H, 7.95; S, 8.85.

3-Sulfopropyl Ethers of Fatty Alcohols

Sulfopropyl ethers were prepared in a manner similar to

TABLE I

Solution Properties of 2-Sulfoethyl Esters and 3-Sulfopropyl Esters, Ethers and Amides

Surfactant	Krafft point, 1%, C	Critical micelle concentration, mmoles/liter	Lime soap dispersing power, %
Sodium 2-sulfoethyl			
Laurate	30	6.4	13
Myristate	39	2.0	9
Palmitate	51	Insoluble	7
Stearate	59	Insoluble	9
Oleate	<0	0.23	9
Potassium 3-sulfopropyl			
Laurate	14	3.75	8
Palmitate	41	0.15	7
Stearate	50	0.08	10
Oleate	<0	0.18	9
Potassium 3-sulfopropoxy			
Dodecane	9	2.14	9
Hexadecane	32	0.13	9
Octadecane	47	0.05	11
Octadecene	<0	0.12	10
Sodium N-3-sulfopropyl			
Lauramide	<0	7.91	7
Palmitamide	44	0.48	4
Stearamide	53	0.14	5
Oleamide	<0	0.34	3

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TABLE II
Detergency^a of Soap Formulation,^b 120 F

Esters, ether and amides	150 ppm			300 ppm		
	EMPA	UST	TFpp	EMPA	UST	TFpp
Sodium 2-sulfoethyl ^c						
Stearate	37.8	8.6	25.0	29.9	6.5	21.7
Tallowate	38.9	8.6	23.5	30.7	6.2	19.6
Potassium 3-sulfopropyl						
Stearate	36.8	8.3	22.9	30.0	6.0	21.0
Sodium 3-sulfopropyl						
Tallowate	37.4	6.7	20.4	29.4	6.2	20.7
Potassium 3-sulfopropoxy						
Octadecane	36.1	8.4	24.1	25.7	4.0	19.5
Sodium N-3-sulfopropyl						
Stearamide	38.8	9.4	25.2	25.8	2.6	8.9
Tallowamide	40.0	9.0	25.1	34.1	7.0	21.9
Control ^d	34.3	7.0	24.4	34.5	7.3	27.0
Soap	35.9	5.9	22.9	15.7	— ^e	— ^e

^aΔR, increase in reflectance after washing.

^b63% Sodium tallowate, 15% sodium silicate, 1% sodium carboxymethylcellulose and 21% test surfactant.

^cFrom Reference 1.

^dCommercially available phosphate built household detergent.

^eΔR was negative.

that described by Hirai et al. (2). The preparation of potassium-3-sulfopropyl octadecyl ether is cited as a typical example. Octadecanol 27.1 g (0.100 mole) was added to a flask containing 120 ml toluene and equipped with a nitrogen bleed. Freshly cut potassium metal 3.91 g (0.100 mole) was added and the mixture stirred vigorously for 3 hr at reflux. The temperature was reduced to 60 C and 12.2 g (0.100 mole) 1,3-propanesultone was added dropwise over a 25 min period. After the addition had been completed, the reaction was allowed to continue for 3 hr. The temperature was then reduced to 40 C, and 400 ml petroleum ether (boiling range 63-70 C) was added to the reaction mass. A 96.5% yield of crude product was obtained by filtration of the reaction mixture at room temperature. The pure product was isolated in 27.4% yield after soxhlet extraction for 3 hr with diethyl ether and two recrystallizations from methanol. Analysis: Calculated for C₂₁H₄₃SO₄K: C, 58.56; H, 10.06; S, 7.45. Found: C, 58.51; H, 10.09; S, 7.47.

N-3-Sulfopropyl Amides of Fatty Acids

3-Sulfopropylated fatty amides were prepared in a manner similar to that described by Hirai et al. (2). The preparation of sodium N-3-sulfopropyl oleamide is cited as a typical example. Sodium methoxide, 3.0 g (0.055 mole), was added to a flask containing 150 ml benzene and equipped with a nitrogen bleed and good mechanical agitation. After the methoxide was completely dispersed, 15.6 g (0.055 mole) oleamide was added, and the material

was refluxed for 3 hr. A 15 ml mixture of benzene and methanol was then removed by slow distillation into a Barrett Receiver over a period of 1 hr. At 60 C, 6.8 g (0.055 mole) 1,3-propanesultone was then added dropwise and the mixture allowed to reflux for 1 hr, 30 min. The reaction mixture was cooled to 40 C, and 300 ml acetone was added. A crude product was obtained in 84.8% yield by filtration at room temperature.

All the sulfopropylated amides contained up to 10 mol % sulfopropylated ester which was easily removed by selected saponification. This was accomplished by refluxing, for 5 min, 15 g of the sulfopropylated amide in 600 ml 60% ethanol containing 0.07 moles sodium hydroxide. The solution was acidified and the fatty acid extracted with petroleum ether (boiling range 63-70 C). The solution was then made alkaline to a pH of 9-10 and allowed to crystallize at -30 C. The filtered solids were subjected to a 2 hr Soxhlet extraction with acetone in order to remove any unreacted primary amide. The product was then recrystallized from 95% ethanol at 0 C giving a 51.7% yield pure product. Analysis: Calculated for C₂₁H₄₀NSO₄Na: C, 59.26; H, 9.47; N, 3.29; S, 7.54. Found: C, 59.22; H, 9.70; N, 3.23; S, 7.68.

Physical and Surface Active Properties

The Krafft point was measured by gradually heating a 1% dispersion until a clear solution was obtained. The critical micelle concentration was measured by the pinacyanole chloride titration (4). The lime soap dispersion tests were run according to the method of Borghetty and Bergman (5). This test gives the percentage of lime soap dispersing agent that must be added to sodium oleate in order to keep the calcium and magnesium soaps formed dispersed in water of 330 ppm hardness expressed as calcium carbonate.

Detergency measurements were carried out in the Terg-O-Tometer operated at 120 F, and 110 cycles per min for 20 min. Five 4 in. circles each of EMPA (cotton) #101, Test Fabrics (cotton-polyester) with permanent press finish and U.S. Testing (cotton) cloth were washed in 1 liter solutions. Detergency was measured by the increase in reflectance, ΔR, after washing.

The detergency of the esters, ethers and amides were compared at two water hardness levels (150 and 300 ppm) in formulation composed of 63% sodium tallowate, 15% sodium silicate (weight ratio SiO₂/Na₂O = 2.4), 1% sodium carboxymethylcellulose and 21% test surfactant. A com-

TABLE III

Rate Constants, Acid and Alkaline Hydrolysis, 60 C

Compound	0.005 M HCl		0.005 M NaOH	
	K ₁ ^a	t _{1/2} ^b , min	K ₂ ^c	t _{1/2} ^b , min
Na 2-Sulfoethyl stearate	0.045 ^d	15 ^d	0.35 ^d	65 ^d
K 3-Sulfopropyl stearate	0.031	25	0.072	300
K 3-Sulfopropoxy octadecane	0.0005		0	
Na 3-Sulfopropyl palmitamide	<0.0005		<0.001	

^aK₁ (First order reaction), $\frac{1}{t} \ln \frac{a}{a-x}$ (min⁻¹).

^bt_{1/2}, Time for 50% hydrolysis.

^cK₂ (Second order reaction), $\frac{1}{t} \frac{x}{a(a-x)}$ (liters/mole/min).

^dFrom Reference 1.

mercially available phosphate built household detergent was also included in Table II at a 0.2% total detergent concentration for comparison.

Hydrolysis Studies

Acid hydrolysis was measured in 100 ml distilled water solutions containing 0.005 moles HCl and 0.005 moles 3-sulfopropyl ester, ether or amide derivative. The temperature was maintained at 60 C. 10 ml samples were withdrawn and titrated with 0.1 N NaOH at suitable intervals using phenolphthalein indicator. The extent of hydrolysis, x , was determined from the increase in acidity, and first order kinetics were calculated according to equation $k_1 = 1/t \ln a/(a-x)$. Time for 50 hydrolysis was determined from the $\log(a-x)$ vs. t plot.

Alkaline hydrolysis was measured at 60 C in 100 ml distilled water solutions containing 0.005 moles NaOH and 0.005 moles 3-sulfopropyl ester, ether or amide. Samples of 10 ml were withdrawn and titrated at suitable intervals with 0.1 N HCl using phenolphthalein indicator. Second order kinetics were calculated according to the equation $k_2 = \frac{1}{t} \cdot \frac{x}{a} \cdot (a-x)$. Time for 50% hydrolysis was determined from the $\frac{1}{(a-x)}$ vs. t plot. The hydrolysis data are tabulated in Table III.

RESULTS AND DISCUSSION

Since the surfactant anion is responsible for the surface active properties, the potassium rather than the sodium derivatives were prepared, in some cases, because of the greater solubility of the intermediate potassium salts in relatively nonpolar reaction solvents. This frequently resulted in faster reaction times and higher yields. Great care was taken in purifying the individual surfactants in order to arrive at reliable surface active data.

In general the overall surface active properties of the sulfopropyl amides were superior to those of the other compounds studied in this investigation. As can be seen in Table I, sulfopropylated esters, ethers and amides are more water soluble as shown by their Krafft points which were lower than those of the sulfoethyl esters. Lime soap dispersing power (LSDP) was of the same order of magnitude for the sulfoethyl esters, sulfopropyl ethers and esters. However the LSDP for the sulfopropyl amides were significantly lower, and thus the amides are better lime soap dispersing agents. Calcium ion stability (6) could not be determined accurately for sulfopropyl compounds due to apparent supersaturation of the calcium salts prior to

precipitation. The critical micelle concentrations (cmc) of the sulfopropyl compounds were lower than those of the corresponding sulfoethyl compounds due to a lengthening of the alkyl chain. The cmc of the sulfopropyl amides were higher than those of the 3 other types of compounds.

The sulfopropyl compounds were more stable to hydrolysis than the sulfoethyl esters. Potassium 3-sulfopropylstearate (Table III) was much more stable to alkaline hydrolysis than sodium 2-sulfoethylstearate, but only slightly more stable to acid hydrolysis. Potassium 3-sulfopropoxyoctadecane and sodium 3-sulfopropylpalmitamide displayed excellent stability to both acid and alkaline hydrolysis.

The detergency behavior of the surfactants in combination with soap is summarized in Table II. The sulfoethyl esters and sulfopropyl esters and ethers performed similarly at each of the two water hardnesses. Sodium N-3-sulfopropyl stearamide was superior to the esters and ethers at 150 ppm water hardness; however at 300 ppm water hardness it did not remain in solution in the Terg-O-Tometer beaker at 120 F, which would explain its poor detergency at this water hardness.

The sulfopropyl tallowamide, a simulated mixture composed of 38% sulfopropyl palmitamide, 15% sulfopropyl stearamide and 47% sulfopropyl oleamide, was superior to all other compounds listed in Table II including the control and soap at 150 ppm water hardness. At 300 ppm water hardness it performed almost as well as the control, whereas the other compounds were clearly inferior to the control at this hardness. The performance of the sulfopropyl tallowamide in a soap-based detergent formulation is thus similar to that of sodium methyl α -sulfotallowate previously described by Bistline and coworkers (7).

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