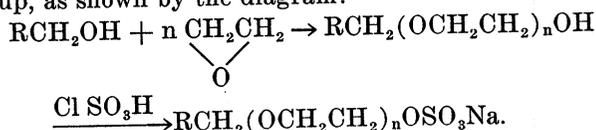


# Synthetic Detergents from Animal Fats. X. Sulfated, Ethenoxylated Tallow Alcohols

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THE SATURATED tallow alcohol sulfates, sodium hexadecyl sulfate, and sodium octadecyl sulfate, are known to be excellent detergents with some limitation in general usefulness because of their low solubility in water at room temperature [about 0.05 and 0.02%, respectively, at 25° (11)]. This solubility is increased by the presence of sodium oleyl sulfate (19) or sodium 9,10-dichlorooctadecyl sulfate (20), perhaps through mixed micelle formation. Usefulness in mixtures with other detergents, in built solutions in hard water, suggests an improved solubility (15).

The sulfation of nonionics, particularly ethenoxy-lated alkylphenols, economizes on the number of ethenoxy groups required and may result in products with better solubility, detergent, and foaming properties (4, 5, 10, 12). Some properties of sodium lauryl ether sulfates have recently been described (2). With respect to tallow derivatives the introduction of ethenoxy groups may therefore be still another means of improving the solubility of tallow alcohol sulfates. Accordingly the present investigation concerns the ethenoxylation of hexadecanol and octadecanol, and sulfation at the terminal hydroxyl group, as shown by the diagram:



It was of special interest to determine, at least approximately, the minimum number,  $n$  (which is also the optimum number), of ethenoxy groups required for improved solubility while retaining excellent detergency characteristics.

## Ethenoxylation and Sulfation

Purified hexadecanol, m.p. 48.8–49.2°,  $n_D^{20}$  1.4350, and octadecanol, m.p. 58.1–58.6°,  $n_D^{20}$  1.4378, were used and the reaction with ethylene oxide was carried out as previously described (22). Reaction with hexadecanol at 195°, using 0.5% potassium hydroxide catalyst, was stopped when the weight increase corresponded to 3.2 ethenoxy groups ( $n_D^{20}$  1.4390). The catalyst was neutralized with concentrated hydrochloric acid, the product was filtered hot to remove potassium chloride, and about 25% unreacted hexadecanol was removed by vacuum distillation at 123° and 0.05 mm. The resulting colorless semi-solid had an average of 3.8 ethenoxy groups, based on hydroxyl content (found 4.13% OH,  $n_D^{20}$  1.4394).

Chlorosulfonic acid was added gradually in 2:1 molar ratio to a stirred solution of 0.27 mole of the ether alcohol in 200 ml. of tetrachloroethylene. The mixture was heated 30 min. at 80°, cooled to 14°, diluted with 100 ml. of cold absolute ethanol, neu-

tralized with 18 N sodium hydroxide, and evaporated to dryness.

The crude product was treated with hot absolute ethanol, filtered to remove most of the insoluble inorganic salts, crystallized at 0°, redissolved in 70% ethanol, and recrystallized at 0° to effect more complete separation from inorganic salts. The yield of purified white product was 48%. Analysis for hydroxyl, sodium, and sulfur, and for active ingredient by titration with standardized hexadecyltrimethylammonium bromide (6) indicated that sulfation was 95% complete. Fractionation occurred during crystallization with some loss of the more soluble and more highly ethenoxyated sulfated ether alcohol so that the average value of  $n$  in the product isolated was about two. Found 0.25% OH, 5.29% Na, 7.76% S.<sup>4</sup> Calculated for  $\text{C}_{16}\text{H}_{33}(\text{OC}_2\text{H}_4)_n\text{OSO}_3\text{Na}$ :  $n=1$ , 5.92% Na, 8.25% S;  $n=2$ , 5.31% Na, 7.41% S;  $n=3$ , 4.83% Na, 6.73% S.

Reaction of ethylene oxide with octadecanol, and vacuum distillation to remove unreacted octadecanol, gave an ether alcohol with an average of 3.5 ethenoxy groups (3.99% OH,  $n_D^{20}$  1.4410). Sulfation with chlorosulfonic acid and purification and isolation as before gave 56% yield of sulfated ethenoxyated octadecanol. Analysis for hydroxyl, sodium, sulfur, and active ingredient indicated 95% sulfation with an average value of about  $n=2$ . Fractionation during crystallization occurred in this case also. Found: 0.26% OH, 5.01% Na, 6.78% S.<sup>4</sup> Calculated for  $\text{C}_{18}\text{H}_{37}(\text{OC}_2\text{H}_4)_2\text{OSO}_3\text{Na}$ , 4.99% Na, 6.96% S.

In a quite similar way octadecanol was ethenoxy-lated to an average of 9.8 ethenoxy groups (2.42% OH,  $n_D^{20}$  1.4469). No unreacted octadecanol was found at this degree of ethenoxylation, and the cream-colored solid was sulfated directly without removal of the alkaline catalyst. The neutralized sulfation product was too soluble for crystallization from organic solvents and was purified only by extraction with a petroleum ether to separate from insoluble inorganic salts. No fractionation was to be expected under these conditions. Analysis indicated about 93% active ingredient, 5% unsulfated ether alcohol, and 2% sodium sulfate. Found 0.18% OH, 3.49% Na, 4.37% S.<sup>4</sup> Calculated for  $\text{C}_{18}\text{H}_{37}(\text{OC}_2\text{H}_4)_{10}\text{OSO}_3\text{Na}$ , 2.83% Na, 3.94% S; calculated for impure  $\text{C}_{18}\text{H}_{37}(\text{OC}_2\text{H}_4)_{10}\text{OSO}_3\text{Na}$  containing 2%  $\text{Na}_2\text{SO}_4$  (indicated by the found gram atom Na/S ratio of 1.11), 3.42% Na, 4.31% S.

## Solubility

The sulfated ethenoxyated tallow alcohols with an average of two and of 10 ethenoxy groups were considerably more soluble in water than the corresponding sodium alkyl sulfates. The sulfated hexadecyl ether alcohol with an average of two ethenoxy groups [sodium hexadecyloxyethoxyethyl sulfate,<sup>5</sup>  $\text{C}_{16}\text{H}_{33}(\text{OC}_2\text{H}_4)_2\text{OSO}_3\text{Na}$ ], gave a clear 10% aqueous solution at 40°, which became a heavy gel at 30°.

TABLE I  
Detergency and Foam Height

Sodium salt of sulfated ether alcohol	Detergency, $\Delta R$ , 60°				Initial foam height (13) mm., 60°			
	90 p.p.m.		300 p.p.m.		90 p.p.m.		300 p.p.m.	
	0.25%	0.05% +0.2%B <sup>b</sup>	0.25%	0.05% +0.2%B <sup>b</sup>	0.25%	0.05% +0.2%B <sup>b</sup>	0.25%	0.05% +0.2%B <sup>b</sup>
C <sub>18</sub> H <sub>33</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> OSO <sub>3</sub> Na.....	34.4	35.9	21.1	34.4	210	200	200	200
C <sub>18</sub> H <sub>37</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> OSO <sub>3</sub> Na.....	37.2	36.8	18.9	36.0	170	130	95	115
C <sub>18</sub> H <sub>37</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>10</sub> OSO <sub>3</sub> Na.....	26.7	27.0	17.4	25.6	115	105	115	125
Sodium alkyl sulfates								
Sodium dodecyl sulfate.....	30.7	29.9	22.9	24.5	205	195	225	195
Sodium hexadecyl sulfate.....	37.5	36.9	36.2	35.7	235	235	120	240
Sodium octadecyl sulfate.....	38.0	37.3	33.7	36.5	205	185	20 <sup>c</sup>	190

<sup>a</sup> Measured as increase in reflectance,  $\Delta R$ , after washing 10 swatches of standard soiled cotton in one liter of detergent solution for 20 min. at 60° and 110 cycles per minute.

<sup>b</sup> B = Builder: 55% Na<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, 24% Na<sub>2</sub>SO<sub>4</sub>, 10% Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, 10% sodium metasilicate, 1% CMC.

<sup>c</sup> Very turbid solution.

More dilute solutions 0.5–3.0%, were somewhat turbid and viscous on standing at room temperature. Sodium octadecyloxyethoxyethyl sulfate<sup>5</sup> [C<sub>18</sub>H<sub>37</sub>(OC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>OSO<sub>3</sub>Na] was not as soluble; a 2.5% solution showed definite precipitation on standing. More dilute solutions, 0.5–1.0%, were well dispersed but somewhat turbid and viscous. In contrast, warm 0.1% solutions of either sodium hexadecyl sulfate or sodium octadecyl sulfate gave definite precipitation on standing at room temperature. The product with 10 ethenoxy groups [C<sub>18</sub>H<sub>37</sub>(OC<sub>2</sub>H<sub>4</sub>)<sub>10</sub>OSO<sub>3</sub>Na] was exceedingly soluble and formed a perfectly clear and stable 10% solution.

The ether alcohol sulfates were also more readily soluble in organic solvents than the corresponding sodium alkyl sulfates. The solubility of the products with two ethenoxy groups, at 25°, was about 1% in lubricating oil or 95% ethanol, 2.5% in benzene or chloroform, and 5% in tetrachloroethylene. The product with 10 ethenoxy groups was somewhat more readily soluble in the organic solvents and gave a 5% solution in the lubricating oil.

### Detergency and Foam Height

The detergent and foaming properties of built and unbuilt solutions of the ether alcohol sulfates, in soft and hard water, were compared with those of the corresponding sodium alkyl sulfates and with sodium dodecyl sulfate. The data are shown in Table I.

Detergency was measured as the increase in reflectance,  $\Delta R$ , after washing 10 swatches of G.D.C. No. 26<sup>6</sup> (7) standard soiled cotton in one liter of the detergent solution in the Terg-O-Tometer.<sup>6</sup> By analysis of variance a difference in  $\Delta R$  of 1.2 to 1.5 was significant with 95% probability (8).

The tallow ether alcohol sulfates with two ethenoxy groups were excellent detergents ( $\Delta R$  34.4–37.2), equal to the corresponding tallow alcohol sulfates ( $\Delta R$  33.7–38.0), except as unbuilt solutions in hard water ( $\Delta R$  18.9–21.1). From solubility and detergency considerations, as well as economy in the number of ethenoxy groups, the value  $n=2$  appears to be near the optimum. The product with 10 ethenoxy groups was a less effective detergent ( $\Delta R$  17.4–27.0) nearly equal however to sodium dodecyl sulfate.

The foaming properties of sulfated ethenoxyethylated hexadecanol were about equal to those of the sodium

alkyl sulfates. Sulfated ethenoxyethylated octadecanol had only moderate foaming properties. Foam height fell to 50 mm. or less within five minutes for the product with 10 ethenoxy groups.

Preliminary compatibility tests (16) suggest the use of the tallow ether alcohol sulfates as sea-water detergents with good foaming properties.

### Surface-Active Properties

Other surface-active and related properties were measured and are recorded in Table II, again in comparison with the sodium alkyl sulfates. The methods for wetting efficiency or sinking time, emulsion stability, calcium stability, and lime-soap dispersing power were those used in previous publications (17, 22).

Of the ether alcohol sulfates, the hexadecyl ether sulfate had the lowest surface-tension and the best wetting properties, the octadecyl ether sulfate with two ethenoxy groups was the best emulsifying agent, and that with 10 ethenoxy groups had the best calcium stability. The three products also appear to have good or excellent general emulsifying characteristics; for comparison the values for a representative tallow alcohol nonionic and a representative commercial anionic surface-active agent are about 1,500 and 200 seconds, respectively (22).

The ether alcohol sulfates have excellent lime-soap dispersing characteristics, comparable to those of disodium 2-sulfoethyl  $\alpha$ -sulfostearate, sodium 2-sulfoethyl oleate, and sodium N-methyl-N-oleoyl taurate (17). This suggests their use in soap-syndet combinations.

The ether alcohol sulfates were found to have excellent metallic ion stability<sup>7</sup> (9). Values of 100 were obtained in all cases (Mg<sup>++</sup>, Al<sup>+++</sup>, Ca<sup>++</sup>, Fe<sup>++</sup>, Ni<sup>++</sup>, Cu<sup>++</sup>, Zn<sup>++</sup>, Ba<sup>++</sup>, Pb<sup>++</sup>), except as follows:

	Al <sup>+++</sup>	Ba <sup>++</sup>
C <sub>16</sub> H <sub>33</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> OSO <sub>3</sub> Na.....	20	100
C <sub>18</sub> H <sub>37</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> OSO <sub>3</sub> Na.....	22	33
C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> Na, for comparison.....	17	13

### Stability to Hydrolysis

Like the sodium alkyl sulfates, the ether alcohol sulfates were completely stable to alkaline hydrolysis but could be hydrolyzed by heating with mineral acids.

The relative ease of hydrolysis on heating 0.001 mole in 20 ml. of 0.05 N HCl for 30 min. at 100° was found to be as follows:

TABLE II  
Surface-Active and Related Properties

Sodium salt of sulfated ether alcohol	Surface and interfacial tension <sup>a</sup> dynes/cm.		Sinking time <sup>a</sup> (14) secs.	Emulsion stability <sup>a</sup> (3) secs.	Ca. stability (21) p.p.m. CaCO <sub>3</sub>	Lime-soap dispersing power (1), %
	S.T.	I.T.				
C <sub>16</sub> H <sub>33</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> OSO <sub>3</sub> Na.....	30.4	8.5	42	810	1340	5
C <sub>18</sub> H <sub>37</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> OSO <sub>3</sub> Na.....	36.2	10.9	280	1540	.... <sup>b</sup>	5
C <sub>18</sub> H <sub>37</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>10</sub> OSO <sub>3</sub> Na.....	38.4	11.7	160	930	1800	5
Sodium alkyl sulfates						
Na dodecyl sulfate.....	49.0	20.3	14	160	720	30
Na hexadecyl sulfate.....	35.0	7.5	180	380	.... <sup>b</sup>	.... <sup>b</sup>
Na octadecyl sulfate.....	40.6 <sup>c</sup>	14.2 <sup>c</sup>	.... <sup>b</sup>	.... <sup>b</sup>	.... <sup>b</sup>	.... <sup>b</sup>

<sup>a</sup> 0.1% solutions in distilled water at 25°.

<sup>b</sup> Not soluble enough for test conditions.

<sup>c</sup> Sodium octadecyl sulfate was not completely in solution at 0.1% concentration.

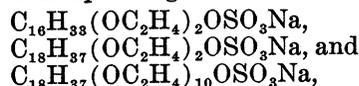
	% hydrolysis
C <sub>16</sub> H <sub>33</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> OSO <sub>3</sub> Na.....	95
C <sub>18</sub> H <sub>37</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> OSO <sub>3</sub> Na.....	88
C <sub>18</sub> H <sub>37</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>10</sub> OSO <sub>3</sub> Na.....	50
C <sub>18</sub> H <sub>33</sub> OSO <sub>3</sub> Na, for comparison.....	54

The products with two ethenoxy groups were more readily hydrolyzed than the product with 10 ethenoxy groups, which was about as stable as sodium hexadecyl sulfate under the conditions of the experiment.

Complete hydrolysis of an ether alcohol sulfate and isolation of the water-insoluble tallow ether alcohol verified the average value  $n=2$ . Ten grams of the sulfated ethenoxyethylated hexadecanol were heated and stirred with 250 ml. of constant boiling hydrochloric acid for three hours at 95°. Successive petroleum ether extraction, followed by countercurrent washing to remove hydrochloric acid and evaporation of solvent, gave a white waxy solid. Found: 5.15% OH,  $n_D^{20}$  1.4367; calculated for C<sub>16</sub>H<sub>33</sub>(OC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>OH, 5.15.

#### Summary

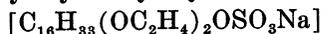
Sulfated ethenoxyethylated tallow alcohols of average composition corresponding to the formulas



were prepared by ethenoxylation and sulfation of hexadecanol and octadecanol.

The incorporation of two ethenoxy groups improved solubility without loss in detergency compared to the corresponding sodium hexadecyl and octadecyl sulfates. With consideration also of economy in the number of ethenoxy groups, two appear to be near the optimum. The product with 10 ethenoxy groups was an even more readily soluble but less effective detergent.

Of the sulfated ethenoxyethylated tallow alcohols, sodium hexadecyloxyethoxyethyl sulfate



had the lowest surface-tension and the best foaming properties; sodium octadecyloxyethoxyethyl sulfate



was the best emulsifying agent; and the product with 10 ethenoxy groups



had the greatest stability in regard to metallic ions and to acid hydrolysis.

All three were excellent lime-soap dispersing agents with good or excellent emulsifying properties and stability in regard to metallic ions.

#### Acknowledgment

The advice and assistance of A. N. Wrigley and F. D. Smith in the ethenoxylation procedure is acknowledged with thanks.

#### REFERENCES

- Borghetty, H. C., and Bergman, C. A., J. Am. Oil Chemists' Soc., 27, 88-90 (1950).
- Braude, G., Egan, R. R., Warren, M., and Galitzin, L., Soap and Chem. Specialties 32, No. 8, 45-50, 77 (1956).
- Briggs, T. R., J. Phys. Chem., 24, 120-6 (1920); Martin, A. R., and Hermann, R. N., Trans. Faraday Soc., 37, 25-29 (1941).
- Brown, C. B., PB 63822, U. S. Department of Commerce.
- Coith, H. S., and Robitschek, F. O., PB 47011, U. S. Department of Commerce.
- Crockett, R. H., J. Soc. Cosmetic Chemists, 6, 124-129 (1955).
- Draves, C. Z., and Sherburne, O. L., Am. Dyestuff Repr., 39, 771-772 (1950).
- Duncan, D. B., "Multiple Range and Multiple F Tests," Virginia Agricultural Experiment Station, Technical Report No. 6 (1953).
- Harris, J. C., A.S.T.M. Bull. No. 141, 49-53 (1946).
- Hoyt, L. F., PB 3868, Office of Technical Services, U. S. Department of Commerce.
- Jones, H. L., Am. Dyestuff Repr., 27, 621-624 (1938).
- Richardson, R. E., Kern, J. G., Murray, R. L., and Sudhoff, R. W., PB 6684, U. S. Department of Commerce.
- Ross, J., and Miles, G. D., Oil and Soap, 13, 99-102 (1941).
- Shapiro, L., Am. Dyestuff Repr., 39, 38-45, 62 (1950).
- Stirton, A. J., Maurer, E. W., and Weil, J. K., J. Am. Oil Chemists' Soc., 33, 290-291 (1956).
- Vaughn, T. H., Hill, E. F., Smith, C. E., McCoy, L. R., and Simpson, J. E., Ind. Eng. Chem., 41, 112-119 (1949).
- Weil, J. K., Bistline, R. G. Jr., and Stirton, A. J., J. Am. Oil Chemists' Soc., 32, 370-372 (1955).
- Weil, J. K., Bistline, R. G. Jr., and Stirton, A. J., J. Am. Oil Chemists' Soc., 34, 100-103 (1957).
- Weil, J. K., Stirton, A. J., and Bistline, R. G. Jr., J. Am. Oil Chemists' Soc., 31, 444-447 (1954).
- Weil, J. K., Stirton, A. J., and Maurer, E. W., J. Am. Oil Chemists' Soc., 32, 148-151 (1955).
- Wilkes, B. G., and Wickert, J. N., Ind. Eng. Chem., 29, 1234-1239 (1937).
- Wrigley, A. N., Smith, F. D., and Stirton, A. J., J. Am. Oil Chemists' Soc., 34, 39-43 (1957).