Synthetic Detergents from Animal Fats. The Sulfation of Tallow Alcohols[1]

J. K. WEIL, A. J. STIRTON, and R. G. BISTLINE JR., United States Department of Agriculture, Agricultural Research Service, Eastern Utilization Research Branch, Philadelphia, Pennsylvania

THE principal long-chain alcohols that may be obtained from tallow or other inedible animal fats by sodium reduction (6, 8) or by catalytic hydrogenolysis (13, 14) are hexadecyl alcohol, octadecyl alcohol, and oleyl and other octadecenyl alcohols. Elaidyl alcohol may be present in tallow alcohols, from elaidates naturally present (21), or from elaidates formed in a preliminary step of selective partial hydrogenation (5, 17, 22), which might be performed to reduce the amount of polyunsaturated compounds. Whether or not elaidyl alcohol may be present in any substantial amount, it is of interest to compare the sulfation of oleyl alcohol with the sulfation of elaidyl alcohol. It is possible the *trans* double bond might be less susceptible to reaction with the sulfating agent.

This paper is concerned with sulfation methods for hexadecyl, octadecyl, oleyl and elaidyl alcohols, and a composite tallow alcohol, also with a comparison of the surface active and detergent properties of the resulting sodium salts of the sulfated alcohols.

The sulfates of the tallow alcohols are good detergents and surface-active agents, but their use has been somewhat limited, apparently because of the low solubility of sodium octadecyl sulfate at room temperature [<0.02% at 25° (7)]. The presence of one double bond in a chain of 18 carbon atoms however markedly improves solubility; sodium oleyl and sodium elaidyl sulfates readily form 10% solutions at room temperature. It seems desirable to select methods which will produce a maximum of the more soluble sulfated alcohols with a minimum of reaction at the double bond during reduction or sulfation.

The sulfation of the saturated primary alcohols is a fairly straight-forward reaction. Sodium dodecyl, tetradecyl, hexadecyl, and octadecyl sulfates were prepared, as described previously (19), by sulfation of the purified alcohols dissolved in chloroform, with chlorosulfonic acid.

The sulfation of unsaturated primary alcohols is however complicated by the ease with which the common sulfating agents will cause reactions to take place at the double bond. A number of special sulfating agents would appear to be suitable for the sulfation of unsaturated alcohols (1, 2, 3, 9, 10, 11, 12, 18). Products from the use of modifications of the usual sulfating agents are now compared to relate the extent of reactions at the double bond with the effect on surface active and detergent properties.

Pure Sodium Oleyl Sulfate and Sodium Elaidyl Sulfate

The preparation of substantially pure sodium oleyl sulfate has been described (19). Sodium elaidyl sulfate was prepared in a similar manner by sulfation of elaidyl alcohol with pyridine · sulfur trioxide. The details follow.

Elaidyl Alcohol. A commercial oleyl alcohol of 69% oleyl alcohol content was isomerized with selenium in 1 hr. at 220-225° and purified in a method similar to that described by Swern, Jordan, and Knight (20). Elaidyl alcohol m.p. 34.6-35.6° was obtained in a yield of 16% based on the oleyl alcohol content of the commercial alcohol. The iodine number was 94.0 (calculated for $C_{18}H_{36}O$, 94.5).

Sodium Elaidyl Sulfate. The method was similar to that used for sodium oleyl sulfate (19) except that it was necessary to warm the reactants above the melting point of elaidyl alcohol to start the reaction. A 93% yield of a slightly impure cream-colored product containing 6.44% sodium was obtained. Further purification by decolorizing a solution in methanol, and cooling to 5°, gave sodium elaidyl sulfate in a yield of 59%. *Analysis.*[2] Calculated for $C_{18}H_{35}NaO_4S$: 58.34% C, 9.52% H, 6.21% Na, 8.65% S, iodine no. 68.5; found, 57.94% C, 9.71% H, 6.20% Na, 8.77% S, iodine no. 68.6.

Special Sulfation Methods for Oleyl and Elaidyl Alcohols

Pyridine · sulfur trioxide has been found to be an excellent sulfating agent for the laboratory preparation of sodium oleyl sulfate (19), and for sodium elaidyl sulfate as well. It was now of interest to use less expensive agents in methods which might sufficiently minimize the extent of reactions involving the double bond. Six sulfating agents were compared: pyridine · sulfur trioxide (19); sulfamic acid (12); dioxane · sulfur trioxide (10); chlorosulfonic acid plus sodium chloride (18); chlorosulfonic acid · urea (3); and sulfuric acid · urea (2). Experiments on direct sulfation with chlorosulfonic acid, sulfur trioxide, and concentrated sulfuric acid were also performed.

On completion of the reaction in each case, n-butanol was added and the mixture was neutralized with 18 N aqueous sodium hydroxide. The n-butanol layer was separated, dried azeotropically, and filtered hot to remove inorganic salts. The product was crystallized from n-butanol at 5°. Purity was estimated from the iodine number, due correction being made for small amounts of saturated alcohols present in the oleyl alcohol. The yield and purity are shown in Table I, and the methods, other than the use of pyridine · sulfur trioxide, are now briefly described.

Sulfamic Acid. A solution of 0.30 mole of sulfamic acid and 0.23 mole of oleyl alcohol in 200 ml. of dimethylformamide was stirred for two hours at 60°. The mixture was neutralized with aqueous sodium

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[1] Presented at the annual meeting of the American Oil Chemists' Society, in San Antonio, Tex., April 12-14, 1954.

[2] Microanalyses for C, H, and S performed by M. J. Bythrow.

TABLE I

The Sulfation of Oleyl and Elaidyl Alcohols. The Effect of Purity on Foam Height (15) and Wetting Properties (16)

Sulfating agent	Sulfation of Oleyl Alcohol				Sulfation of Elaidyl Alcohol			
	Yield, %	Purity, %	Foam height, mm.[b]	Sinking time 0.1%, 25°, seconds	Yield, %	Purity, %	Foam height, mm.[b]	Sinking time 0.1%, 25°, seconds
Pyridine · SO_3	54	96	226	19	59	100	202	20
NH_2SO_3H	61	93	198	17	....	....	....	....
Dioxane · SO_3	63	90	224	19	74	94	209	30
$ClSO_3H + NaCl$	42	66	209	21	45	73	210	26
$ClSO_3H \cdot CO(NH_2)_2$	93	87	217	19	75	91	224	21
$H_2SO_4 \cdot CO(NH_2)_2$	58	54	213	30	....	....	....	....
SO_3	52	....[a]	73	179	....	....	....	....
$ClSO_3H$	20	....[a]	0	48	....	....	....	....

[a] Low iodine numbers indicated extensive reaction involving the double bond.

[b] Immediate values, 0.1% solutions in hard water of 100 p.p.m. at 60°. There was no fall in foam height when measured after 5 minutes, except for the reaction product from SO_3.

hydroxide, dimethylformamide was partly recovered by distillation at reduced pressure, and the product was crystallized from an n-butanol extract as a pale yellow solid.

Dioxane · Sulfur Trioxide (10). Liquid sulfur trioxide, 0.15 mole, was slowly added, with mechanical agitation, to 0.23 mole of dioxane in 200 ml. of carbon tetrachloride; 0.13 mole of elaidyl alcohol was then added, and the mixture was heated one hour at 60°. The cooled mixture was neutralized, and the product was crystallized from an n-butanol extract as a light cream-colored solid.

Chlorosulfonic Acid Plus Sodium Chloride (18). Chlorosulfonic acid, 0.13 mole, added slowly with cooling and stirring to 0.25 mole of sodium chloride, gave a white paste of the complex with evolution of hydrogen chloride. The paste was slowly added with stirring to 0.10 mole of elaidyl alcohol. At the end of the reaction the mixture was neutralized, and the product was recovered from the n-butanol extract.

Chlorosulfonic Acid · Urea (3). Chlorosulfonic acid, 0.133 mole, was slowly added to a slurry of 0.185 mole of urea in 200 ml. of chloroform. The reaction was exothermic, and a clear solution was obtained. Oleyl alcohol, 0.115 mole, was added, the mixture was refluxed for one hour, cooled, and neutralized. A white product was recovered from the n-butanol extract.

Sulfuric Acid · Urea (2). Urea, 0.100 mole was dissolved in 0.306 mole of 100% sulfuric acid. The solution was cooled, and 0.112 mole of oleyl alcohol was slowly added, keeping the temperature below 40°. At the end of the reaction the mixture was poured on cracked ice and neutralized with sodium hydroxide. The product was recovered from an n-butanol extract.

Direct Sulfation

Experiments with chlorosulfonic acid under the conditions used in the sulfation of the saturated alcohols, with sulfur trioxide dissolved in sulfur dioxide at —10°, and with concentrated sulfuric acid at 5-10° gave dark products with inferior surface-active and detergent properties. The reactions were carried out in conventional laboratory apparatus. The low iodine number of the products indicated reactions involving the double bond.

Sulfation of Tallow Alcohol

It appears from Table I that the *trans* double bond of elaidyl alcohol is only slightly less reactive than the double bond of oleyl alcohol under the sulfation conditions. The special sulfating agents were at least partially successful in causing the reaction to take place preferentially at the hydroxyl group. Two of the methods, the use of $ClSO_3H + NaCl$, and the use of $ClSO_3H \cdot CO(NH_2)_2$, were selected as the means of preparing tallow alcohol sulfates from tallow alcohol.

The tallow alcohol[3] used had the following analysis: saponification no. 8.2, acid no. 1.5, hydroxyl no. 6.4, iodine no. 54.1. The sulfation was carried out as described for oleyl and elaidyl alcohols, but no attempt was made to purify the product. Solvent was removed by evaporation. Extraction of samples of the crude neutralized product with ethanol showed the content of active ingredient to be 60 and 66%, from the use of $ClSO_3H + NaCl$, and $ClSO_3H \cdot CO(NH_2)_2$, respectively.

Surface Active and Detergent Properties

The pure sodium alkyl sulfates, the pure sodium alkenyl sulfates, the products from the use of various sulfating agents, and the unpurified sulfated tallow alcohol were examined. Data were obtained on surface and interfacial tension, foam height, wetting properties, and detergency.

Surface and Interfacial Tension

The surface tension *vs.* concentration curve for sodium elaidyl sulfate is shown in Figure 1. Measurements were made at 25° with the Du Noüy tensiometer. The curve is quite similar to a previous one for sodium oleyl sulfate (19), but the values for sodium elaidyl sulfate are slightly higher. In each case there is a minimum, attributable to small amounts of impurities.

Table II presents the surface tension, and the interfacial tension against a refined mineral oil, of 0.1% solutions of six alcohol sulfates at 25°. The values of Table II are those which may be found at concentrations greater than the critical micelle concentration, with the exception of the value for sodium dodecyl sulfate. At 0.25%, which is about the critical micelle concentration for sodium dodecyl sulfate, the surface tension is 37.4 dynes per centimeter. The high values for sodium octadecyl sulfate are probably due to incomplete solution. The unsaturated 18 carbon atom homologs effectively lower surface and interfacial tension.

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[3] Prepared by Ethyl Corporation.

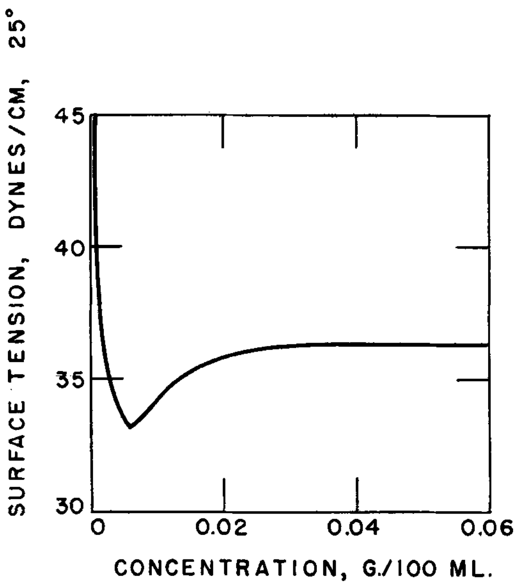

FIG. 1. Surface tension of sodium elaidyl sulfate.

Foam Height

Foam height measurements by the Ross-Miles method (15) at 60° are shown in Tables I and II.

Table II lists the values for six pure alcohol sulfates, at 0.25% concentration in distilled water, measured immediately and again after five minutes. Table II also lists the immediate values at 0.1% concentration in hard water of 100 p.p.m. At 0.25% concentration in distilled water the foam height decreased in five minutes for sodium dodecyl sulfate and sodium tetradecyl sulfate; the values for sulfates derivable from tallow remained the same. At 0.1% concentration in 100 p.p.m. the immediate values for sodium hexadecyl sulfate and sodium octadecyl sulfate were the lowest.

TABLE II

Surface and Interfacial Tension and Foaming Properties of Six Alcohol Sulfates

Alcohol sulfates[a]	Surface and interfacial tension, dynes/cm. 0.1% solutions, 25°		Foam height, mm. at 60°(15)		
			0.25% in distilled water		0.1% in water of 100 p.p.m. (as $CaCO_3$)
	S.T.	I.T.	Immediate	After 5 min.	Immediate[c]
NaDDS	49.0	20.3	220	175	240
NaTDS	25.3	9.1	231	184	246
NaHDS	35.0	7.5	244	240	178
NaODS	40.6[b]	14.2[b]	227	227	151
NaOS	35.0	7.4	246	240	226
NaES	36.1	6.3	243	241	202

[a] The abbreviations are for sodium dodecyl, tetradecyl, hexadecyl, octadecyl, oleyl, and elaidyl sulfates, respectively.

[b] Sodium octadecyl sulfate was not in complete solution, at 0.1% at 25°.

[c] The foam height remained at essentially the same values after 5 minutes.

The values for the six alcohol sulfates at 0.1% concentration in 100 p.p.m. were not changed significantly when measured again after five minutes.

Table I lists the immediate values for the products of the sulfation of oleyl and elaidyl alcohols, using eight different sulfating agents. The measurements were made on 0.1% solutions in hard water of 100 p.p.m. Except for the products of direct sulfation, using sulfur trioxide or chlorosulfonic acid, the foaming properties were satisfactory and remained the same when measured again after five minutes.

Wetting Properties

Wetting properties were measured, using a 9-in. length of 1¼-in. binding tape, a 1-g. hook, and a 40-g. anchor (16). The tests were made on 0.1% solutions in distilled water at 25°. The sinking time for sodium dodecyl, tetradecyl, hexadecyl, and octadecyl sulfates was 13, 12, 59, and 280 seconds, respectively. Pure sodium oleyl sulfate and sodium elaidyl ~~sulfate~~ were better wetting agents than sodium hexadecyl sulfate or sodium octadecyl sulfate. In general, the least pure sulfates of the unsaturated alcohols were the least effective wetting agents, as shown in Table I.

Detergency

Detergency was measured in the Terg-O-Tometer, using A.C.H. No. 114[4] standard soiled cotton of average initial reflectance 27.0, relative to the reflectance of magnesium oxide as 100. Ten 2¼-in. x 3¼-in. swatches were washed in one liter of hard water of 100 p.p.m., detergent concentration 0.1%, for 20 minutes at 60°, at 110 cycles per minute, load ratio 0.00924 g. per milliliter.

The sulfated alcohol preparations are listed in Table III in the order of their detergent efficiency as measured by the increase in reflectance, △ R, after washing. For comparison, the value of △ R for a 0.1% solution of sodium palmitate in distilled water was 41.5.

TABLE III

Detergency of Sodium Salts of Sulfated Alcohols
Measured in the Terg-O-Tometer with 10 swatches/liter of solution at 110 cycles/minute, 20 minutes at 60°C. 0.1% Solutions in water of 100 p.p.m. (as $CaCO_3$).

No.		Sulfating agent	% Purity of sulfation product	△ R[a]
1	NaODS	$ClSO_3H$	....	38.6
2	NaES	Pyridine · SO_3	100	37.6
3	NaOS	Pyridine · SO_3	96	37.1
4	NaOS	Dioxane · SO_3	90	37.1
5	NaES	$ClSO_3H \cdot CO(NH_2)_2$	91	36.6
6	NaOS	$ClSO_3H \cdot CO(NH_2)_2$	87	36.0
7	NaHDS	$ClSO_3H$	....	35.9
8	NaOS	NH_2SO_3H	93	35.8
9	NaES	$ClSO_3H + NaCl$	73	35.7
10	NaOS	$ClSO_3H + NaCl$	66	35.4
11	NaES	Dioxane · SO_3	94	35.0
12	NaTDS	$ClSO_3H$	....	34.2
13	NaOS	$H_2SO_4 \cdot CO(NH_2)_2$	54	33.0
14	Sulfated tallow alcohols	$ClSO_3H \cdot CO(NH_2)_2$	66[b]	30.0
15	NaDDS	$ClSO_3H$	....	28.6
16	Sulfated tallow alcohols	$ClSO_3H + NaCl$	60[b]	27.3
17	NaOS	$ClSO_3H$	....[c]	16.0
18	NaOS	SO_3	....[c]	11.7
19	Water	....	....	10.3

[a] For comparison, the △ R value for 0.1% sodium palmitate in distilled water was 41.5.

[b] Estimated % active ingredient.

[c] Low iodine numbers indicated extensive reaction involving the double bond.

Differences in △ R values of 0.9 were significant with at least 95% probability. Some correlation between purity and detergency is evident, but there are

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[4] American Conditioning House, Inc. The mention of this type of standard soiled cotton does not constitute a recommendation by the Department of Agriculture of this test cloth over that produced by any other manufacturer.

two discrepancies. The △ R values for sodium oleyl sulfate and sodium elaidyl sulfate, of 93 and 94% purity, respectively, are lower than might be expected.

TABLE IV

Summary of Properties of Sodium Salts of Sulfated Alcohols

Sulfating agent		Purity %	Foam height (15), immediate, 0.1%, 60°, hard water of 100 p.p.m., mm.	Sinking time (16), 0.1%, 25°, distilled water, seconds	Detergency Terg-O-Tometer, 0.1%, 60°, hard water of 100 p.p.m., △ R
NaDDS[1]	$ClSO_3H$	....	240	13	28.6
NaTDS[2]	$ClSO_3H$	....	246	12	34.2
NaHDS[3]	$ClSO_3H$	....	177	59	35.9
NaODS[4]	$ClSO_3H$	....	151	280	38.6
NaOS[5]	Pyridine · SO_3	96	226	19	37.1
NaES[6]	Pyridine · SO_3	100	202	20	37.6
NaOS	NH_2SO_3H	93	198	17	35.8
NaOS	Dioxane · SO_3	90	224	19	37.1
NaES	Dioxane · SO_3	94	209	30	35.0
NaOS	$ClSO_3H + NaCl$	66	209	21	35.4
NaES	$ClSO_3H + NaCl$	73	210	26	35.7
NaOS	$ClSO_3H \cdot CO(NH_2)_2$	87	217	19	36.0
NaES	$ClSO_3H \cdot CO(NH_2)_2$	91	224	21	36.6
NaOS	$H_2SO_4 \cdot CO(NH_2)_3$	54	213	30	33.0
NaOS	SO_3	....[a]	73	179	11.7
NaOS	$ClSO_3H$	....[a]	0	48	16.0

[1, 2, 3, 4, 5, 6] Abbreviations for sodium dodecyl, tetradecyl, hexadecyl, octadecyl, oleyl, and elaidyl sulfates, respectively.

[a] Low iodine numbers indicated extensive reaction involving the double bond.

Similar results were obtained at 0.25% concentration in hard water of 300 p.p.m., and with another standard soiled cotton [G.D.C. No. 26 (4)] at 0.1% in hard water of 100 p.p.m., and at 0.25% in 300 p.p.m.

Summary

Sodium oleyl sulfate (or the trans isomer) is a desirable component in a mixture of sulfated tallow alcohols, principally because of its ready solubility in water at room temperature.

The use of moderate sulfating agents, which can be thought of as complexes formed with either sulfur trioxide, chlorosulfonic acid, or sulfuric acid, has been shown to give products having good detergent and surface-active properties. Desirable properties are generally related to the purity of the product and to the extent to which side reactions at the double bond are minimized or avoided.

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CORRECTION

In the paper, "Estimating Carbonyl Compounds in Rancid Fats and Foods," J. American Oil Chemists' Society, *31*, 88 (1954), the a_M for saturated monocarbonyl compounds reported has been found to be low. Using repeatedly recrystallized derivatives of five n-aliphatic aldehydes, C_6-C_{12}, the following values are obtained: at 430 mμ 21,000, and at 460 mμ 16,300. Recheck on the unsaturated aldehyde, crotonal, shows no change for the previously reported values of 21,350 and 28,100, respectively.

The equations given for the calculation of concentrations when measurements are made in 1-cm. cuvettes with the Beckman DU Spectrophotometer become:

$$\text{Unsaturated} = \frac{3.067\ A_{460} - 2.381\ A_{430}}{.469}$$

and

$$\text{Saturated} = 3.067\ A_{460} - 1.724\ \text{unsaturated}.$$

Authors of the paper are A. S. Henick, M. F. Benca, and J. H. Mitchell Jr., Quartermaster Food and Container Institute for the Armed Forces, Chicago, Ill.