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OXYETHYLATED DIOLS, NITRILES AND SOAPS

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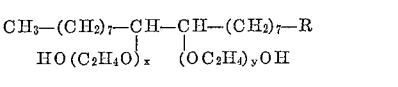
This invention relates to the preparation of surface active agents and particularly relates to nonionic compounds and hybrid nonionic-anionic compound (nonionic soaps).

A typical nonionic surface active agent, or surfactant, has a large hydrophobic moiety in the molecule in combination with a large hydrophilic moiety. The latter is usually a polyoxyethylene grouping. The surface active properties vary with the hydrophobic moiety and with the number of units in the polyoxyethylene grouping. An object of the present invention is to prepare new combinations of hydrophobic and hydrophilic moieties.

Attempts have previously been made to prepare a nonionic soap consisting of a large hydrophobic moiety in combination with both a carboxylate-alkali metal grouping and an oligo- or poly-alkylene oxide moiety. Reacting ethylene oxide with an hydroxy acid or its simple ester does not give the desired nonionic soaps. Reaction occurs only at the carboxyl or carboxylate group to give as a product a mixture of monoesters, diesters, and polyethylene glycols. Another object of the present invention is to prepare nonionic soaps.

Procedures to oxyethylate long-carbon-chain secondary monohydroxy alcohols such as 9-octadecanol are discouraging, resulting under acid catalysis in large amounts of undesired by-products, and under alkaline catalysis in a low yield of highly oxyethylated molecules admixed with a large portion of unreacted parent alcohol. We have discovered that a significant improvement in initiation of the oxyethylation reaction occurs when the monohydroxy secondary alcohol is replaced by a vicinal secondary dihydroxy alcohol such as 9,10-octadecanediol.

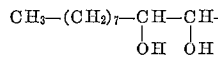
A surface active agent of the present invention is a compound of the formula



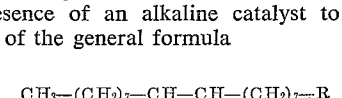
wherein R may be CH_3, CN, or COOM, where M is an alkali metal or ammonium radical, and the average of the sum of x and y is about from 4 to 16.

The oxyethylated diols, oxyethylated dihydroxystearonitriles, and nonionic soaps of the present invention have certain surface active properties which are significant improvements over the products resulting from oxyethylation of primary monohydroxy alcohols or acids of the same carbon chain length. For example, oxyethylated octadecanol with an average of 12 units of oxyethyl groups has a wetting time by the Shapiro standard tape method of over 100 seconds. In contrast, oxyethylated 9,10-octadecanediol with an average of 12 oxyethyl groups (compound of the general formula in which R is methyl and the average sum of x and y is 12) has a wetting time of only 6 seconds. Oxyethylated 9,10-octadecanediols with an average of 4 oxyethyl groups were exceptionally effective emulsifying agents and emulsion stabilizers. In general, a compound of the formula has low surface tension and interfacial tension values, signifying favorable surface active properties.

In general according to the present invention a mid-chain vicinal dihydroxy long carbon chain compound, such as a compound of the formula



wherein R is CH_3 or CN, and ethylene oxide, are heated in the presence of an alkaline catalyst to produce a compound of the general formula



wherein R is CH_3 or CN and the average of the sum of x and y is about from 4 to 16.

The reaction proceeds over a considerable range of temperature, the rate increasing with temperature, so that in order to minimize reaction time a temperature of 120° C. or higher, preferably about 160° C., is recommended.

Various alkalies such as potassium hydroxide, sodium methoxide, or sodium ethoxide, may be used as the catalyst for the oxyethylation reaction.

The number of units of ethylene oxide combining per molecule, or an average basis, is regulated by adding a weight of ethylene oxide calculated to provide a product with the desired units of oxyethyl groups. Course of the reaction may be followed by various means, such as increase in weight of the product mixture.

In one embodiment of the present invention a nonionic soap is prepared by combining a vicinal dihydroxynitrile such as threo-9,10-dihydroxystearonitrile, with ethylene oxide in the presence of an alkaline catalyst and substantially in the absence of air and water, and heating to produce an oxyethylated long carbon chain nitrile containing an average of about from 4 to 16 oxyethyl groups per molecule, and saponifying the oxyethylated nitrile to produce a nonionic soap.

The oxyethylated nitrile may be used as a surface active agent as the nitrile, or may be used in the preparation of a nonionic soap, depending upon the properties desired in the product.

In a prefered method for preparing a nonionic soap an oxyethylated nitrile is refluxed in aqueous alcohol with excess alkali until ammonia is no longer evolved, the dilute alcoholic solution is contacted with an ion-exchange resin to remove alkali and provide a solution of the "nonionic" acid, the acid is exactly neutralized with alkali, as by adding a solution of sodium hydroxide, potassium hydroxide, lithium hydroxide, or ammonium hydroxide, and the solvents evaporated. Although the nonionic soap has the salt forming characteristics of a soap, in other respects it has typical nonionic characteristics. Unlike soap it is not easily precipitated by hard water or various metal ions.

A typical oxyethylation procedure is exemplified with the oxyethylation of *dl*-9,10-octadecanediol.

EXAMPLE I

Racemic (*dl*)-9,10-octadecanediol (M.P. 78.5–79.4° C.) had been previously prepared from pelargonic acid. A graduated reservoir was charged with liquid ethylene oxide and freed of air by alternate introduction of nitrogen and boiling of ethylene oxide under vacuum, and the

valve in the line connecting to the reaction flask was then closed. The reaction flask, 500-ml. size containing a glass-enclosed stirring bar, was charged with 11.25 g. (0.0393 mole) of *dl*-9,10-octadecanediol and 104.7 mg. of 85% KOH (4 mole percent). The contents of the reaction flask were purged of air and water by heating and stirring at 140° C. with alternate introduction of nitrogen and evacuation (about 25 mm.) for several cycles. The nitrogen and vacuum-line valves to the reaction flask were closed, the volume of liquid ethylene oxide in the reservoir recorded (45.0 ml.), and the valve from the reservoir to the reaction flask opened, so that ethylene oxide gas entered the reaction flask. Pressure of the ethylene oxide gas was maintained at 6.7 p.s.i.g. (about 21 lbs./in.^{2} total pressure) by controlling heat applied to the reservoir. The temperature of the magnetically stirred reaction mixture was brought to and maintained at 160° C. The progress of oxyethylation was followed by the decreasing volume of liquid ethylene oxide, density taken as 0.87 g./ml. After 90 minutes the reaction was stopped for a weight check at 95% of the desired uptake. A final brief reaction gave 31.75 g. of a product with 11.9 oxyethylene units per mole of original octadecanediol. The weight increase of the reaction flask, which checked with the decrease in the reservoir volume, was taken as the final measure of oxide combined. After neutralization of the catalyst in isopropyl alcohol solution, the alcohol was removed by vacuum evaporation.

EXAMPLES II–VIII

In a manner similar to that of Example I, meso-9,10-octadecanediol, also prepared from pelargonic acid, was oxyethylated to contain an average of about 4, 8, 12 and 16 units of oxyethyl groups per molecule, and *dl*-9,10-octadecanediol was oxyethylated to contain an average of about 4, 8, and 16 units of oxyethyl groups per molecule.

When the products contained more than 2% unreacted diol, the residual diol was destroyed by oxidation. A major part of unreacted meso diol could be removed first by crystallization.

Referring to Example III, meso-9,10-octadecanediol oxyethylated to $x+y=4.00$ was found to contain 20.30% unreacted octadecanediol. By crystallization of product mixture (31 g.) from ether at 0° C. and then at −20° C., 5.50 g. of meso-octadecanediol, out of 6.29 g. expected, was removed. The remaining product in 175 ml. of ether was shaken repeatedly with 4.0 g. (7 equivalents/equivalent) of periodic acid in 250 ml. of water, with which it formed an emulsion. After 1.3 hrs., 100 ml. of a saturated solution of potassium iodide was added; the iodine was immediately reduced with thiosulfate solution. After boiling off the ether and heating the mixture to 60° C., the aqueous layer was saturated with sodium sulfate and separated. After three more washings at 60° C. with saturated solutions of sodium sulfate, the organic layer was freed from nonaldehyde by distillation at 0.05 mm., leaving oxyethylated product devoid of parent diol.

The reason for the unreacted octadecanediol is that under alkaline-catalyzed oxyethylation, the first derived ethylene glycol monoether formed, being more acidic than the parent alcohol, tends to react with ethylene oxide more readily than does the parent alcohol. This tendency is measurable by the Weibull-Nycander distribution constant, which for a long chain secondary monohydroxy alcohol such as 9-octadecanol is about 20; for a typical long-chain primary alcohol about 3. The Weibull-Nycander distribution constant for meso-9,10-octadecanediol is about 7, and for *dl*-9,10-octadecanediol is only about 3, the same magnitude as for a long chain primary alcohol. These values are especially important in indicating the amount of parent alcohol left unreacted in preparing oxyethylated products containing a low number of oxyethyl groups (as in Examples IV to VI). While less unreacted starting glycol in the desired product is obtained when the diol is the *dl* mixture rather than the meso compound in structure, the use of either vicinal secondary glycol is a marked improved over starting with a monohydroxy secondary alcohol.

EXAMPLE IX

Threo-9,10-dihydroxystearonitrile for use in oxyethylation reactions was prepared as follows: Commercial oleonitrile was redistilled and 184.5 g. of the middle fractions, B.P. 140–145° C. at 0.05 mm. Hg pressure, n_D^{20} 1.4564–1.4568, iodine value 96.2, was dissolved in 555 ml. of 98–100% formic acid in a 2-neck, 1-liter reaction flask equipped with thermometer well, dropping funnel, mechanical stirrer, and ice bath. With stirring of the reaction mixture, maintained by the ice bath at 35–40° C., there was added over a period of about 45 minutes 80.7 g. (1.05 times the stoichiometric quantity) of 31% hydrogen peroxide. After 4 hours' reaction time at 35–40° C., the reaction mixture was poured into ice and water. The organic layer was separated, combined with ether extracts of the water layer, and the ether solvent evaporated to give 228 g. of crude hydroxy-formoxystearonitrile. Saponification with dilute sodium hydroxide removed the formoxy group, and threo-9,10-dihydroxystearonitrile, M.P. 74.7–75.7° C., was separated from the saponification mixture by filtration. As proof of structure a sample was hydrolyzed with 10% aqueous alcoholic sodium hydroxide to an acid, M.P. 93.4–94.8° C., shown by melting point, mixed melting point and infrared spectrum to be threo-9,10-dihydroxystearic acid.

Threo - 9,10 - dihydroxystearonitrile (31.78 g.) was charged to a glass reaction flask fitted in the thermometer well and containing a glass-enclosed magnetic stirrer bar. To it was added 4 mole percent of potassium hydroxide (0.282 g. of 85% KOH pellets). After removal of water and air at 130° C. and reduced pressure, the molten mixture at 160° C. was stirred in contact with an atmosphere of ethylene oxide, maintained at 7 pounds per square inch, until 28.1 g. of ethylene oxide (or 5.97 moles per mole of dihydroxystearonitrile) had been fixed. The 59.9 g. of reaction product was dissolved in 300 ml. of isopropyl alcohol; the catalyst was removed by neutralizing with the calculated amount of hydrochloric acid and filtration; and then evaporation of the solvent left 58.7 g. of dry polyoxyethyl-threo - 9,10 - dihydroxystearonitrile, containing an average of 5.97 oxyethyl groups per molecule.

EXAMPLES X AND XI

Following the procedure of Example IX, but varying the amount of ethylene oxide combined with the dihydroxynitrile, products containing an average of about 4 and 8 oxyethyl groups per molecule, respectively, were prepared.

The Weibull-Mycander distribution constant for the oxyethylation of threo-9,10-dihydroxystearonitrile was about 2.5.

EXAMPLE XII

Twenty grams of the product of Example IX, polyoxyethyl-threo-9,10-dihydroxystearonitrile containing an average of about 6 oxyethyl groups, was saponified by refluxing 117 hours in 60 ml. 90% ethanol-10% water containing 2.463 grams of dissolved sodium. The aqueous alcoholic solution was passed through a column containing ion-exchange resin to remove the sodium and convert the product to a "nonionic" acid. The acid was exactly neutralized with sodium hydroxide (pH 9.0) and the solvent evaporated to give 18.3 g. of nonionic soap.

EXAMPLES XIII AND XIV

In a manner similar to that of Example XII, the oxyethylated nitriles of Examples X and XI were hydrolyzed and converted to the sodium salts.

Some of the surface active properties of oxyethyated compounds prepared are summarized in Table I.

SURFACE ACTIVE PROPERTIES OF COMPOUNDS OF THE FORMULA

$$CH_3-(CH_2)_7-\underset{HO(C_2H_4O)_x}{CH}-\underset{(OC_2H_4)_yOH}{CH}-(CH_2)_7-R$$

WHEREIN R MAY BE CH_3, CN, OR COONa, AND THE AVERAGE OF THE SUM OF x AND y IS ABOUT FROM 4 TO 16

Example No.	Surface active agent	Average of x plus y	Wetting time [a], 0.1%, seconds	Surface tension, 0.1%, dynes/cm.	Interfacial tension, 0.1%, dynes/cm.	Foam height, immediate, 0.25%, 60° C., mm.	Emulsion stability [c], 2% in light petrolatum
	Oxyethylated 9,10-octadecanediols						
3	meso	[b] 4	25	26.0	1.6	15	4 days.
4	dl	[b] 4	87	26.0	1.9	7	2 days.
5	meso	[b] 8	17	26.6	1.7	40	1,500 sec.
6	dl	[b] 8	23	26.9	2.2	40	510 sec.
2	meso	[b] 12	6.1	26.9	2.1	100	140 sec.
1	dl	[b] 12	6.3	27.5	2.4	105	190 sec.
7	meso	16	14	28.7	3.5	100	70 sec.
8	dl	16	15	30.1	4.1	125	80 sec.
10	oxyethylated-threo-9,10-dihydroxystearonitriles.	4	19	31.4	5.0	0	200 sec.
9		6	14	34.8	7.4	0	200 sec.
11		8	8.8	33.1	3.7	2	100 sec.
13	Nonionic soap	4	29	31.4	5.0	65	90 sec.
14	do	8	300	33.1	3.7	30	80 sec.

[a] Shapiro standard tape method.
[b] Purified by removal of unreacted diol.
[c] Atlab emulsion tester, time for 10% separation from emulsion from 25 ml. 2% solution in mineral oil in the 25 ml. of water.

All of the oxyethylated compounds of Table I are liquids at room temperature and are readily miscible with water, an advantage over polyoxyethylene derivatives of fatty acids and fatty alcohols which are waxy solids at room temperature.

We claim:

1. A compound of the formula

$$CH_3-(CH_2)_7-\underset{HO(C_2H_4O)_x}{CH}-\underset{(OC_2H_4)_yOH}{CH}-(CH_2)_7-R$$

wherein R is selected from the group consisting of CH_3, CN, and COOM, M is selected from the group consisting of Na, K, Li, and NH_4, and the average of the sum of x and y is a number about from 4 to 16.

2. A compound of the formula of claim 1 in which R is CH_3.

3. The compound of claim 2 in which the average of the sum of x and y is about 4.

4. The compound of claim 2 in which the average of the sum of x and y is about 8.

5. The compound of claim 2 in which the average of the sum of x and y is about 12.

6. The compound of claim 2 in which the average of the sum of x and y is about 16.

7. A compound of the formula of claim 1 in which R is CN.

8. The compound of claim 7 in which the average of the sum of x and y is about 4.

9. The compound of claim 7 in which the average of the sum of x and y is about 6.

10. The compound of claim 7 is which the average of the sum of x and y is about 8.

11. A compound of the formula of claim 1 in which R is COOM.

12. The compound of claim 11 in which M is sodium and the average of the sum of x and y is a number about from 4 to 16.

13. The compound of claim 12 in which the average of the sum of x and y is about 4.

14. The compound of claim 12 in which the average of the sum of x and y is about 6.

15. The compound of claim 12 in which the average of the sum of x and y is about 8.

16. A process comprising heating a compound of the formula

$$CH_3-(CH_2)_7-CHOH-CHOH-(CH_2)_7-R$$

wherein R is selected from the group consisting of CH_3 and CN, with at least about a 4 to 1 molar ratio of ethylene oxide in the presence of an alkaline catalyst to produce an oxyethylated compound of the formula

$$CH_3-(CH_2)_7-\underset{HO(C_2H_4O)_x}{CH}-\underset{(OC_2H_4)_yOH}{CH}-(CH_2)_7-R$$

wherein R is eselected from the group consisting of CH_3 and CN and the average of the sum of x and y is a number about from 4 to 16.

17. A process comprising heating threo-9,10-dihydroxystearonitrile with at least about a 4 to 1 molar ratio of ethylene oxide in the presence of an alkaline catalyst to produce an oxyethylated stearonitrile of the formula

$$CH_3-(CH_2)_7-\underset{HO(C_2H_4O)_x}{CH}-\underset{(OC_2H_4)_yOH}{CH}-(CH_2)_7-CN$$

in which the average of the sum of x and y is a number about from 4 to 16, heating the oxyethylated nitrile in aqueous alcohol with excess alkali of the formula MOH wherein M is selected from the group consisting of Na, K, Li, and NH_4 to hydrolyze the nitrile and to produce an alkaline salt of the formula

$$CH_3-(CH_2)_7-\underset{HO(C_2H_4O)_x}{CH}-\underset{(OC_2H_4)_yOH}{CH}-(CH_2)_7-COOM$$

wherein the average of the sum of x and y is a number about from 4 to 16, and M is selected from the group consisting of Na, K, Li and NH_4.

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