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ALKALI-STABLE SURFACE ACTIVE ESTERS OF α-SULFOCARBOXYLIC ACIDS

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8 Claims. (Cl. 260—400)

ABSTRACT OF THE DISCLOSURE

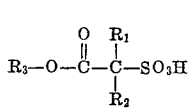
Surface-active agents which are stable in alkaline solutions comprising esters of alpha-sulfocarboxylic acids and salts thereof, wherein the alpha-carbon atoms has no hydrogen atoms attached thereto. The disclosed surface active agents have the desirable property of resisting saponification under alkaline conditions and are suitable as emulsifying agents in strongly alkaline systems.

DISCLOSURE

This invention relates to new and improved surface active agents which are stable in alkaline solutions. More particularly, it relates to surface active agents comprising esters of certain α-sulfocarboxylic acids, and salts thereof, in which the α-carbon atom has no hydrogen atoms attached thereto.

Surface active agents comprising compounds having a sulfonic acid group intermediately linked to a hydrophobic group by means of an ester group are known. Examples of such compounds include sulfonated succinic acid esters and esters of sulfoacetic acid, both of which are available commercially. Products of this type possess, in general, excellent surface active properties, rendering them useful as wetting agents and emulsifying agents. The products of this type heretofore known, however, are easily saponified under alkaline conditions, rendering them unsuitable for use, for example, in laundry detergent formulations in which alkaline builders are normally used. For the same reason, the known detergents cannot be used as emulsifying agents in strongly alkaline systems.

In accordance with the invention, there are provided surface active agents having greatly improved resistance to saponification. These compounds comprise esters of certain α-sulfocarboxylic acids and salts thereof. In general, the surface active agents of the invention contain a sulfonic acid group intermediately linked to a hydrophobic group by an ester group in which the remaining valences of the α-carbon atom are filled by hydrocarbon radicals, i.e., the α-carbon atom contains no hydrogen atom directly linked thereto. The compounds of the invention comprise esters of certain sulfocarboxylic acids, and salts thereof with suitable bases, said acid having the formula



wherein R_1 and R_2 are both straight or branched chain aliphatic hydrocarbon radicals each having from 1 to about 10 carbon atoms; R_3 is a straight or branched chain aliphatic hydrocarbon radical having about 8 to about 24 carbon atoms; the total number of carbon atoms in R_1 plus R_2 being 2 to about 14, and the total number of carbon atoms in R_1 plus R_2 plus R_3 being about 10 to about 30.

We have found that the surface active agents of the invention have the desirable property of resisting saponification under alkaline conditions and are, therefore, suitable for use in formulations wherein other α-sulfocarboxylic acid esters break down and, therefore, cannot be used.

The advantages of the compounds of the invention are illustrated in the following specific examples.

Example 1

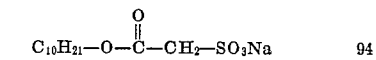
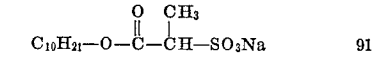
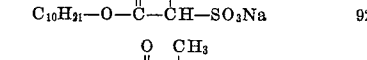
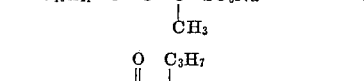
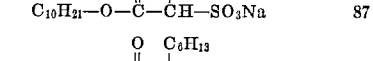
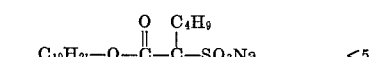
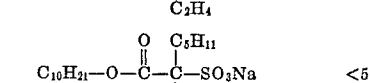
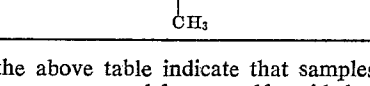
A number of esters of α-sulfocarboxylic acids, some coming within the scope of the invention and others being illustrative of the prior art, were prepared and subjected to a saponification test to determine their resistance to saponification in alkaline solution.

In the first step of the test procedure, the α-sulfocarboxylic acid was esterified with decanol as follows:

Two moles of the alcohol were heated at 150° C. with 1 mole of the monosodium salt of the acid and 5 g. of aluminum sulfate. The water of reaction was condensed and collected in a Dean-Stark tube. When 1 mole of water was collected, 2 g. of sodium carbonate was added to the reaction solution. The solution was then concentrated to a paste under 1 mm. pressure at 100° C. The products were then crystallized from ethanol and dried at 100° C.

After preparation in this manner, the compounds were subjected to a saponification test to determine their stability to alkaline solution. The test consisted of dissolving a 1 g. sample of the ester in 40 ml. of 0.1 N sodium hydroxide. After refluxing for 1 hour, the solution was cooled to 25° C. and titrated to the neutral point with 0.1 N sulfuric acid. The percentage of the sample which saponified was then calculated and is listed in the following table.

TABLE I

Sample:	Structure	Percent Saponified
A		94
B		91
C		92
D		8
E		87
F		82
G		<5
H		<5

The data in the above table indicate that samples D, G, and H, which were prepared from α-sulfo acids having no hydrogen atom attached to the α-carbon of the acid and which are representative of the compounds of the invention, had remarkably greater stability to alkaline solution than the other samples.

The compounds listed in Table I above were then subjected to a test for their ability as wetting agents. In this test, 2/10 g. of the ester and 0.2 g. of sodium polyphosphate were dissolved in 200 ml. of water in a 1 pint Mason jar. A swatch of 65–35 Dacron-cotton shirting material, 1 in. x 1 in., was placed on the surface of each

solution. The time required for the swatch to become wet and sink below the surface of the solution was measured. The rate at which the swatch became wet and submerged was a measure of the wetting power of the detergent formulation. The Mason jars were then stoppered and placed in a launderometer for 30 min. at 160° C. The solutions were cooled to room temperature and the wetting test was repeated. The results of the tests are shown in the following table.

TABLE II

	Time Required for Swatch to Sink (Sec.)	
	Before Heating	After Heating
Sample:		
A	7	<600
B	6	<600
C	4	<600
D	4	5
E	3	<600
F	4	<600
G	2	2
H	2	3

It will be seen from Table II that compounds D, G, and H, which contain no hydrogen atom on the α-carbon atom in accordance with the invention, retained their surface active properties, whereas the surface active properties of the other compounds were destroyed by heating in the presence of the sodium polyphosphate, a typical alkaline builder.

Example 2

Two moles of 2,2-dimethyldecanol and 1 mole of α-sulfoisobutyric acid, monosodium salt, were heated with 4 g. of titanium tetrabutoxide (an esterification catalyst) for 3 hours at the reflux temperature (220 to 240° C.). Eighteen g. of water was condensed and separated in a Dean-Stark tube. The excess alcohol was then removed by distillation at reduced pressure. Residual alcohol and color were removed by steam distillation in the presence of charcoal. The charcoal was removed by filtration. The water was evaporated, and 362 g. of a white flake was obtained. The product was found to be a powerful wetting agent. When subjected to the wetting test described in Example 1, the swatch sank in 3 sec. The surface active properties were not altered by the 160° C. heat treatment in the presence of sodium polyphosphate. A 1% solution had a surface tension of 22.3 degrees/cm. and an interfacial tension with mineral oil of 2.1 degrees/cm.

The resistance to saponification of the ester was further tested by dissolving a 1 g. sample thereof in 40 ml. of 0.1 N sodium hydroxide and refluxing for 1 hour at atmospheric pressure. The solution was then cooled to 25° C. and titrated to the neutral point with 0.1 N sulfuric acid. Less than 5% of the sample saponified during the saponification treatment.

Example 3

Three moles of 2-ethylhexanol, 3 moles of 2-ethyl-2-sulfohexanoic acid, and 300 ml. of benzene were refluxed for 30 min. Fifty-four ml. of water was condensed and separated in a Dean-Stark tube. The solution was divided into 3 equal portions. The samples (designated X, Y, Z) were neutralized as follows. Sample X was neutralized with aqueous sodium hydroxide. Sample Y was neutralized with aqueous potassium hydroxide, and Sample Z was neutralized with butyl amine. The samples were isolated by evaporating off the volatile material at 150° C. under reduced pressure (2 mm.). All of the samples were water soluble and were good wetting agents. They were stable to saponification by sodium hydroxide as determined by the stability test described in Example 1. The amine salt (Z) was soluble in hydrocarbons. It was found to be a good dispersing agent for fuel oils. The sodium and potassium salts were excellent emulsifying agents for oil in water emulsions.

Example 4

Six moles of 2-ethylhexanol, 3 moles of the monosodium salt of 2-ethyl-2-sulfohexanoic acid, and 5 g. of toluenesulfonic acid were heated at 190° C. until 36 ml. of water was removed by azeotropic distillation. The toluenesulfonic acid was neutralized with sodium bicarbonate, then the excess 2-ethylhexanol was removed by vacuum distillation. The resulting 2-ethylhexyl-2-ethyl-2-(sodium-sulfo)hexanoate contained 53.2% carbon, 8.6% hydrogen, 9.1% sulfur, and 6.5% sodium. A 1% water solution had a surface tension of 21.9 degrees/cm. and an interfacial tension with mineral oil of 4.0 degrees/cm. When subjected to the saponification test described in Example 1, less than 5% of the sample saponified. The results of the wetting test indicated that the sample was extremely stable to the alkaline conditions encountered in most commercial detergents. For example, when the sample was tested by the method described in Example 1, the swatch sank in 2 seconds. No change in wetting time was observed after the 160° C. heat treatment.

Example 5

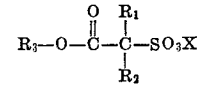
A mixture of neoalcohols containing about 17% $C_4H_9(CH_3)CH_2OH$, 14% $C_6H_{13}C(CH_3)_2CH_2OH$, 13% $C_8H_{17}C(CH_3)_2CH_2OH$, 11% $C_{10}H_{21}C(CH_3)_2CH_2OH$, 9% $C_{12}H_{25}C(CH_3)_2CH_2OH$, 9% $C_{14}H_{29}C(CH_3)_2CH_2OH$, 8% $C_{16}H_{33}C(CH_3)_2CH_2OH$, 9% $C_{18}H_{37}C(CH_3)_2CH_2OH$

and

10% $C_{20}H_{41}C(CH_3)_2CH_2OH$

was esterified with α-sulfoisobutyric acid by the method described in Example 2. When subjected to the stability test described in Example 1, less than 5% of the sample saponified. A 1% water solution of the product had a surface tension of 23.2 and an interfacial tension with mineral oil of 5.2 degrees/cm.

The α-sulfocarboxylic acid esters of the invention can be prepared in several ways which will be apparent to those skilled in the art. For example, a hydrophobic alcohol, which can be either straight chain or branched chain and desirably contains about 8 to 24 carbon atoms, can be heated with the α-sulfocarboxylic acid and an azeotroping agent such as benzene. After the reaction, the progress of which can be followed by the amount of water generated in the reaction, the sulfonic acid group is neutralized with sodium bicarbonate or any other suitable basic reactant. Suitable reactants include the carbonates, bicarbonates, and hydroxides of the alkali metals, such as sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium hydroxide, potassium carbonate, and potassium bicarbonate, for example, ammonia, lower aliphatic amines such as methyl amine, ethyl amine, propyl amine, isopropylamine and butyl amine, lower alkanolamines such as mono- di-, and tri-ethanolamine, β-hydroxypropylamine, delta hydroxybutylamine, and the like. The base used for neutralizing the α-sulfocarboxylic acid esters of the invention can be any of the bases known to those skilled in the art to be useful for this purpose. Thus in the general formula for the salts of our novel compounds,



X can be any cation forming a water soluble salt.

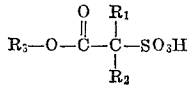
Another method for preparing the esters of the invention comprises heating a suitable hydrophobic alcohol with a mono-salt, such as the monosodium salt, of the α-sulfocarboxylic acid in the presence of an esterifica-

tion catalyst such as toluene sulfonic acid or titanium tetrabutoxide.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications will be obvious to those skilled in the art.

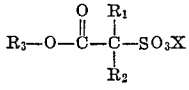
What is claimed is:

1. A compound having the formula



wherein R_1 and R_2 are alkyl having from 1 to 10 carbon atoms, R_3 is alkyl having from 8 to 24 carbon atoms, the total number of carbon atoms in R_1 and R_2 being from 2 to 14 and the total number of carbon atoms in R_1, R_2, and R_3 being from 10 to 30.

2. A surface active compound of the formula:



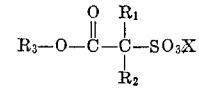
wherein X is a cation selected from the class consisting of an alkali metal ammonium, a lower alkyl amine, and a lower alkanolamine, and R_1–R_3 are as previously defined in claim **1**.

3. The compound of claim **2** in which said cation is ammonium.

4. The compound of claim **2** in which said cation is an alkyl amine having 1–4 carbon atoms.

5. The compound of claim **2** in which said cation is a lower alkanolamine containing from 1–3 alkanol groups and wherein each of said alkanol groups contain from 1–4 carbon atoms.

6. A surface active compound having the formula:



wherein R_1 and R_2 are alkyl having from 1 to 10 carbon atoms, R_3 is alkyl having from 8 to 24 carbon atoms, the total number of carbon atoms in R_1 and R_2 being from 2 to 14, the total number of carbon atoms in R_1, R_2, and R_3 being from 10 to 30, and X is an alkali metal.

7. The compound of claim **6** in which X is sodium.

8. The compound of claim **6** in which X is potassium.

References Cited

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