

2,806,044

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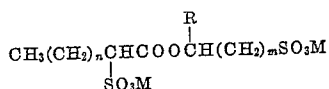
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8 Claims. (Cl. 260—400)

(Granted under Title 35, U. S. Code (1952), sec. 266)

A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all governmental purposes, throughout the world, with power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to surface-active compounds of the sulfonated ester type wherein an α -sulfonated long-chain fatty acid is esterified with certain hydroxyalkane-sulfonates. These esters may be represented by the formula



wherein n is an integer from 9 to 19, m is an integer from 1 to 2, R is a member selected from the group consisting of hydrogen and methyl, and M is a member selected from the group consisting of hydrogen, an alkali metal NH_4 , $\text{NH}_3(\text{C}_2\text{H}_4\text{OH})$, $\text{NH}_2(\text{C}_2\text{H}_4\text{OH})_2$ and $\text{NH}(\text{C}_2\text{H}_4\text{OH})_3$.

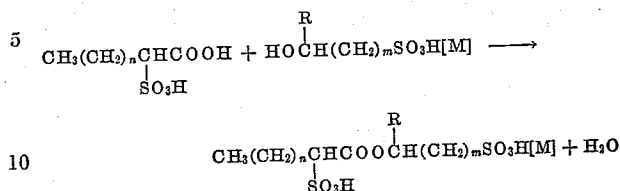
The esters having the formula shown above constitute a new and especially valuable family of surface-active compounds. They are highly soluble in water and are effective solubilizers for more difficultly soluble surface active agents such as the sodium soaps of palmitic, stearic and longer-chain fatty acids, the long-chain alcohol sulfates and sulfonated fatty acids. These esters have the valuable property of being insensitive to dissolved salts such as are found in hard water or sea water; consequently they are especially valuable for use in compositions designed for use in such waters. They not only are not precipitated by the salts in such water but also have a stabilizing effect on and help prevent the precipitation of soaps and other surface-active compounds that otherwise would be precipitated by such salts.

A major advantage of the esters of this invention is their extreme stability to hydrolysis in the presence of acid, base or heat. All other ester type surface-active compounds are more or less easily hydrolyzed in the presence of water, especially if heated or if in the presence of acid or alkali. There are innumerable applications in which a surface-active agent is needed that will withstand these conditions, as for instance, in metal cleaning, wool scouring, textile finishing, dyeing, mordanting, etc. For these applications, our esters are particularly suitable.

The detergent properties of our esters are excellent; yet they may be greatly improved by use of conventional builders, particularly the phosphates. Thus, a highly effective detergent composition may be made from as little as one part of ester to four parts of builder. Such high tolerance of builders enables the preparation of very inexpensive, yet highly effective detergent compositions.

The compounds of this invention may be conveniently

prepared by the direct esterification of the α -sulfonated fatty acid with the hydroxyalkanesulfonate:



Neutralization of this product with an appropriate base yields the desired product. The α -sulfonated fatty acid may be prepared by any known process, as for example, the action of sulfur trioxide or chlorosulfonic acid on lauric, myristic, palmitic, stearic, behenic or similar fatty acid. The hydroxyalkanesulfonate may also be prepared by any of several known methods, as for instance, the reaction of sulfites and bisulfites with appropriate alkylene oxides or olefinic compounds.

alkylene oxides or olefinic compounds.

Since the α -sulfonated acid reagent is strongly acidic, no added catalyst is needed in making the esters. It is very helpful to conduct the esterification under conditions such that the water produced is removed from the reaction zone as fast as formed. This may be done by use of an inert solvent that distills azeotropically with water, such as toluene, carbon tetrachloride, ethylene chloride, or the like.

30 Preparation of the esters of the invention is illustrated by the following examples:

EXAMPLE I

Disodium 2-sulfoethyl α-sulfosterate

A mixture of 0.2 g. mole each of α -sulfostearic acid and sodium isethionate and 250 ml. of toluene was refluxed, with stirring, while the water distilled azeotropically was collected continuously. The reaction was complete after 6 hrs., at which time 6 ml. of water had been collected. The mixture was cooled, diluted with 200 ml. of ethanol and neutralized with 18 N aqueous NaOH. Evaporation of the toluene and ethanol left 103 g. of crude product which was extracted with 400 ml. of water, leaving a small amount of the sparingly soluble sodium α -sulfostearic acid as a residue. After evaporating the aqueous solution to dryness, the ester was taken up in 75% aqueous ethanol, decolorized with carbon, and twice crystallized at -15° C. The purified product thus obtained in 66% yield was a white solid having the analysis shown in Table I.

EXAMPLE II

Disodium 1-methyl-2-sulfoethyl α-sulfostearate

Sodium 2-hydroxypropanesulfonate, M. P. 225° C., was prepared from 1,2-propylene oxide and sodium bisulfite by a conventional procedure [Lambert and Rose, J. Chem. Soc., 1949, 46-91. This compound was then treated with α -sulfostearic acid as described in Example I to produce the desired 1-methyl-2-sulfoethyl α -sulfostearate.

EXAMPLE III

Disodium 3-sulfopropyl α -sufostearate

Allyl alcohol and α -sulfostearic acid were heated together to form allyl α -sulfostearate. The sodium salt of this compound was treated with a mixture of sodium sulfite and sodium bisulfite in the presence of oxygen to form the desired product. This procedure is substantially that described by Kharasch et al., *J. Org. Chem.*, 3, 175-192 (1938), for sulfonating allyl alcohol.

EXAMPLES IV AND V

Disodium 2-sulfoethyl α-sulfopalmitate and -behenate

When the α-sulfostearic acid used in Example I was replaced with α-sulfopalmitic or α-sulfo-behenic acid, respectively, the corresponding esters were obtained.

The elementary analyses of the compounds produced in the above examples are shown in the following table.

TABLE I.—ANALYSES OF ESTERS

$$\text{CH}_3(\text{CH}_2)_n\text{CHCOOCH}(\text{CH}_2)_m\text{SO}_2\text{Na}$$

$$\text{SO}_2\text{Na}$$

Example	n	m	R	Analysis, Percent			
				C	H	Na	S
I	15	1	H	46.4	7.4	8.8	12.0
II	15	1	CH ₃	47.5	7.6	8.5	11.5
III	15	2	H	44.1	8.9	8.7	12.8
IV	13	1	H	44.1	8.9	9.4	12.8
V	19	1	H	44.1	8.9	8.0	12.8

While the above examples show the sodium salts of the disulfonic acids, the free acids or the potassium, ammonium or amine salts are easily made. Thus, the free acid results from the reaction of isethionic acid with an α-sulfo acid, and the product may then be neutralized with the appropriate alkali, ammonia or an amine to give the corresponding salts.

The potassium salts are quite similar in properties to the sodium salts. The ammonium and amine salts are even more soluble than the alkali metal salts and in general are somewhat better foaming agents. Otherwise their surface-active properties are similar to those of the alkali metal salts. The salts of ethanolamine, diethanolamine and triethanolamine are particularly desirable because of their low cost and excellent surface-active properties.

EXAMPLE VI

Surface active properties

Some of the surface active properties of esters of our invention are shown in Table II.

TABLE II.—SURFACE ACTIVE PROPERTIES OF DISODIUM 2-SULFOALKYL α-SULFO-PALMITATES AND α-SULFOSTEARATES

Ester	Product of Example No.	Surface and Interfacial tension, 0.25% solns. in distd. water 25° C., dynes/cm.		Ca Stability, p. p. m. CaCO ₃ ¹	Lime Soap Dispersing Power, Percent ²	Foam Height, 0.25% solns. in 300 p. p. m., 60° C., Immediate mms. ³	Sinking Time, 0.1% solns. in distd. water 25° C., seconds ⁴
		S. T.	I. T.				
Disodium 2-sulfoethyl α-sulfopalmitate	IV	35.2	9.8	>1,800	5 ⁴	202	134
Disodium 2-sulfoethyl α-sulfostearate	I	35.8	11.6	>1,800	5	223	102
Disodium 1-methyl-2-sulfoethyl α-sulfostearate	II	46.9	14.5				

¹ B. G. Wilkes and J. N. Wickert, Ind. Eng. Chem. 29, 1234-9 (1937).

² H. C. Borghetty and C. A. Bergman, J. Am. Oil Chemists' Soc. 27, 88-90 (1950).

³ J. Ross and G. D. Miles, Oil & Soap 18, 99-102 (1941).

⁴ L. Shapiro, Am. Dyestuff Reprtr. 39, 38-45, 62 (1950).

⁵ 0.00125 g. dispersed the Ca soap formed from 0.025 g. of Na oleate.

Metallic ion stability, measured by the method of Harris [J. C. Harris, ASTM Bull. No. 141, 49-53 (1946)], gave values of 100 for Mg⁺⁺, Al⁺⁺⁺, Ca⁺⁺, Fe⁺⁺, Ni⁺⁺, Cu⁺⁺, Zn⁺⁺ and Pb⁺⁺ for disodium 2-sulfoethyl α-sulfopalmitate and disodium 2-sulfoethyl α-sulfostearate. The esters were therefore not precipitated under the test conditions.

Table II shows that the esters lower surface tension and interfacial tension (against a refined mineral oil). The high calcium stability values, tolerance to water of

greater than 1800 p. p. m. (as CaCO₃) show the esters can be used in the hardest waters. The lime soap dispersing power values showed that 5% by weight of the esters, based on the sodium oleate test soap, dispersed the calcium oleate formed with hard water. The immediate foam height was high. The wetting properties shown by sinking time indicate the esters are primarily detergents rather than extremely effective wetting agents.

EXAMPLE VII

Detergency

Detergency of built and unbuilt esters, compared to two well known and widely used detergents, sodium 2-sulfoethyl oleate and to sodium dodecyl sulfate, was measured in hard water of 300 p. p. m. using a standard soiled cotton (A. C. H. No. 114) in a standard laboratory scale washing machine (Terg-O-Tometer). Ten swatches, 2½ in. x 3¼ in., were washed in 1 liter of detergent solution for 20 minutes at 60° C., at 110 cycles per minute. Detergency was measured as ΔR, the increase in reflectance after washing. A difference in ΔR values of 0.9 was significant with at least 95% probability.

TABLE III.—DETERGENCY OF DISODIUM 2-SULFOETHYL α-SULFOPALMITATES AND α-SULFOSTEARATES

	Detergency, ΔR		
	0.05	0.10	0.25
30 Total detergent concn., percent.	27.1	29.2	29.7
Disodium 2-sulfoethyl α-sulfostearate (I)	27.1	29.2	29.7
0.10% I+0.15% A ¹			34.1
0.10% I+0.15% B ²			37.9
0.05% I+0.20% A			35.1
0.05% I+0.20% B			34.2
Disodium 2-sulfoethyl α-sulfopalmitate (IV)	24.4	26.9	29.8
0.05% IV+0.20% A			23.7
0.05% IV+0.20% B			27.2
0.05% I+0.05% IV			28.4
0.05% I+0.05% IV+0.15% A			33.9
0.025% I+0.025% IV	27.1		
0.025% I+0.025% IV+0.20% A			34.0
Sodium 2-sulfoethyl oleate (VI)		18.3	27.7
0.05% VI+0.20% A			33.0
40 Sodium dodecyl sulfate			25.4

¹ Builder A: Na₂SO₄ 71.11%, Na₂P₂O₇ 8.33, Na₄P₂O₇ 8.33, NaBO₂·4H₂O 5.56, Na metasilicate 5.56, CMC 1.11.

² Builder B: Na₂P₂O₇ 55%, Na₂SO₄ 24, Na₄P₂O₇ 10, Na metasilicate 10, CMC 1.

The detergency of disodium 2-sulfoethyl α-sulostearate was considerably improved by builder A and builder B. Disodium 2-sulfoethyl α-sulfopalmitate was improved by B, but not by A. Mixtures of the two esters (I and IV) responded favorably to building with A or B. Sodium 2-sulfoethyl oleate, without builder, was not nearly as good a detergent, at 0.10% concentration, as disodium 2-sulfoethyl α-sulfostearate (I) or disodium 2-sulfoethyl α-sulfopalmitate (IV), or a mixture of I and IV. The presence of builder A improved the detergency of sodium

2-sulfoethyl oleate, but the built mixture was not as good a detergent as 0.05% disodium 2-sulfoethyl α -sulfostearate+20% A, or as 0.025% I+0.025% IV+0.20% A. Further, sodium 2-sulfoethyl oleate is not as well suited for building with the alkaline builders A or B since it is considerably more susceptible to hydrolysis in alkaline solutions than are the esters of our invention.

The two best detergent compositions of Table III are those containing 40% and 20% of disodium 2-sulfoethyl α -sulfostearate as the active ingredient.

Washing tests with a different standard soiled cotton (G. D. C. No. 26) led to the same general conclusions. Disodium 1-methyl-2-sulfoethyl α -sulfostearate appeared to have detergent properties intermediate between those of disodium 2-sulfoethyl α -sulfostearate and disodium 2-sulfoethyl α -sulfopalmitate.

EXAMPLE VIII

Stability to hydrolysis in acid and alkaline solutions of the esters of our invention compared to sodium 2-sulfoethyl oleate, is shown by values of the rate constants, in Table IV.

TABLE IV.—RATE OF HYDROLYSIS OF DISODIUM SULFOALKYL α -SULFOPALMITATES AND α -SULFOSTEARATES AT 100° C.

	Acid Hydrolysis k_1^*	Alkaline Hydrolysis k_2^{**}
Disodium 1-methyl-2-sulfoethyl α -sulfostearate (II).....	0.0051.....	0.13
Disodium 2-sulfoethyl α -sulfopalmitate (IV).....	too rapid to measure accurately.	1.0
Sodium 2-sulfoethyl oleate (VI).....	too rapid to measure accurately.	4.3

* k_1 =first order rate constant= $\frac{1}{t} \ln \frac{a}{a-x}$, in reciprocal minutes.

** k_2 =second order rate constant= $\frac{1}{t} \frac{x}{a(a-x)}$, in liters-moles⁻¹-minutes.⁻¹

The rate of hydrolysis in acid solution was measured by heating 0.01 mole of the ester in 100 ml. of N/3 sulfuric acid at 100° C., and titrating 10 ml. samples at selected intervals. The rate of hydrolysis of disodium 2-sulfoethyl α -sulfopalmitate was found to correspond to a first order reaction and to be quite slow. In comparison, sodium 2-sulfoethyl oleate was hydrolyzed so rapidly under these conditions that the rate was not subject to accurate measurement.

The rate of alkaline hydrolysis was measured by heating 0.01 mole of the ester in 100 ml. of 0.1 N. sodium hydroxide at 100° C., and titrating 10 ml. samples at selected intervals. Alkaline hydrolysis was found to correspond to a second order reaction. Sodium 2-sulfoethyl oleate was hydrolyzed about 4 times as fast as disodium 2-sulfoethyl α -sulfopalmitate. Disodium 1-methyl-2-sulfoethyl α -sulfostearate, an ester of a secondary alcohol, was most resistant to hydrolysis. Sodium 2-sulfoethyl oleate was hydrolyzed about 33 times as fast as disodium 1-methyl-2-sulfoethyl α -sulfostearate.

EXAMPLE IX

The esters of our invention can be advantageously used in combinations with soap, as shown in the following washing experiments carried out as described in Example VII.

TABLE V.—DETERGENCY OF BUILT COMBINATIONS OF SOAP AND DISODIUM 2-SULFOETHYL α -SULFOSTEARATE IN HARD WATER (300 p.p.m.)

	Detergency, ΔR		
Total detergent concn., percent.....	0.05	0.10	0.25
Disodium 2-sulfoethyl α -sulfostearate (I).....	27.1	29.2	29.7
0.10% I+15% B ¹	—	—	37.9
0.05% I+20% B.....	—	—	34.2
0.05% I+0.05% Na palmitate +15% B.....	—	—	38.9
Sodium palmitate.....	—	20.8	—

¹ Builder B: Na₂P₂O₁₀ 55%, Na₂SO₄ 24, Na₄P₂O₇ 10, Na metasilicate 10, CMC 1.

The combination of disodium 2-sulfoethyl α -sulfostearate, sodium palmitate, and builder gave a well dispersed mixture in hard water with excellent detergency.

EXAMPLE X

The esters of our invention can be advantageously used in combination with other synthetic detergents. This behavior is shown in washing experiments (Table VI) carried out as described in Example VII.

TABLE VI.—DETERGENCY OF BUILT SYNTHETIC DETERGENT MIXTURES IN HARD WATER (300 P. P. M.)

Expt. No.		Detergency, ΔR		
	Total detergent concn., percent.....	0.05	0.10	0.25
1.....	Disodium 2-sulfoethyl α -sulfostearate (I).....	27.1	29.2	29.7
2.....	Disodium α -sulfopalmitate (VII).....	—	18.8	32.4
3.....	0.02% I+0.08% VII.....	—	27.1	—
4.....	0.05% I+0.20% A ¹	—	—	35.1
5.....	0.05% I+0.20% B ²	—	—	34.2
6.....	0.10% VII+0.15% A.....	—	—	23.7
7.....	0.10% VII+0.15% B.....	—	—	25.9
8.....	0.02% I+0.08% VII+0.15% B.....	—	—	30.9
9.....	0.25% I+0.025% VII+0.20% A.....	—	—	31.6

¹ Builder A: Na₂SO₄ 71.11%, Na₃P₂O₁₀ 8.33, Na₄P₂O₇ 8.33, NaBO₂·4H₂O 5.56, Na metasilicate 5.56, CMC 1.11.

² Builder B: Na₂P₂O₁₀ 55%, Na₂SO₄ 24, Na₄P₂O₇ 10, Na metasilicate 10, CMC 1.

Building with A or B markedly improved the detergency of a mixture of disodium 2-sulfoethyl α -sulfostearate and disodium α -sulfopalmitate (experiments 3, 8 and 9) to produce good detergents readily soluble in hard water.

EXAMPLE XI

The esters of our invention have detergent properties in sea water. Washing experiments were carried out in the Launder-Ometer, with 1 swatch of standard soiled cotton in 100 ml. of detergent solution, and 30 ¼-inch stainless steel balls, rotating the jars at 42 R. P. M. for 30 minutes at 140° F. Detergency was expressed as ΔR , the increase in reflectance after washing. The results are shown in Table VII. The total detergent concentration was 0.25%. The synthetic sea water was prepared as described by Vaughn et al. [T. H. Vaughn, E. F. Hill, C. E. Smith, L. R. McCoy and J. E. Simpson, Ind. Eng. Chem. 41, 112-19 (1949)].

The esters of our invention are among the best detergents in sea water, of the list of Table VII. They form clear foaming solutions in sea water and may be built with inorganic builders or with urea.

TABLE VII.—DETERGENCY IN SEA WATER

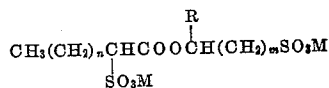
[Total detergent concentration 0.25%]

	Detergency, ΔR
Disodium 2-sulfoethyl α -sulfostearate (I).....	20.2
Disodium 2-sulfoethyl α -sulfopalmitate (IV).....	20.3
Sodium 2-sulfoethyl oleate (VI).....	18.7
0.05% I+0.20% B ¹	18.5
0.05% I+0.20% urea.....	17.9
0.05% IV+0.20% B.....	18.1
0.05% VI+0.20% urea.....	9.1
Sodium N-methyl-N-oleyl taurate.....	20.0
Sulfated monoglyceride of coconut oil.....	19.0
Polyoxyalkylene derivative of sorbitan monooleate.....	16.9
Sodium oleyl sulfate.....	13.9

¹ Builder B: Na₂P₂O₁₀ 55%, Na₂SO₄ 24, Na₄P₂O₇ 10, Na metasilicate 10, CMC 1.

We claim:

1. A compound having the formula



wherein n is an integer from 9 to 19, m is an integer from 1 to 2, R is a member selected from the group consisting of hydrogen and methyl, and M is a member selected from the group consisting of hydrogen, an alkali metal, NH₄, NH₂(C₂H₄OH), NH₂(C₂H₄OH)₂, and NH(C₂H₄OH)₃.

2. A compound as in claim 1 wherein M is an alkali metal.

3. A compound as in claim 1 wherein M is sodium.

4. Disodium 2-sulfoethyl α -sulfostearate.

5. Disodium 2-sulfoethyl α -sulfopalmitate.

6. Disodium 2-sulfoethyl α -sulfobehenate.

7. Disodium 1-methyl-2-sulfoethyl α -sulfostearate.

8. Disodium 3-sulfopropyl α -sulfostearate.

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