

Oxypropylation of Fatty Alcohols, and the Sulfation Products¹

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Abstract

Reaction of propylene oxide, rather than ethylene oxide, with fatty alcohols, gives a higher yield (50%) of mono-oxyalkylation product because the secondary alcohol formed is less reactive than the primary alcohol formed with ethylene oxide. Rate of further reaction is about half the rate of the parent primary alcohol. Distribution of propylene oxide reaction products follows the Weibull-Nycander equation.

Analysis of reaction products was accomplished by gas-liquid chromatography of the acetylated ether alcohol mixtures. Pure mono-oxypropylated alcohols $\text{ROCH}_2\text{CHOHCH}_3$ and in some cases di-oxypropylated alcohols $\text{R}[\text{OCH}_2\text{CH}(\text{CH}_3)]_2\text{OH}$ were separated by fractional distillation.

Individual ether alcohols and products with a known average number of oxypropyl groups were sulfated and evaluated in terms of Krafft point, critical micelle concentration, detergency, foam height and lime soap dispersing properties. Incorporation of one oxypropyl group was more effective than the same degree of oxyethylation, and improved solubility with no significant loss in foaming and detergency. Ether alcohol sulfates from propylene oxide are stable to alkaline hydrolysis and nearly equal to the sulfates from ethylene oxide in their stability to acid hydrolysis.

Introduction

A STUDY OF LONG CHAIN ether alcohol sulfates $\text{R}(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3\text{Na}$ (1,10) has shown that solubility increases with the number of oxyethyl groups, n , but detergency decreases, particularly when n is greater than 2.

Since the alkali catalyzed reaction of ethylene oxide with fatty alcohols proceeds at a rate proportional to the acidity of the hydroxylic hydrogen, the product ether alcohol is more reactive than the parent alcohol. Wrigley (12) has shown that the distribution constant, or ratio of reaction rate of ether alcohol to parent alcohol has a value of 3. Because of this unfavorable ratio direct oxyethylation does not produce high yields of product with a desired small number of oxyethyl groups.

Propylene oxide has been shown to add to methanol under alkaline catalysis to give only 1-methoxypropanol-2 (6). Secondary alcohols formed by the reaction of long chain primary alcohols with propylene oxide would be expected to be less acidic and less reactive than the parent alcohol. The lower distribution constant would increase the amount of mono-oxypropylated product at the expense of unreacted parent alcohol and give smaller amounts of polyoxypropylated alcohols.

The effect of the additional methyl branch derived from propylene oxide is difficult to predict but one could expect a general lowering of melting point and lower Krafft point since the methyl branch interferes with close packing of aliphatic chains.

The purpose of this paper is, therefore, to study

the alkali-catalyzed reaction of propylene oxide with fatty alcohols and the composition of reaction products, to determine distribution constants and to isolate pure compounds for characterization. Both the pure ether alcohols and oxypropylation reaction mixtures are sulfated and evaluated as detergents and surface active agents.

Experimental

Materials

Normal primary alcohols purified from good commercial grades by redistillation and low temperature crystallization from acetone had the following constants: dodecanol, n_D^{25} 1.4409; tetradecanol, n_D^{20} 1.4383, mp 37.4–38.4C; hexadecanol, n_D^{20} 1.4351, mp 49.3–49.6C; octadecanol n_D^{20} 1.4380, mp 57.9–58.4C. Purity by gas-liquid chromatography (GLC) was 97–99%. The propylene oxide was reagent grade bp 34–35C.

Oxypropylation

The reaction of propylene oxide with fatty alcohols is illustrated by the oxypropylation of octadecanol. Octadecanol, 228 g (0.844 moles) and 1.2 g of KOH were stirred and heated to 160C while passing a stream of dry N_2 over the reaction mixture. Propylene oxide 66.2 g (1.14 moles, mole ratio 1.35) was added dropwise during 1.5 hr, keeping the mixture at 160–175C, under efficient reflux to retain propylene oxide. The catalyst was neutralized with 1.75 ml concentrated HCl, the product dissolved in ethyl ether, washed, and ether removed on the steam bath. A fraction (60 g) of the reaction mixture was retained for analysis and sulfation, and the remainder was distilled as described below. The product from this experiment was found to contain an average of 1.12 oxypropyl groups/mole with the distribution shown in Table II.

Acetylation

Pure ether alcohol fractions or the oxypropylation reaction mixtures were converted to the acetate esters by the method of Gildenberg and Trowbridge (5). The ether alcohol was refluxed 20 min with 50–100 mole % excess of acetic anhydride. Use of greater than 100% excess gave no more rapid or complete conversion to the acetate. Excess acetic anhydride and acetic acid were removed under pressures less than 1 mm in a rotary evaporator heated in a boiling water bath. This method was satisfactory for analytical samples and for the larger scale preparation of ether alcohol acetates.

TABLE I
Properties of Individual Ether Alcohols and Their Acetates*

| Compound | Ether alcohol | | Acetate | |
|---|----------------------|------------|----------------------|------------|
| | $fp, ^\circ\text{C}$ | n_D^{20} | $fp, ^\circ\text{C}$ | n_D^{20} |
| $\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CHOHCH}_3$ | 25 | 1.4269 | | |
| $\text{C}_{14}\text{H}_{29}\text{OCH}_2\text{CHOHCH}_3$ | 33 | 1.4307 | | |
| $\text{C}_{14}\text{H}_{29}[\text{OCH}_2\text{CH}(\text{CH}_3)]_2\text{OH}$ | 3 | 1.4307 | | |
| $\text{C}_{16}\text{H}_{33}\text{OCH}_2\text{CHOHCH}_3$ | 39 | 1.4330 | 15 | 1.4348 |
| $\text{C}_{16}\text{H}_{33}[\text{OCH}_2\text{CH}(\text{CH}_3)]_2\text{OH}$ | 19 | 1.4330 | 10 | 1.4355 |
| $\text{C}_{18}\text{H}_{37}\text{OCH}_2\text{CHOHCH}_3$ | 41 | 1.4352 | 28 | 1.4375 |

* Analyses for C and H agreed with theoretical values with an average deviation less than 0.2%.

¹ Presented at the AOCs Meeting in Cincinnati, 1965.
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TABLE II

Distribution of Products^a in the Reaction of Propylene Oxide with Fatty Alcohols^b

| | Dodec- anol | Tetra- decanol | Hexadecanol | | | Octa- decanol |
|--|----------------|-------------------|-------------|-------|-------|------------------|
| Moles Propylene Oxide | | | | | | |
| Moles alcohol ($v = m/n_{00}$) | 0.92 | 1.74 | 0.80 | 1.20 | 1.46 | 1.12 |
| Mole fraction of alcohol (n_0/n_{00}) | 0.284 | 0.055 | 0.380 | 0.199 | 0.130 | 0.213 |
| Mole fraction of 1st derivative (n_1/n_{00}) | 0.544 | 0.397 | 0.468 | 0.495 | 0.459 | 0.512 |
| Mole fraction of 2nd derivative (n_2/n_{00}) | 0.144 | 0.347 | 0.129 | 0.229 | 0.272 | 0.212 |
| Mole fraction of 3rd derivative (n_3/n_{00}) | 0.025 | 0.158 | 0.020 | 0.065 | 0.103 | 0.063 |
| Mole fraction of 4th derivative (n_4/n_{00}) | 0.003 | 0.045 | 0.003 | 0.012 | 0.029 | 0.000 |
| Mole fraction of 5th derivative (n_5/n_{00}) | 0.000 | 0.011 | 0.000 | 0.000 | 0.007 | 0.000 |
| Distribution constant ^c ($C = k/k_0$) | 0.37 | 0.41 | 0.52 | 0.49 | 0.50 | 0.45 |

^a Found by GLC of the acetates.^b Catalyzed by 0.5% KOH at 160–175°C.^c Distribution constant of the Weibull-Nycander equation,

$$C = \frac{v - 1 + n_0/n_{00}}{\ln \frac{n_{00}}{n_0} - 1 + \frac{n_0}{n_{00}}}$$

Separation of Derivatives by Distillation

Ether alcohol reaction products and their acetates were separated by distilling through a column 1.5 in. in diameter and 1 ft long filled with Cannon 0.24 in. stainless steel protruded packing. Distillations were conducted at 0.3–0.6 mm pressure using a capillary N₂ bleed. Conversion of ether alcohols to the acetate permitted a sharper separation. Dioxypropylated hexadecanol was separated by conversion to the acetate, distillation, and alkaline hydrolysis.

Table I describes the individual ether alcohols and their acetates. It was surprising to find that the refractive index was the same for the first and second derivatives of both tetradecanol and hexadecanol (1.4307 and 1.4330). Differences were found, however, at other temperatures as shown by the following measurements: C₁₄H₂₉OCH₂CHOHCH₃, n_D^{20} 1.4379,

TABLE III

Distribution of Products, C₁₆H₃₃[OCH₂CH(CH₃)₁OH, in the Reaction of Propylene Oxide with Hexadecanol^a

| | Calculated by the Weibull- Nycander (6) equation | Found, mole fractions | |
|----------------------------|---|------------------------------|--|
| | | By GLC of the acetates | By fractional distillation of the acetates |
| Parent alcohol, $i = 0$ | | 0.130 | 0.121 |
| 1st derivative, $i = 1$ | 0.461 | 0.459 | 0.444 |
| 2nd derivative, $i = 2$ | 0.274 | 0.272 | 0.263 |
| 3rd derivative, $i = 3$ | 0.102 | 0.103 | 0.121 |
| 4th derivative, $i = 4$ | 0.027 | 0.029 | 0.040 |
| 5th derivative, $i = 5$ | 0.006 | 0.007 | 0.010 |

^a Reaction catalyzed by 0.5% KOH at 160–175°C, molar ratio $v = 1.46$, distribution constant $C = 0.50$.

d_4^{20} 0.8503, molar refractivity 84.85 (theory 84.87); C₁₄H₂₉[OCH₂CH(CH₃)₂OH, n_D^{20} 1.4381, d_4^{20} 0.8677, molar refractivity 100.61 (theory 101.47). Similar results were obtained at 35°C.

Gas-Liquid Chromatography

Reaction mixtures were analyzed and the purity of separated fractions was verified by GLC analysis. An F & M Model 720 dual column chromatograph fitted with a commercial 8 ft 20% SE-30 Silicone Gum Rubber column was used. The oven was operated isothermally at 280°C for all of the ether alcohol acetate samples. Distribution of products by GLC, as the acetates, is shown in Table II and compared with theoretical values and separation by distillation in Table III.

Sulfation

A 10% molar excess of ClSO₃H was added dropwise to a stirred solution of the individual ether alcohol in cold CCl₄. The reaction mixture was warmed to room temperature with continuous stirring, diluted with an equal volume of cold 95% ethanol and neutralized with 18N NaOH. The pure ether alcohol sulfates were crystallized from the neutralized solution and recrystallized from absolute ethanol after removing insoluble inorganic salts from the boiling solu-

TABLE IV
Surface Active Properties of Pure Ether Alcohol Sulfates

| | cmc mmoles ^a per liter | Krafft point, 1% solu- tion, °C | Ca ⁺⁺ stabil- ity (11), ppm CaCO ₃ | Lime soap disper- sing power (2) % | Detergency, 60C, ΔR ^b | | Foam height (7), 60C, mm. | |
|---|---|---|--|---|-------------------------------------|---|------------------------------|---|
| | | | | | 0.25%, distilled water | 0.05% + 0.2% builder, ^c 300 ppm | 0.25%, distilled water | 0.05% + 0.2% builder, ^c 300 ppm |
| C ₁₂ H ₂₅ OCH ₂ CHCH ₃ OSO ₃ Na | 2.69 | clear at zero | >1800 | 14 | 21 | 22 | 200 | 210 |
| C ₁₄ H ₂₉ OCH ₂ CHCH ₃ OSO ₃ Na | 0.58 | 14 | >1800 | 8 | 23 | 26 | 215 | 220 |
| C ₁₄ H ₂₉ [OCH ₂ CH(CH ₃) ₂ OSO ₃ Na | 0.36 | clear at zero | >1800 | 9 | 20 | 23 | 210 | 200 |
| C ₁₆ H ₃₃ OCH ₂ CHCH ₃ OSO ₃ Na | 0.16 | 27 | 780 | 8 | 25 | 27 | 200 | 185 |
| C ₁₈ H ₃₇ OCH ₂ CHCH ₃ OSO ₃ Na | 0.07 | 43 | ^d | 8 | 30 | 28 | 160 | 95 |
| C ₁₈ H ₃₇ OCH ₂ CH ₂ OSO ₃ Na | 0.11 | 46 | ^d | 9 | 29 | 29 | 160 | 100 |
| C ₁₂ H ₂₅ OSO ₃ Na | 6.8 ^e | 16 | 650 | 30 | 23 | 18 | 220 | 185 |
| C ₁₆ H ₃₃ OSO ₃ Na | 0.42 ^e | 45 | ^d | 40 | 29 | 28 | 245 | 240 |
| C ₁₈ H ₃₇ OSO ₃ Na | 0.11 ^e | 56 | ^d | ^d | 34 | 28 | 225 | 190 |

^a Pinacyanole chloride method.^b ΔR = increase in reflectance after washing standard soiled cotton (4) in the Terg-O-Tometer.^c Builder: 55% Na₃P₂O₇, 24% Na₂SO₄, 10% Na₄P₂O₇, 10% Na metasilicate, 1% CMC.^d Not soluble enough for the test conditions.^e Measured at 50°C.

TABLE V
 Surface Active Properties of Ether Alcohol Sulfate Mixtures

| Ether alcohol sulfate product | Ca ⁺⁺ stability (11), ppm CaCO ₃ | Lime soap dispersing power (2) | Wetting time (3) 0.1% distilled water, seconds | Detergency, 60C, ΔR ^a | | Foam height (7), 60C, mm | |
|---|--|--------------------------------|--|----------------------------------|---|--------------------------|-------------------------------|
| | | | | 0.25% distilled water | 0.05% + 0.2% builder ^b 300 ppm | 0.25% distilled water | 0.05% + 0.2% builder, 300 ppm |
| C ₁₂ H ₂₅ [OCH ₂ CH(CH ₃) _{0.02} OSO ₃ Na | >1800 | 17 | 6 | 22 | 27 | 190 | 210 |
| C ₁₄ H ₂₉ [OCH ₂ CH(CH ₃) _{1.45} OSO ₃ Na | >1800 | 10 | 18 | 25 | 26 | 210 | 220 |
| C ₁₆ H ₃₃ [OCH ₂ CH(CH ₃) _{1.20} OSO ₃ Na | 650 | 7 | 80 | 26 | 27 | 205 | 180 |
| C ₁₆ H ₃₃ [OCH ₂ CH(CH ₃) _{2.28} OSO ₃ Na ^c | >1800 | 5 | >300 | 25 | 22 | 170 | 110 |
| C ₁₈ H ₃₇ [OCH ₂ CH(CH ₃) _{1.12} OSO ₃ Na | d | 8 | d | 29 | 27 | 170 | 110 |

^a ΔR = increase in reflectance after washing standard soiled cotton (4) in the Terg-O-Tometer.

^b Builder: 55% Na₂P₂O₇, 24% Na₂SO₄, 10% Na₄P₂O₇, 10% Na metasilicate, 1% CMC.

^c Fractions containing unreacted hexadecanol and first derivative removed before sulfation.

^d Not soluble enough for the test conditions.

tion. Yields of purified ether alcohol sulfates were 75–80%. Analyses for Na and S agreed with theoretical values with an average deviation of 0.07% Na and 0.20% S. Properties are recorded in Table IV.

Unseparated ether alcohol mixtures were sulfated and neutralized in the same way, evaporated to dryness and used without further purification for the evaluation of detergent and surface active properties shown in Table V.

Evaluation of Detergent and Surface Active Properties

The methods were those used in earlier publications (1,10). Calcium stability was measured by the method of Wilkes and Wickert (11), lime soap dispersing power by the method of Borghetty and Bergman (2), wetting time by the Dravés test (3) and foam height by the Ross-Miles test (7). The critical micelle concentration (cmc) was measured by the pinacyanole chloride dye titration method, and the Krafft point was measured as the temperature at which a 1% dispersion became a clear solution on gradual heating. Detergency was measured as the increase in reflectance, ΔR, after washing 10 swatches of standard soiled cotton (4) in 1 liter of detergent solution in the Terg-O-Tometer for 20 min at 60C and 110 cpm. The results are recorded in Tables IV and V.

Stability to Hydrolysis

Like normal primary alcohol sulfates the ether alcohol sulfates from either ethylene oxide or propylene oxide are stable to saponification with boiling 2N alcoholic KOH but may be hydrolyzed in hot acid solution. First order kinetics of acid hydrolysis were determined by heating 0.05 N solutions of ether alcohol sulfates from propylene oxide in 0.05 N HCl at 80C, following the course of reaction by titrating the additional acid produced by hydrolysis. Table VI shows these data compared to similar measurements on sodium octadecyloxethyl sulfate and sodium hexadecyl sulfate.

Biodegradability

Ease of biodegradation was measured by the river water die-away test (9). Like the normal primary alcohol sulfates and the ether alcohol sulfates from ethylene oxide, the ether alcohol sulfates from propylene oxide were all very soft and degraded completely in less than 3 days, in most cases less than 2 days.

Discussion

Products from the oxypropylation of dodecanol, tetradecanol, hexadecanol and octadecanol containing

an average of 0.80 to 1.74 oxypropyl groups per mole were acetylated and analyzed by GLC with the results shown in Table II.

In studying the reaction of ethylene oxide with short-chain primary alcohols Weibull and Nycander (8) assumed the ether alcohol R(OC₂H₄)_iOH (i = 1) to have a reactivity different from the parent alcohol but the same as all other ether alcohols (i = 2,3, etc.). From this they derived equations which describe the distribution of products and permit the calculation of the distribution constant C, the ratio of reactivity of ether alcohol to parent alcohol. We have calculated C for the oxypropylation of long-chain alcohols, and as recorded in Table II it ranges from 0.37 to 0.52, but for hexadecanol varies only from 0.49 to 0.52. The reason for somewhat different values for different homologs is unknown but the important fact is that the value of C is only about one-sixth of the value previously reported (12) for the reaction of ethylene oxide with a long-chain primary alcohol.

The distribution constants of Table II were calculated from the first equation of Weibull and Nycander (footnote c, Table II) which is dependent only on the analysis for unreacted alcohol n₀/n_∞, and the total amount of propylene oxide added. To verify the relation of GLC analysis to normal distribution, Weibull and Nycander's second equation

$$n_i/n_{\infty} = c^{i-1}/(c-1)^{i-1} \left\{ \begin{array}{l} n_0/n_{\infty} - (n_0/n_{\infty})^c \sum_{j=0}^{i-1} \\ 1/j! [(c-1) \ln n_{\infty}/n_0]^j \end{array} \right\}$$

was used to calculate a theoretical distribution of products. Table III illustrates excellent agreement of calculated distribution with distribution found by GLC and fractional distillation. In general, values shown in Table II and theoretical values agreed within 0.5%.

 TABLE VI
 Rate Constants for Acid Hydrolysis^a

| Compound | k ₁ ^b min. ⁻¹ | Time for 50% hydrolysis, min |
|--|--|------------------------------|
| C ₁₆ H ₃₃ OCH ₂ CHCH ₃ OSO ₃ Na | 0.0075 | 90 |
| C ₁₈ H ₃₇ OCH ₂ CHCH ₃ OSO ₃ Na | 0.0071 | 92 |
| C ₁₈ H ₃₇ OCH ₂ CH ₂ OSO ₃ Na | 0.0051 | 125 |
| C ₁₆ H ₃₃ OSO ₃ Na | 0.0037 | 210 |

^a 0.05 N solution in 0.05 N HCl at 80C.

^b k₁ (first order reaction) = $\frac{1}{t} \ln \frac{a}{a-x}$.

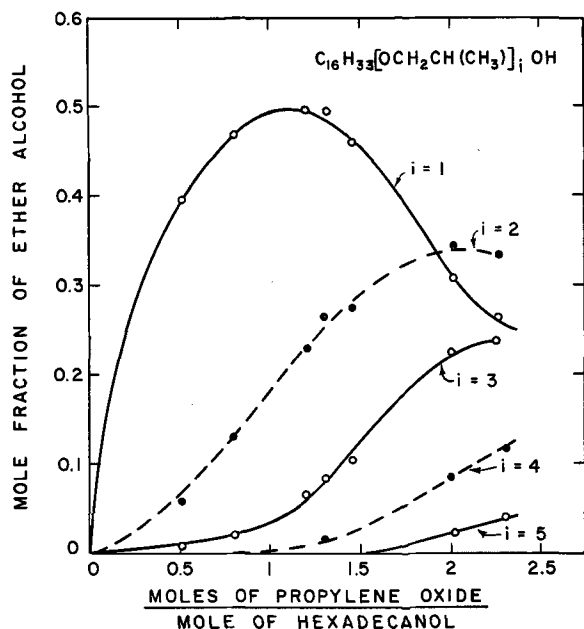


Fig. 1. Reaction of propylene oxide with hexadecanol.

Fig. 1 shows that the maximum yield of the desired first derivative is obtained when the average number of oxypropyl groups is about one. Increase in second derivative is rapid at about this stage with a corresponding loss in parent alcohol.

Although data on product distribution are consistent with oxirane ring opening to give the secondary alcohol $\text{ROCH}_2\text{CHOHCH}_3$, more direct evidence was sought by oxidation. Chromic acid oxidation by heating a purified ether alcohol with an equimolar amount of CrO_3 in glacial acetic acid for 5 min at 80°C gave a neutral fraction (90%) containing unreacted ether alcohol and a ketone, presumably the alkoxy acetone $\text{ROCH}_2\text{COCH}_3$; and an acid fraction (6%) identified as the normal fatty acid corresponding to the parent alcohol. The ketone could not be isolated in a pure state but was recognized by characteristic infrared absorption for the carbonyl group and by reaction with hydroxylamine and 2,4-dinitrophenylhydrazine. No evidence for ring opening to form the primary alcohol $\text{ROCH}(\text{CH}_3)\text{CH}_2\text{OH}$ was found.

Surface Active Properties

Table IV lists the solution and surface active properties of some pure ether alcohol sulfates. A comparison of Krafft points, the temperature at which a 1% turbid dispersion changes sharply to a clear solution on gradual heating, shows that oxypropylation increases solubility over that of the parent alcohol sulfate, to a greater extent than oxyethylation.

Insertion of an oxypropyl group lowers cmc's to a greater extent than is true of an oxyethyl group (8) consistent with the view that the oxypropyl group is more hydrophobic. As in the case of oxyethylation, a second oxypropyl group has less effect. This may be related to coiling in the ether chain.

There is an expected logarithmic relation between chain length of the parent alcohol and cmc, which does not hold as well at the very low cmc value for sodium 2-octadecyloxy-1-methylethyl sulfate. Fig. 2 shows the extent of this deviation.

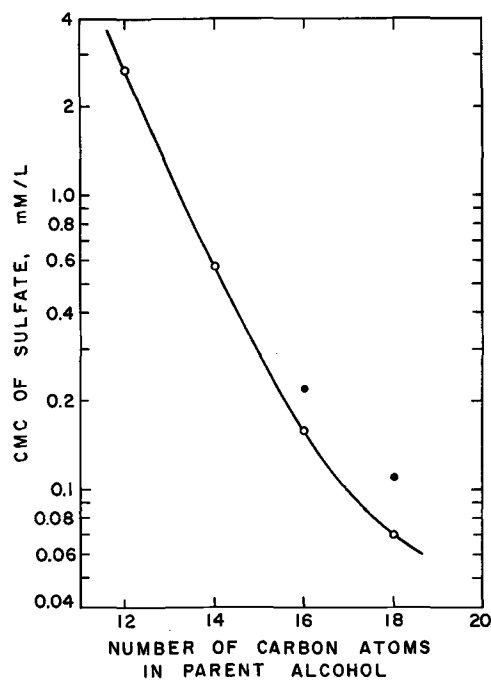


Fig. 2. Critical micelle concentration of ether alcohol sulfates: \circ $\text{ROCH}_2\text{CH}(\text{CH}_3)\text{OSO}_3\text{Na}$; \bullet $\text{ROCH}_2\text{CH}_2\text{OSO}_3\text{Na}$.

The ether alcohol sulfates generally have good foaming and detergent properties, not very different from the parent alcohol sulfates. Oxyalkylation of sodium octadecyl sulfate decreases foam height. The presence of two oxypropyl groups, in the tetradecanol derivative, increases solubility but decreases detergency.

Products from the propylene oxide reaction were also sulfated directly without separation of unreacted parent alcohol from oxypropyl derivatives, and their properties are shown in Table V.

Foaming and detergent properties are generally good and similar to those of the pure ether alcohol sulfates of Table IV. Products from hexadecanol and octadecanol have good lime soap dispersing properties. Removal of fractions containing unreacted hexadecanol and the first derivative, prior to sulfation, gave a product containing a larger average number of oxypropyl groups, somewhat less effective as a detergent in hard water.

ACKNOWLEDGMENTS

Assistance in evaluation of surface active properties by M. V. Nuñez-Ponzoa; in gas-liquid chromatographic analysis by F. D. Smith. Analyses for C, H and S by Lois C. Donio and Judith A. Porta.

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[Received November 17, 1965]