Synthetic Detergents From Animal Fats. Disodium Alpha-Sulfopalmitate and Sodium Oleyl Sulfate[1,3]

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ALTHOUGH synthetic detergents derived from oleic, palmitic, and stearic acids, the constituent acids of tallow and grease, were early developments in the history of the surface active agents, those from coconut oil and petroleum sources are now more important in volume of production. With increasing availability of substantially pure fat acids and simple derivatives the possibility of producing synthetic detergents from animal fats can now be re-explored. The lower solubility of palmitic and stearic acid derivatives, if it is considered a disadvantage, might be improved by blending with other detergents or builders.

We have selected two types of anion active compounds to prepare and evaluate for detergent properties. One of these, disodium α-sulfopalmitate, may be derived from the saturated, and the other, sodium oleyl sulfate, from the unsaturated constituents of animal fats.

Disodium α-Sulfopalmitate

Disodium α-sulfopalmitate, $CH_3(CH_2)_{13}CH(SO_3Na)CO_2Na$, is an example in which the properties of the carboxyl group have been modified by the introduction of an adjacent solubilizing sulfonic acid group to overcome the instability of sodium palmitate in hard water.

The α-sulfonation of saturated fat acids has been accomplished in the past by leading sulfur trioxide vapor over the surface of a carbon tetrachloride solution (8), by the reaction of chlorosulfonic acid or sulfur trioxide with the molten acid (9), by refluxing with chlorosulfonic acid in a carbon tetrachloride solution (21) by sulfonation of the soap, acid, alkyl ester, or amide with sulfur trioxide in sulfur dioxide solution (2, 14), and by the reaction of sulfites with α-bromo acids (1, 13).

The sulfonating agent used in the present work was liquid sulfur trioxide. The method is similar to one described to us by E. E. Gilbert (7).

Commercially pure palmitic acid was further purified by twice crystallizing from acetone at 0°. The product melted at 61.5-62.0° and had a neutralization equivalent of 256.9.

Sulfan B[4] was added dropwise in 1.6 molar ratio in 15 minutes to a stirred solution of one mole of palmitic acid in 1300 ml. of tetrachloroethylene, at 15°C. The reaction was only slightly exothermic. The mixture was heated to 60°, cooled, poured into water, neutralized with sodium hydroxide, and filtered. After crystallization from hot water, disodium α-sulfopalmitate was obtained as a white crystalline powder, in a yield of 83%, containing 8.21% S. The theoretical value for $C_{16}H_{30}Na_2O_5S$ is 8.43% S.

Sodium α-Sulfopalmitic Acid

The disodium salt was converted to sodium α-sulfopalmitic acid $CH_3(CH_2)_{13}CH(SO_3Na)CO_2H$, by heating with excess dilute sulfuric acid. The product crystallized from hot water or 75% ethanol was a white crystalline powder, neutralization equivalent 358.7 (theoretical value 358.5), less soluble in water than the disodium salt. The n-butyl and n-amyl esters were prepared in low yields by azeotropic removal of water from a system containing sodium α-sulfopalmitic acid, excess of the alcohol, xylene, and β-naphthalenesulfonic acid as a catalyst. The triethanol-ammonium salt was prepared in aqueous solution by neutralizing sodium α-sulfopalmitic acid with triethanolamine.

α-Sulfonated Lauric, Myristic, and Stearic Acids

Lauric, myristic, and stearic acids were sulfonated in the same manner as described for palmitic acid and converted to the mono- and disodium salts. Unsulfonated fat acid can be removed after sulfonation by partial neutralization to form the monosodium salt and extraction of the fat acid with acetone. Analysis gave the following values which can be compared with the calculated values in parentheses:

$C_{10}H_{21}CH(SO_3Na)CO_2H$, N.E.[5] 304.1 (302.4), % S 10.51 (10.60)

$C_{10}H_{21}CH(SO_3Na)CO_2Na$, % S 10.02 (9.89)

$C_{12}H_{25}CH(SO_3Na)CO_2H$, N.E. 333.4 (330.4), % S 9.39 (9.70)

$C_{12}H_{25}CH(SO_3Na)CO_2Na$, % S 8.97 (9.10)

$C_{16}H_{33}CH(SO_3Na)CO_2H$, N.E. 386.0 (386.5), % S 8.10 (8.30)

$C_{16}H_{33}CH(SO_3Na)CO_2Na$, % S 7.85 (7.85)

Sodium Oleyl Sulfate

Sodium oleyl sulfate is an example in which the carboxyl group is replaced by the $-CH_2OSO_3Na$ group and the molecule is further solubilized by the presence of a double bond. Sodium oleyl sulfate has not been as well characterized as the sodium alkyl sulfates of the saturated alcohols, principally because the usual sulfating agents react both with the double bond and the hydroxyl group of oleyl alcohol. The use of special sulfating agents to favor sulfation of the hydroxyl group is described in the following patents: sodium pyrosulfate and pyridine (10); chlorosulfonic acid and pyridine (18); complexes of sulfur trioxide or chlorosulfonic acid with metal chlorides or sulfates (20); dioxane-sulfur trioxide (11); sulfuric acid-urea complex (3); ammonium bisulfate (12); chlorosulfonic acid and ethyl acetate (6); sulfur trioxide-sodium nitrite complex (23).

We were principally concerned in the preparation of substantially pure sodium oleyl sulfate and have found that pyridine-sulfur trioxide is satisfactory for that purpose.

Pyridine-sulfur trioxide was prepared from pyridine and chlorosulfonic acid (19) in a yield of 70%.

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[1] Report of a study in which certain phases were made under the Research and Marketing Act of 1946.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

[3] Presented at the meeting of the American Oil Chemists' Society, Chicago, Ill., in October 1951.

[4] Stabilized liquid sulfur trioxide.

[5] Neutralization equivalent.

Purified oleyl alcohol prepared from commercial oleyl alcohol by fractional vacuum distillation and crystallization from acetone at 0°, —45°, and —10° (22) had an iodine number of 93.6, n_D^{30} 1.4581. The estimated purity was 98%, and the principal impurity was hexadecanol.

Pyridine-sulfur trioxide, 2 moles, and 1.7 moles of oleyl alcohol, were thoroughly stirred together manually for one hour. The reaction was exothermic. The homogeneous paste formed was dissolved in 2,700 ml. of butanol and 450 ml. of water and made slightly alkaline with 18 N sodium hydroxide. The butanol layer was dried azeotropically and filtered hot to remove sodium sulfate. An equal volume of butanol was added, the butanol solution was cooled to 5°C., precipitated sodium oleyl sulfate was filtered off, and adhering solvent was removed in a vacuum oven at 65°C. under a nitrogen atmosphere. Sodium oleyl sulfate was obtained as a hard white mass with a slight yellow cast, in a yield of 70%. Analysis gave the following values: iodine number 67.5, 58.31% C, 9.67% H, 6.38% Na, 8.67% S. The values calculated for $C_{18}H_{35}NaO_4S$ are: iodine number 68.5, 58.35% C, 9.52% H, 6.21% Na, 8.65% S. The estimated purity is 95% or greater. Suspected impurities are small amounts of sodium hexadecyl sulfate, disulfated material, and unsulfated oleyl alcohol or hexadecanol. Storage at room temperature for one year showed no decrease in iodine number or development of peroxides.

Sodium Dodecyl, Tetradecyl, Hexadecyl, and Octadecyl Sulfates

The sodium alkyl sulfates of the saturated alcohols were prepared for comparison. The commercial alcohols were purified by vacuum distillation and low temperature crystallization from acetone. A 10% excess of chlorosulfonic acid was slowly added to a stirred mixture of the alcohol and twice the weight of chloroform at 5-15°C. Stirring was continued for one hour at room temperature, ice and butanol were added, and the mixture was neutralized with aqueous sodium hydroxide. The butanol layer was dried azeotropically, filtered to remove inorganic salts, and the sodium alkyl sulfate was crystallized at room temperature. Analysis for sulfur agreed with the theoretical values.

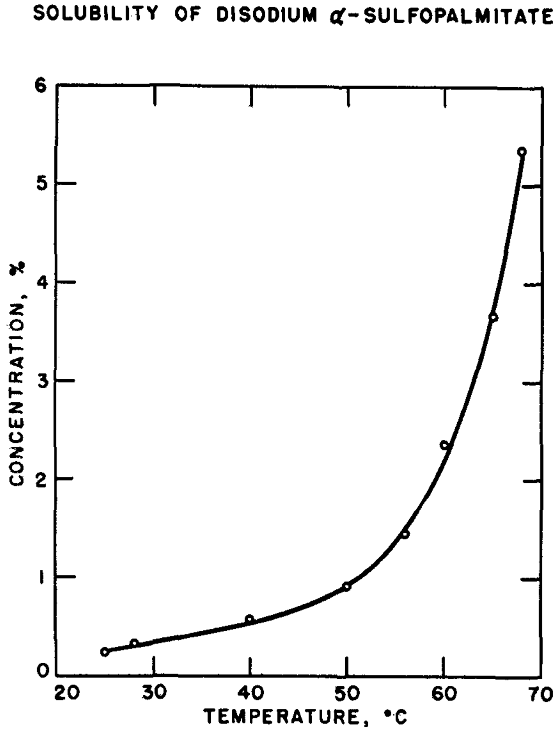

FIG. 1. Solubility of disodium α-sulfopalmitate.

Solubility

Solubility, surface tension, wetting time, foam height, and detergency measurements were made on disodium α-sulfopalmitate, sodium oleyl sulfate, and related compounds.

Figure 1 presents the solubility of disodium α-sulfopalmitate in distilled water. Samples of 0.5-7.0 g. and 100 ml. of water were placed in Ball-Mason jars and rotated three hours at constant temperature in the Launder-Ometer. The contents were filtered rapidly without significant temperature change during filtration, the residue was dried and weighed, and the solubility was calculated. The solubility is fairly low at room temperature (0.25%) but increases rapidly with temperature to 2.36% at 60°C.(140°F.) and 5.36% at 68°C.(154°F.). Disodium α-sulfolaurate and disodium α-sulfomyristate are considerably more soluble, disodium α-sulfostearate is less soluble, and the monosodium salts are less soluble than corresponding disodium salts.

Sodium oleyl sulfate is quite soluble, but the solubility is difficult to measure. A 20% solution forms a clear gel at room temperature. The solubility of sodium alkyl sulfates of the saturated alcohols has been reported by Dreger and co-workers (5).

Surface Tension

The surface tension of aqueous solutions of α-sulfonated compounds and sodium oleyl sulfate was measured at 25°C. at concentrations up to 0.25%, with a DuNoüy tensiometer. The results are presented in Figure 2.

Disodium α-sulfolaurate and disodium α-sulfomyristate hardly exhibit surface active properties in distilled water, but surface tension decreases with

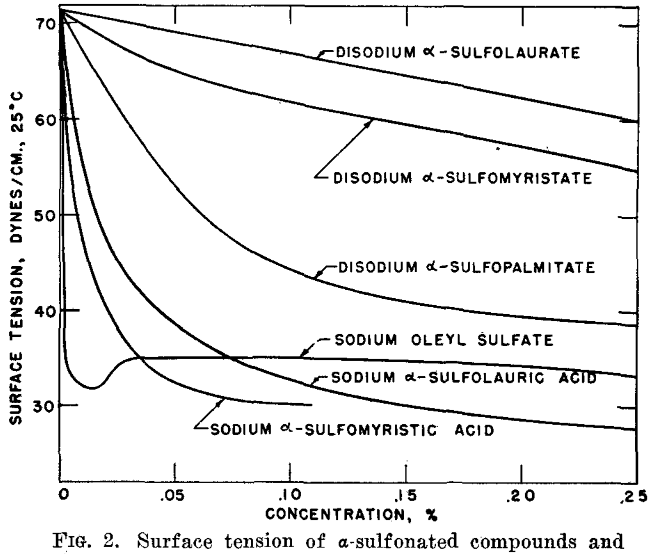

FIG. 2. Surface tension of α-sulfonated compounds and sodium oleyl sulfate.

increase in molecular weight from disodium α-sulfolaurate to disodium α-sulfomyristate and disodium α-sulfopalmitate. The surface tension of the corresponding monosodium salts, sodium α-sulfolauric acid, and sodium α-sulfomyristic acid, is considerably lower. Sodium α-sulfopalmitic acid, disodium α-sulfostearate, and sodium α-sulfostearic acid are not very soluble at 25°C., and surface tension was measured only at low concentrations. The values at 0.01% were 44.4, 55.9, and 44.3 dynes/cm., respectively.

The minimum in the surface tension curve for sodium oleyl sulfate is probably due to impurities.

Wetting Properties

Wetting properties were measured by a tape test method (17), using standard 1¼-inch binding tape, 9 inches long, a 1-g. hook and 40-g. anchor. The time in seconds required for sinking was recorded for concentrations from 0.1 to 0.4% at 30°C. The results are presented in Figure 3.

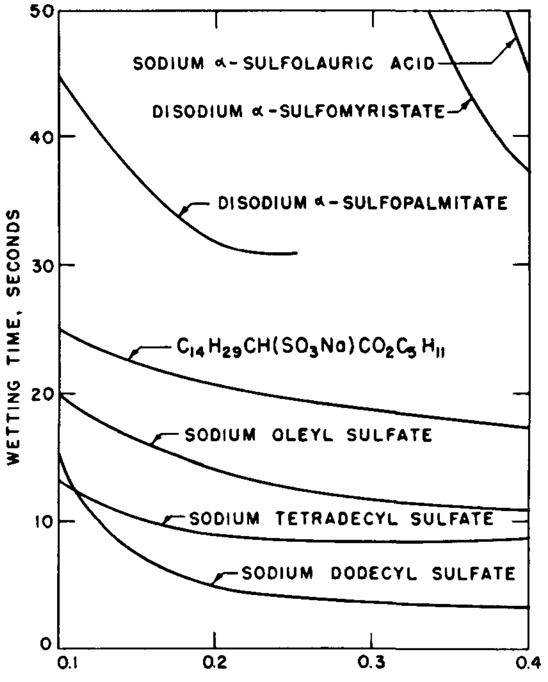

FIG. 3. Wetting properties of α-sulfonated compounds and sodium alkyl sulfates.

Disodium α-sulfolaurate is not a wetting agent in distilled water, disodium α-sulfomyristate has wetting properties in a slight degree, and disodium α-sulfopalmitate is a fair wetting agent, showing improvement with increase in molecular weight. Sodium α-sulfolauric acid is the only one of the four homologous monosodium salts sufficiently soluble to give a wetting time of less than 50 seconds. The amyl ester of the sodium salt of α-sulfopalmitic acid is the best wetting agent of the α-sulfonated compounds.

Sodium dodecyl sulfate is the best wetting agent. In general, wetting properties of sodium alkyl sulfates of the saturated alcohols decrease with increase in molecular weight. At 0.10% the values for sodium hexadecyl sulfate and sodium octadecyl sulfate are 60 and 289 seconds, respectively.

Foam Height

The foam height measurements by the Ross-Miles method (16) at 30 and 60°C. and 0.125 and 0.25% concentration are recorded in Table I. Disodium α-sulfolaurate, disodium α-sulfomyristate, and sodium α-sulfolauric acid have practically no foam under these conditions. The foam height of disodium α-sulfostearate, sodium α-sulfopalmitic acid, and sodium α-sulfostearic acid was not measured because of limited solubility.

TABLE I

Foam Height, cm.

	Temperature, °C.			
	30		60	
	Concentration, %			
	,125	.25	.125	.25
Disodium α-Sulfopalmitate	1	6	2	15
Disodium α-Sulfostearate	....	....	2	....
Sodium α-Sulfomyristic Acid	1	1	13	16
Sodium α-Sulfopalmitic Acid	....	....	1	....
$C_{14}H_{29}CH(SO_3Na)CO_2C_5H_{11}$	9	7	9	10
$C_{14}H_{29}CH(SO_3Na)CO_2NH(C_2H_4OH)_3$	1	3	1	10
Sodium Oleyl Sulfate	16	16	18	18
Potassium Oleyl Sulfate	12	13	14	14

Sodium oleyl sulfate has the highest and most compact and stable foam.

Detergency

Detergency was measured in the Launder-Ometer by washing a 2½ by 3¼-inch piece of G.D.C. No. 26 standard soiled cotton (4) in 100 ml. of detergent solution for 30 minutes at 140°F., in the presence of 30 ¼-inch stainless steel balls. The washed pieces were rinsed in water of the same hardness, partially dried and ironed. Reflectance at 560 mμ relative to magnesium oxide as 100 was measured with a General Electric recording spectrophotometer. The number of replicates was five or greater. Percentage of detergency was calculated from the formula,

$$\%\ D = \frac{\text{R after} - \text{R before}}{\text{R unsoiled} - \text{R before}} \times 100 = \frac{\Delta R \times 100}{88.1 - 18.6} =$$

1.44 ΔR, where ΔR is the increase in reflectance after washing. Pure sodium palmitate had an average percentage of detergency of 73.5 at 0.25% concentration in distilled water. Tables II and III present the order of detergent efficiency, average percentage of detergency and standard error.[6] Detergency tests in a Launder-Ometer with a standard soiled cloth apply to a particular soil removal and are suggestive and not conclusive.

TABLE II

Detergency, 140°F., in Distilled Water

	Order	% D	$\sqrt{\frac{\Sigma(D_i - D)^2}{n(n-1)}}$
.25% Disodium α-Sulfopalmitate	3	52.5	1.12
.125% Disodium α-Sulfopalmitate	6	26.5	1.88
.25% Sodium Dodecyl Sulfate	4	37.6	0.91
.25% Sodium Oleyl Sulfate	1	74.3	1.01
.125% Sodium Oleyl Sulfate	2	66.5	1.07
.25% Commercial Alkylarylsulfonate	5	31.1	1.18
Distilled Water	7	22.5	0.74

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[6] Standard error, $E = \sqrt{\frac{\Sigma(D_i - D)^2}{n(n-1)}}$ where D is the average per cent detergency, D_i the value for an individual experiment, and n the number of replicates.

TABLE III

Detergency, 140°F., in Hard Water

	100 P.P.M.			300 P.P.M.		
	Order	% D	Standard Error	Order	% D	Standard Error
.25% Disodium α-Sulfopalmitate	2	54.8	1.32	1	49.8	1.90
.125% Disodium α-Sulfopalmitate	3	46.0	1.37	4	33.4	1.16
.25% Sodium Dodecyl Sulfate	5	34.1	2.13	6	28.8	1.17
.25% Sodium Oleyl Sulfate	1	67.5	1.34	2	45.6	2.09
.125% Sodium Oleyl Sulfate	4	45.3	0.72	3	39.9	1.53
.25% Commercial Alkylarylsulfonate	6	33.3	1.45	5	30.9	0.95
Hard Water	7	4.5	0.95	7	6.3	0.38

In distilled water solutions (Table II) sodium oleyl sulfate is the best detergent. At 0.125% concentration it is better than 0.25% solutions of disodium α-sulfopalmitate, sodium dodecyl sulfate, and a commercial alkylarylsulfonate. The difference in average percentage of detergency for any pair of the six detergents of Table II is greater than twice the square root of the sum of the squares of the two standard errors, and there is 95% probability that the differences are significant ($D_A - D_B > 2\sqrt{E_A^2 + E_B^2}$) (15). The detergency of disodium α-sulfopalmitate is considerably reduced with decrease in concentration.

In hard water of 100 p.p.m. as calcium carbonate (Table III), sodium oleyl sulfate is the best detergent, at 0.25% concentration. The difference in average percentage of detergency is significant, with 95% probability, for all comparisons except two. The difference in values for 0.125% solutions of disodium α-sulfopalmitate and sodium oleyl sulfate is less than 1.0 and is not significant. This is also true of sodium dodecyl sulfate compared with the commercial alkylarylsulfonate.

In hard water of 300 p.p.m. the difference in average percentage detergency is significant, with 95% probability, for all comparisons except three. The difference is significant with only 80-90% probability in the comparison of disodium α-sulfopalmitate with sodium oleyl sulfate at 0.25% concentration (the two best detergents), and the comparison of the commercial alkylarylsulfonate with sodium dodecyl sulfate and 0.125% disodium α-sulfopalmitate.

Summary

Disodium α-sulfopalmitate and homologous compounds were prepared by sulfonation of the fat acid with liquid sulfur trioxide. Sodium oleyl sulfate was prepared in an estimated 95% purity by sulfation of oleyl alcohol with pyridine-sulfur trioxide. The solubility, surface tension, wetting, foaming, and detergent properties of these and related compounds were measured.

Disodium α-sulfopalmitate is potentially inexpensive, has adequate surface active properties, is a good detergent in hard and soft water, but has limited solubility at room temperature (0.25% at 25°C.). The lauric and myristic homologs are less surface active, but more soluble. Disodium α-sulfostearate is less soluble.

Sodium oleyl sulfate has excellent solubility, and surface active properties and is an excellent detergent in soft water. It is not quite so efficient in hard water although no insoluble calcium salts are formed.

The future of the two compounds will depend upon successful formulation with builders or combinations with soap or other detergents.

Acknowledgment

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