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SURFACE-ACTIVE ACETALS AND FORMALS

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14 Claims. (Cl. 260—609)

The present invention concerns specific surface-active acetals and formulas. It is further concerned with specific surface-active acetals and formals that are stable under alkaline or neutral conditions but which may be altered by acidic conditions. This alteration may particularly take the form of changing an oil-soluble, surface-active compound to a water-soluble, surface-active compound. In addition, a water-soluble, surface-active compound may be changed to one of less or substantially no surface activity. This invention also concerns a method for the preparation of the specific surface-active acetals and formals.

The acid-sensitive, non-ionic, surface-active acetals and formulas of this invention may be represented by the formula

$$R^1A\overset{R^2}{\underset{|}{C}}H(OCH_2CH_2)_nAZ$$

in which R^1 represents an alkyl group of eight to eighteen carbon atoms, R^2 is a hydrogen atom or a methyl group, A is a chalcogen having an atomic weight of sixteen to thirty-two, i.e., oxygen or sulfur, n is an integer from six to fifty, and Z is an alkyl group of eight to eighteen carbon atoms, an alkenyl group of eight to eighteen carbon atoms, or an alkylphenyl group in which the alkyl portion has from eight to twenty-four carbon atoms.

R^1 may typically be octyl, nonyl, decyl, dodecyl, octadecyl, or the like in any of the known spatial configurations such as normal, iso, or tertiary.

R^2 has been stated as representing a hydrogen atom or a methyl group. When R^2 represents hydrogen a formal structure is obtained and when R^2 represents a methyl group an acetal structure is obtained.

The integer n varies from six to about fifty. When n ranges from about six to twelve the product is oil-soluble and when n ranges from thirteen to about fifty the product is substantially water-soluble.

Z may represent an alkyl group of eight to eighteen carbon atoms, such as octyl, nonyl, decyl, dodecyl, pentadecyl, and octadecyl. Z may also represent an alkenyl group of eight to eighteen carbon atoms, such as octenyl, nonenyl, decenyl, dodecenyl, hexadecenyl, and octadecenyl. Z further may represent an alkylphenyl group in which the alkyl portion contains eight to twenty-four carbon atoms and may be in the form of one or more alkyl groups as long as the restriction as to range of carbon atoms is adhered to. Typical alkylphenyl representations of Z include octylphenyl, nonylphenyl, dodecylphenyl, octadecylphenyl, dioctylphenyl, dinonylphenyl, octylnonylphenyl, didodecylphenyl, and decyldodecylphenyl. The alkyl and alkenyl representations of Z as well as the alkyl portion of the alkylphenyl representation of Z may exhibit any of the known spatial configurations, such as normal, iso, or tertiary. The alkenyl groups may have the double bond in any of the possible locations. The alkyl group or groups, as the case may be, in the alkylphenyl representation of Z, may be positioned at any of the possible locations on the benzene ring. Particularly

useful are those representations of Z that include octyl, nonyl, dodecyl, octadecyl, octenyl, decenyl, dodecenyl, octadecenyl, octylphenyl, nonylphenyl, dodecylphenyl, dioctylphenyl, and dinonylphenyl.

A wide variety of non-ionic, surface-active agents is known in the art and usually these are stable in acid, basic, and neutral media. In many applicaitons it is necessary or at least highly desirable to remove or change the surface activity of an agent at some critical point in the operation. For example, if an ordinary, non-ionic, surface-active agent is used ot remove oils and waxes from raw wool by emulsification, there is obtained an emulsion in water which is not easily broken, either for the recovery of the oils and waxes or purposes of disposal. Also, the effluent from commercial laundries using non-ionic detergents remains highly surface active causing many troublesome problems of foaming and disposal. Further, when non-ionic, surface-active agents are used for the recovery of petroleum, there is obtained an emulsion which is not easily broken without the use of certain complex and expensive demulsifying agents. The present compounds can be used in all of the above situations by employing a step in which the objectionable emulsions are treated with dilute acids which, since there is an alteration in the surface-active properties of the present compounds, permits the ready and effective conclusion of the operations described heretofore. The subject compounds may also be used in the preparation of emulsion polymers which can well be coagulated, if desired, in fiber form by treatment with dilute acids. The present compounds are useful general purpose detergents that exhibit low foam, good detergency, and high cloud points.

The two high molecular weight hydrophobic groups in the compounds of this invention contribute to the oil-solubility of the molecule up to quite high molecular weights as represented by the number of oxyethylene units. For this reason, it is possible to prepare compounds which are initially oil-soluble and water-insoluble, with sufficient surface activity to function as emulsifying and suspending agents. Solutions of these compounds may be altered by acidic conditions in water to convert them to water-soluble surface-active compounds. Thus, the surface activity can be transferred from the oil phase to the water phase. Another advantage of these compounds is the small amount of foam which is generated in water solutions.

The present compounds are preferably prepared by reacting a compound having the formula

$$R^1A\overset{R^2}{\underset{|}{C}}HX$$

with one having the formula

$$ZA(CH_2CH_2O)_nH$$

in which X is chlorine or bromine. The reaction is conducted in the presence of a strongly basic inorganic neutralizing agent. Among the basic agents that may be employed are the alkali metals, such as sodium and potassium, the alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide, or lithium hydroxide, alkaline earth metal hydroxides, such as barium hydroxide, calcium hydroxide, and strontium hydroxide, alkali metal carbonates, such as sodium carbonate, potassium carbonate, and the like. The basic agent should be present in an amount somewhat greater than an equivalent amount of the reactants in order to assure the complete neutralization of the hydrochloric or hydrobromic acid formed in the reaction.

As an alternative method for preparing members having acetal structures, there may be used a reaction between a specific vinyl ether with a defined alcohol in the

presence of an acidic catalyst. In this instance the reactants may be represented by the formulas

$$R^1ACH{=}CH_2$$

and

$$ZA(CH_2CH_2O)_nH$$

and the acidic catalyst may typically be concentrated hydrochloric acid, concentrated sulfuric acid, syrupy phosphoric acid, boron trifluoride, or boron trifluoride coordinated complexes.

The compounds of this invention are prepared by conducting the reaction in the temperature range of about 40° C. to 100° C., preferably 50° C. to 70° C. When a halogenated reactant is employed the reaction is exothermic in nature. It is preferable to add to the reaction system the alcohol reactant and the acidic catalyst or basic agent, as the case may be, and then introduce the other reactant, the vinyl ether or the halogenated compound, as the case may be. Such a procedure assures a maximization of yields and minimization of undesired side reactions. Reaction time is not critical but generally will vary from about thirty minutes to two hours or more, depending largely on the individual reactants employed. A solvent is not required in this reaction but sometimes, in order to aid in the separation of the inorganic salt byproduct formed when the halogenated reactant is employed, it may be advantageous to employ a volatile inert organic solvent, such as benzene, toluene, or the like.

Typical reactants that may be employed include

$C_8H_{17}OCH_2Cl$

$C_9H_{19}OCH_2Br$

$C_{10}H_{21}O\underset{\displaystyle CH_3}{\underset{|}{C}}HCl$

$C_{12}H_{25}OCH_2Cl$

$C_{12}H_{25}SCH_2Cl$

$C_{14}H_{29}O\underset{\displaystyle CH_3}{\underset{|}{C}}HBr$

$C_{16}H_{33}OCH_2Cl$

$C_{18}H_{37}O\underset{\displaystyle CH_3}{\underset{|}{C}}HCl$

$C_{18}H_{37}SCH_2Br$

$C_8H_{17}OCH{=}CH_2$

$C_{10}H_{21}OCH{=}CH_2$

$C_{12}H_{25}SCH{=}CH_2$

$C_{12}H_{25}OCH{=}CH_2$

$C_{14}H_{29}OCH{=}CH_2$

$C_{18}H_{37}SCH{=}CH_2$

$C_{18}H_{37}OCH{=}CH_2$

$C_8H_{17}O(CH_2CH_2O)_6H$

$C_8H_{15}O(CH_2CH_2O)_8H$

$C_8H_{17}C_6H_4O(CH_2CH_2O)_9H$

$C_{12}H_{25}O(CH_2CH_2O)_{15}H$

$C_{12}H_{23}O(CH_2CH_2O)_{20}H$

$C_{12}H_{25}S(CH_2CH_2O)_{15}H$

$C_8H_{17}S(CH_2CH_2O)_6H$

$(C_8H_{17})_2C_6H_3O(CH_2CH_2O)_{25}H$

$C_{12}H_{25}C_6H_4O(CH_2CH_2O)_{30}H$

$(C_{12}H_{25})_2C_6H_3O(CH_2CH_2O)_{40}H$

$C_{14}H_{29}O(CH_2CH_2O)_{45}H$

$C_{18}H_{37}O(CH_2CH_2O)_{48}H$

and

$C_{18}H_{35}O(CH_2CH_2O)_{50}H$

The reactants of this invention are known compounds or readily prepared by known methods. In a preparation of the ethoxyalcohol reactants having six to fifty ethoxy units, there is frequently obtained a mixture of compounds having different members of ethoxy units. This is known in the art and is no deterrent to the present reaction since satisfactory and useful compounds are formed from the mixture of compounds in the same way as the individual compounds. It is to be understood, therefore, that the integer n stands for either the number of ethoxy units in a single compound or an average value in a mixture of compounds.

At the conclusion of the reaction, if a halogenated reactant is used, the halide salt formed as a reaction byproduct is removed by filtration. The product is obtained as the filtrate. If a solvent has been employed, as indicated previously, it may be removed by stripping in a conventional manner. Even if a solvent has not been employed during the course of the reaction, the use of one is often advantageous in the isolation of the product in order to facilitate the removal of the inorganic halide salt formed. When a vinyl ether reactant is used the reaction medium is neutralized at the conclusion of the reaction by the addition of sodium hydroxide or the like. The resulting neutralization product may be removed by filtration, if desired, but since the amount of such is relatively small and does not interfere with the desired product no further operations of isolation are usually conducted.

The products of this invention, having the utilities previously stated, possess the hydrophobic-hydrophilic balance required for a substance to exhibit surface activity. As has been presented previously it is frequently desirable to employ a surface-active material at one stage of a process and not have such material interfere at a later stage of the process. The present compound may be used as valuable surface-active agents at one stage of a process and then chemically altered to change its surface-active characteristics at a later stage of the process, as will be apparent hereinafter. The present compounds are quite stable in alkaline or neutral media, but may be chemically altered in an acidic media particularly at temperatures approaching about 100° C. Hydrochloric acid or the like is particularly convenient and effective for use in this respect and the change is effected usually in a manner of minutes, such as five or ten, depending largely on the temperatures and compounds involved. The present compound is split into three fragments, one an oily, water-insoluble compound of no surface activity; one a volatile aldehyde; and the third, a water soluble, surface-active compound.

The compounds of this invention, as well as the methods for their preparation, may be more fully understood from the following examples which are offered by way of illustration and not by way of limitation. Parts by weight are used throughout.

Example 1

There are placed in a reaction vessel eight parts of powdered potassium hydroxide and sixty parts of t—$C_8H_{17}C_6H_4O(CH_2CH_2O)_9H$. The system is heated to 60° C. and over a period of one and one-half hours there are introduced twenty-three parts of chloromethyl lauryl ether. The reaction mixture is then heated to 75° C. for one hour. It is diluted with two hundred parts of toluene and the inorganic salts are then removed by filtration. The toluene layer is stripped to give a yellow liquid identified as dodecoxy t-octyl-phenoxynonaethoxymethane,

$$C_{12}H_{25}OCH_2O(CH_2CH_2O)_9C_6H_4{-}t{-}C_8H_{17}$$

This product is soluble in hydrocarbon oils. When it is used at a concentration of 0.1% by weight in an insecticidal oil base, the oil can be emulsified with water.

In a similar manner there are prepared

$$C_8H_{17}OCH_2O(CH_2CH_2O)_{25}C_6H_3(C_9H_{19})_2$$

$$C_{18}H_{37}OCH_2O(CH_2CH_2O)_{50}C_6H_3(C_{12}H_{25})_2$$

and

$$C_8H_{15}O(CH_2CH_2O)_6CH_2OC_8H_{17}$$

Example 2

There are introduced into a reaction vessel eighty parts of $C_{18}H_{35}O(CH_2CH_2O)_{12}H$ and five parts of powdered sodium hydroxide. The system is heated to 60° C. and there is then added twenty-five parts of

$$C_{12}H_{25}O\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}H$$

The mixture is heated for thirty minutes at 70° C. and the hot solution is filtered to remove inorganic salts. The filtrate is a yellow liquid, which is identified as 1-(dodecoxy) - 1 - (octadecenyloxydodecaethoxy)ethane, $C_{12}H_{25}OCH(CH_3)O(CH_2CH_2O)_{12}C_{18}H_{35}$.

There are prepared in like manner

$$C_{18}H_{37}OCH_2O(CH_2CH_2O)_{50}C_8H_{17}$$

and

$$C_{18}H_{37}OCH_2O(CH_2CH_2O)_{12}C_{18}H_{37}$$

Example 3

Into a reaction vessel are placed seventy-three parts of $t—C_{12}H_{25}S(CH_2CH_2O)_{12}H$ and eight parts of powdered potassium hydroxide. There is then added twenty-seven parts of chloromethyl t-dodecyl sulfide, the temperature being maintaiend at about 50° C. The reaction mixture is heated briefly to 75° C., and then diluted with two hundred parts of toluene. The inorganic salts are filtered off and the toluene removed by heating at 100° C. under vacuum. The product is an oil-soluble liquid, which confers emulsifying properties on, for example, insecticidal hydrocarbon oils. It is identified as t-dodecylthiodecaethoxymethyldodecyl sulfide,

$$t—C_{12}H_{25}SCH_2(OCH_2CH_2)_{12}SC_{12}H_{25}—t$$

In a similar manner there are prepared

$$t—C_{12}H_{25}SCH_2O(CH_2CH_2O)_{20}C_{14}H_{29}$$

$$t—C_8H_{17}SCH(CH_3)O(CH_2CH_2O)_6C_6H_4—t—C_8H_{17}$$

and

$$t—C_{18}H_{37}OCH_2O(CH_2CH_2O)_{49}CH_2CH_2SC_{18}H_{37}$$

Example 4

There is added to a reaction vessel thirty-nine parts of $C_8H_{17}O(CH_2CH_2O)_6H$. Concentrated hydrochloric acid is introduced until a pH of two is obtained. There is then added at steam bath temperature, dropwise with stirring, 21.2 parts of dodecylvinyl ether. More acid is introduced during the addition in order to maintain acidity at a level of pH 2. The mixture is stirred and heated at 60° C. for two additional hours and is then made alkaline with about five drops of aqueous 50% sodium hydroxide solution. The resulting product is soluble in hydrocarbon oils and confers surface activity thereon, for example, for the preparation of oil in water emulsions. The product is identified as 1-dodecyloxy-1-(octoxyhexaethoxy)ethane.

In a similar manner there are made

$$C_{18}H_{37}OCH(CH_3)(OCH_2CH_2)_{36}SC_{12}H_{25}$$

and

$$C_{12}H_{25}OCH(CH_3)O(CH_2CH_2O)_9C_6H_4C_9H_{19}$$

We claim:

1. A composition of matter having the formula

$$R^1A\underset{\displaystyle R^2}{\overset{\displaystyle |}{\underset{|}{C}}}H(OCH_2CH_2)_nAZ$$

in which R^1 is an alkyl group of 8 to 18 carbon atoms, R^2 is a member of the group consisting of a hydrogen atom and a methyl group, A is a chalcogen having an atomic weight of 16 to 32, n is an integer from 6 to 50, and Z is a member of the group consisting of alkyl groups of 8 to 18 carbon atoms, alkenyl groups of 8 to 18 carbon atoms, and alkylphenyl groups in which the alkyl portion has from 8 to 24 carbon atoms.

2. A composition of matter having the formula

$$R^1O\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{C}}}H(OCH_2CH_2)_nOZ$$

in which R^1 and Z are alkyl groups of 8 to 18 carbon atoms and n is an integer from 6 to 50.

3. A composition of matter having the formula

$$R^1O\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{C}}}H(OCH_2CH_2)_nOZ$$

in which R^1 is an alkyl group of 8 to 18 carbon atoms, n is an integer from 6 to 50, and Z is an alkenyl group of 8 to 18 carbon atoms.

4. A composition of matter having the formula

$$R^1O\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{C}}}H(OCH_2CH_2)_nOZ$$

in which R^1 is an alkyl group of 8 to 18 carbon atoms, n is an integer from 6 to 50, and Z is an alkylphenyl group in which the alkyl portion has from 8 to 24 carbon atoms.

5. A composition of matter having the formula

$$R^1OCH_2(OCH_2CH_2)_nOZ$$

in which R^1 and Z are alkyl groups of 8 to 18 carbon atoms and n is an integer from 6 to 50.

6. A composition of matter having the formula

$$R^1OCH_2(OCH_2CH_2)_nOZ$$

in which R^1 is an alkyl group of 8 to 18 carbon atoms, n is an integrer from 6 to 50, and Z is an alkenyl group of 8 to 18 carbon atoms.

7. A composition of matter having the formula

$$R^1OCH_2(OCH_2CH_2)_nOZ$$

in which R^1 is an alkyl group of 8 to 18 carbon atoms, n is an integer from 6 to 50, and Z is an alkylphenyl group in which the alkyl portion has from 8 to 24 carbon atoms.

8. A composition of matter having the formula

$$C_{12}H_{25}OCH_2O(CH_2CH_2O)_9C_6H_4—t—C_3H_{17}$$

9. A composition of matter having the formula

$$C_{12}H_{25}OCH(CH_3)O(CH_2CH_2O)_{12}C_{18}H_{35}$$

10. A composition of matter having the formula

$$t—CH_{12}H_{25}SCH_2(OCH_2CH_2)_{12}SC_{12}H_{25}$$

11. A composition of matter having the formula

$$C_8H_{17}OCH_2O(CH_2CH_2O)_{25}C_6H_3(C_9H_{19})_2$$

12. A composition of matter having the formula

$$C_{18}H_{37}OCH_2O(CH_2CH_2O)_{50}C_8H_{17}$$

13. A method for preparing a compound having the formula

$$R^1A\underset{\displaystyle R^2}{\overset{\displaystyle |}{\underset{|}{C}}}H(OCH_2CH_2)_nAZ$$

in which R^1 is an alkyl group of 8 to 18 carbon atoms, R^2 is a member of the group consisting of a hydrogen atom and a methyl group, A is a chalcogen having an atomic weight of 16 to 32, n is an integer from 6 to 50, and Z is a member of the group consisting of alkyl groups of 8 to 18 carbon atoms, alkenyl groups of 8 to 18 carbon atoms, and alkylphenyl groups in which the alkyl portion has from 8 to 24 carbon atoms, which comprises bringing together in a reacting temperature in the range of about 40° to 100° C. in the presence of a strongly

basic inorganic neutralizing agent a compound having the formula



with one having the formula

$$ZA(CH_2CH_2O)_nH$$

in which X is a halogen having an atomic weight of about 35.5 to 80.

14. A method according to claim 13 in which the reacting temperature is about 50° to 70° C.

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UNITED STATES PATENT OFFICE

Certificate of Correction

Patent No. 2,905,720 September 22, 1959

Peter L. de Benneville et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 47, Claim 8, the formula should appear as shown below instead of as in the patent:

$$C_{12}H_{25}OCH_2O(CH_2CH_2O)_9C_6H_4—t—C_8H_{17}$$

column 6, line 53, Claim 10, the formula should appear as shown below instead of as in the patent:

$$t—C_{12}H_{25}SCH_2(OCH_2CH_2)_{12}SC_{12}H_{25}$$

Signed and sealed this 22nd day of March 1960.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.

UNITED STATES PATENT OFFICE

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