TABLE II

Direct Estimation of Total Monoglycerides with the Aid of Various Catalysts
Reaction Time: 30 min.

Material	Solvent	Catalyst	Amount of catalyst per 100 ml of solution (solvent + periodic acid reagent)	% Total monoglycerides found	% Total monoglycerides by Brokaw et al. technique
2-Monostearin	Chloroform	56% HClO₄	0.2 ml	100.4	98.4
2-Monostearin	Chloroform	56% HClO₄	0.1 ml	76.8	......
1-Monostearin	Chloroform	56% HClO₄	0.1 ml	99.9	99.5
90% 1-Monostearin + 10% 2-monostearin	Chloroform	56% HClO₄	0.1 ml	99.4	99.5
80% 1-Monostearin + 20% 2-monostearin	Chloroform	56% HClO₄	0.1 ml	98.8	98.7
70% 1-Monostearin + 30% 2-monostearin	Chloroform	56% HClO₄	0.1 ml	95.5	99.4
2-Monostearin	Chloroform	Toluene-p-sulfonic acid	0.5 g	98.5	......
2-Monostearin	Chloroform	Magnesium perchlorate	0.3 g	48.4	......
2-Monostearin	Chloroform	Aluminum perchlorate	0.3 g	49.6	......
2-Monostearin	Chloroform	Calcium perchlorate	0.3 g	45.7	......
Technical linseed oil monoglyceride	Chloroform	56% HClO₄	0.1 ml	55.7	47.7
Technical linseed oil monoglyceride	Carbon tetrachloride	56% HClO₄	0.1 ml	47.9	......

of their insufficient solubility in this solvent. Thus the solvent had to be varied according to circumstances.

If the technique is used in conjunction with the Partition method a 50 ml aliquot of the chloroform or carbon tetrachloride solution washed free from glycerol is mixed with 50 ml of the periodic acid reagent containing 0.3% water.

One tenth ml of 56% perchloric acid is added and after 30 min the monoglyceride content is determined as in the Pohle and Mehlenbacher method.

The percentage of total monoglycerides is calculated from the actual consumption of periodic acid without the use of the multiplication factor of 1.15.

Results obtained with some of the catalysts mentioned appear in Table II and the hydrolytic action of perchloric acid is shown in Table III. The isomerizing effect of metallic perchlorates is probably due to their acidic character in the solvent system employed. The continued consumption of periodic acid in the presence of perchloric acid after the oxidation of all 1-monoglycerides seems to indicate that the aldehydic oxidation products are subjected to further oxidation as such or, what is more likely, are hydrolyzed with the subsequent oxidation of the glycolic aldehyde formed.

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TABLE III

Consumption of Periodic Acid by 1-Monostearin in the Presence of Perchloric Acid

Time of reaction (hr)	Moles of periodic acid consumed by 1 mol. of 1-monostearin	
	Addition of 0.2 ml 56% HClO₄ per 100 ml of solution	Control
½	1.02	1.00
1	1.06	1.00
24	1.38	1.01
30	1.63	1.01

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Sodium Salts of Alkyl Esters of a-Sulfo Fatty Acids. Wetting, Lime Soap Dispersion, and Related Properties[1]

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A series of esters of the general formula $RCH(SO_3Na)$-CO_2R' of 14–19 carbon atoms prepared by the a-sulfonation of propionic, butyric, pelargonic, lauric, myristic, palmitic, and stearic acids and esterification with normal primary alcohols were compared for critical micelle concentration, surface and interfacial tension, Ca^{++} stability, wetting properties, foam height, detergency, and lime soap dispersing properties. Comparison of position isomers showed that as the hydrophilic portion moved from the center toward either end, cmc and wetting efficiency decreased, surface and interfacial tension increased, and Ca^{++} stability and lime soap dispersing properties improved.

A coconut oil fatty acid forerun sulfonated with SO_3 vapor and esterified with 2-ethylhexanol gave a product with useful wetting properties in soft and hard water.

SODIUM ALKYL a-sulfopalmitates and stearates have been shown to be useful surface active agents, quite resistant to acid or alkaline hydrolysis (9). A recent investigation of sodium alkyl a-sulfopelargonates has shown that the hexyl, heptyl, capryl, and 2-ethylhexyl esters in particular are superior wetting agents (8). This investigation has been extended to other esters of the same general formula $RCH(SO_3M)CO_2R'$, based on propionic, butyric, lauric, and myristic acids and normal primary alcohols, to better relate structure with useful properties. Sodium alkyl sulfoacetates are related compounds and the dodecyl ester is a commercial surface active agent.

Esters containing from 14 to 19 carbon atoms were prepared and examined for solubility, critical micelle concentration, surface and interfacial tension, Ca⁺⁺ stability, wetting properties, detergency, foam height, and lime soap dispersion properties. An experiment on direct sulfonation of coconut fatty acid foreruns and esterification with 2-ethylhexanol was included.

Sodium n-alkyl a-sulfopropionates and butyrates were prepared through the barium salt of the sulfo fatty acid (2); sodium n-alkyl a-sulfolaurates and myristates by esterification of the isolated a-sulfolauric or myristic acid (12). The examples which follow illustrate the methods.

The sulfonation and esterification of coconut oil fatty acid foreruns is also described. This experiment demonstrates it is possible to sulfonate a mixture of fatty acids directly without use of solvent, to esterify without isolation of the sulfo acids and obtain a useful wetting agent.

Synthesis

Sodium Dodecyl a-Sulfobutyrate. A stirred mixture of 0.1 mole (30.4 g) of barium a-sulfobutyrate, 0.11 mole (20.4 g) of dodecanol, 11 g of concentrated sulfuric acid (0.11 mole H_2SO_4) and 200 ml of toluene was refluxed 3 hr with azeotropic removal of water, and neutralized with alcoholic NaOH. After removal of barium sulfate by filtration and unreacted dodecanol by ether extraction of an aqueous alcohol solution, the extracted solution was evaporated to give sodium dodecyl a-sulfobutyrate in a yield of 63%.

Sodium Ethyl a-Sulfomyristate. A solution of 0.08 mole (25 g) of a-sulfomyristic acid in 200 ml of ethanol was refluxed 6 hr, neutralized with 18 N NaOH, chilled to $-20C$, and filtered. The crude product was taken up in ethanol, a small amount of disodium a-sulfomyristate was removed by filtration, and sodium ethyl a-sulfomyristate was crystallized from aqueous ethanol at $-20C$ in a yield of 62%.

Sodium Salt of 2-Ethylhexyl Ester of a-Sulfonated Coconut Oil Fatty Acids Forerun. The commercial coconut oil fatty acid forerun was a mixture of 42% caprylic, 28% capric, 24% lauric, 6% myristic acid, neutralization equivalent 169.3, with an average composition corresponding to capric acid.

A mixture of sulfur trioxide vapor, 1.12 moles (90 g) and nitrogen, was passed into 0.95 mole (161 g) of the semiliquid forerun at 14C with agitation. The temperature of the viscous reaction mixture reached a maximum of 64C. Toluene and 2-ethylhexanol were added and the sulfonated fatty acids were esterified; water was removed azeotropically. The reaction mixture was neutralized with NaOH and the product was isolated after recovery of solvent as the sodium salt of the 2-ethylhexyl ester of a-sulfonated coconut oil fatty acid forerun. Analysis: calculated for $C_{18}H_{35}NaO_5S$, 5.95% Na, 8.30% S; found: 6.44% Na, 7.61% S.

Properties

The esters, with several of their properties, are listed in Table I, for comparison with pelargonates, palmitates, and stearates. The lower molecular weight n-alkyl a-sulfolaurates and myristates, like the sodium alkyl a-sulfopalmitates and stearate (11), have definite melting points. From analyses for sodium (or potassium) and sulfur the average deviation from the cal-

TABLE I
Surface Active Properties

RCH(SO₃M)CO₂R'	R	R'	Number of C atoms R+R'+2	mp	cmc [a] millimoles per liter	Surface and interfacial tension 0.2%, 25C dynes/cm		Ca⁺⁺ stability (14) ppm	Wetting time (5) 0.1%. 25C seconds		Lime soap dispersion power (3)%
						S.T.	I.T.		Distilled water	300 ppm	
Na decyl a-sulfobutyrate	2	10	14	....[b]	9.6	36.9	13.7	>1800	9.9	8.1	>100
Na amyl a-sulfopelargonate	7	5	14	....[b]	15.6	40.3	18.9	630	12.1	5.3	>100
Na ethyl a-sulfolaurate	10	2	14	118.0–119.2°	7.8	31.9	7.9	>1800	10.5	5.4	>100
Na dodecyl a-sulfopropionate	1	12	15	....[b]	3.2	38.6	10.2	>1800	5.6	4.8	22
Na hexyl a-sulfopelargonate	7	6	15	....[b]	6.9	26.8	7.1	360	2.2	1.4	65
Na propyl a-sulfolaurate	10	3	15	52.6–53.4°	5.3	35.5	9.5	>1800	3.2	2.0	40
Na methyl a-sulfomyristate	12	1	15	125.0–126.0°	2.8	39.9	10.9	>1800	12.5	6.5	9
Na dodecyl a-sulfobutyrate	2	12	16	....[b]	1.9	36.8	9.1	>1800	5.5	4.4	14
Na heptyl a-sulfopelargonate	7	7	16	....[b]	4.5	26.6	5.7	440	0	3.0	27
Na butyl a-sulfolaurate	10	4	16	94.4–95.0°	2.8	33.8	8.7	730	1.6	1.5	22
Na ethyl a-sulfomyristate	12	2	16	118.0–119.2°	1.9	36.9	10.1	>1800	6.7	5.0	8
Na tetradecyl a-sulfopropionate	1	14	17	....[b]	0.77	35.7	7.8	>1800	8.8	12.2	8
Na octyl a-sulfopelargonate	7	8	17	....[b]	2.1	25.7	4.5	500	1.3	10.8	14
Na amyl a-sulfolaurate	10	5	17	....[b]	1.7	31.1	6.9	500	1.6	4.9	11
Na propyl a-sulfomyristate	12	3	17	55.0–55.8°	1.1	35.6	8.5	>1800	5.0	3.8	9
Na methyl a-sulfopalmitate	14	1	17	180.9–182.8°	0.4	39.0	9.7	>1800	25.0	15.5	9
Na tetradecyl a-sulfobutyrate	2	14	18	....[b]	0.45	34.8	6.9	>1800	15.1	17.3	8
Na nonyl a-sulfopelargonate	7	9	18	195° dec.	1.2	25.4	3.8	500	3.8	33.0	8
Na salt of 2-ethylhexyl ester of a-sulfo coconut f.a. forerun	8	8	18	....	....	25.3	1.5	500	3.5	8.7	15
Na hexyl a-sulfolaurate	10	6	18	....[b]	0.87	28.1	4.6	570	2.2	40.0	10
K butyl a-sulfomyristate	12	4	18	168.0–168.8°	0.63	31.6	4.5	500	4.8	5.2	9
Na ethyl a-sulfopalmitate	14	2	18	95.2–96.7°	0.34	36.4	8.0	>1800	12.0	36.0	8
K hexadecyl a-sulfopropionate	1	16	19	....[b]	0.22	35.5	5.3	900	58.0	>300	8
Na decyl a-sulfopelargonate	7	10	19	....[b]	0.49	25.0	3.0	610	6.0	105.0	9
Na heptyl a-sulfolaurate	10	7	19	....[b]	0.50	24.5	2.1	620	17.1	72.0	10
Na amyl a-sulfomyristate	12	5	19	53.2–54.0°	0.34	31.5	4.9	700	6.1	30.0	9
Na propyl a-sulfopalmitate	14	3	19	63.3–65.1°	0.26	35.0	6.5	>1800	21.9	17.2	8
Na methyl a-sulfostearate	16	1	19	179.8–180.0°	0.08	39.0	8.4	800	47.0	91.0	9

[a] Critical micelle concentration, Pinacyanole Chloride method (4).
[b] No definite mp below 200C.

culated values was 0.12% in sodium (or potassium) and 0.13% in sulfur.

Solubility. The aqueous solubility of the esters listed in Table I ranged from 1% to 20% or greater except that the solubility of sodium decyl α-sulfopelargonate and potassium hexadecyl α-sulfopropionate was only about 0.5% at room temperature.

Most of the esters easily form 10% solutions in ethanol, chloroform, and petroleum ether but methyl esters and the propionates and butyrates are not very soluble in petroleum ether. Only eight esters of Table I are soluble to the extent of 5–10% or more in mineral oil: sodium tetradecyl α-sulfopropionate, sodium decyl α-sulfobutyrate, sodium decyl α-sulfopelargonate, sodium amyl, hexyl and heptyl α-sulfolaurates, sodium butyl α-sulfomyristate and potassium amyl α-sulfomyristate. Solubility in mineral oil increases with molecular weight and esters of 20 carbon atoms or more, such as sodium octyl α-sulfolaurate, sodium hexyl α-sulfomyristate, and sodium hexyl α-sulfopalmitate (not shown in Table I) form 10% solutions.

Critical Micelle Concentration. The critical micelle concentration, cmc, was measured by the pinacyanole chloride method (4). These values should be considered preliminary until corroborated by other methods such as surface tension and conductivity. A plot of the values for the pelargonates (8) as log cmc against the total number of carbon atoms has given a straight line with slope −.30 about equal to minus the logarithm of 2 (7).

Values for the propionates, butyrates, laurates, and myristates gave straight lines but with slopes of −.29, −.33, −.24, −.23, respectively.

Values for the sodium methyl, ethyl, propyl, and amyl α-sulfo esters of Table I gave straight lines with slopes of −.39, −.34, −.33, −.33, respectively.

The cmc is a function of the number of carbon atoms and the position of the hydrophilic portion in the molecule. The more symmetrical molecules, the pelargonates, and also sodium heptyl α-sulfolaurate have the highest cmc in the particular group of isomers.

Surface and Interfacial Tension. Surface and interfacial tension of 0.2% solutions in distilled water at 25C were measured with the duNoüy tensiometer. Pelargonates and laurates gave the lowest values.

Calcium Stability. Calcium stability measured on 0.5% solutions by a modified Hart method (14) ranged from about 400 to >1800 ppm as CaCO$_3$. The less symmetrical compounds have greater calcium stability.

Wetting Time. Wetting time was measured by the Draves test (5) on 0.10% solutions in distilled water and in hard water of 300 ppm at 25C using a 5 g cotton skein and 3 g hook. These values are shown in Table I and graphs of wetting time against concentration for representative esters are shown in Figures 1 and 2. Esters of 15–17 carbon atoms are the best wetting agents. Wetting time in seconds at 0.05 and 0.10% concentration for the six most efficient wetting agents in soft and hard water is shown in Table II.
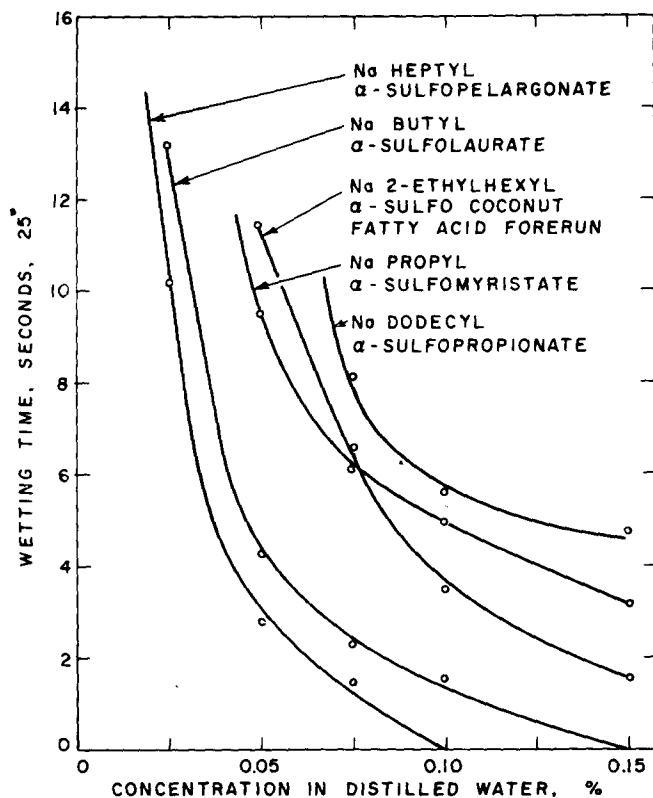
Foam Height. The foam height of 0.25% solutions

FIG. 1. Wetting time vs. concentration, distilled water.

in distilled water and in hard water of 300 ppm was measured by the Ross-Miles test at 60C (1). Most of the esters of 15–18 carbon atoms had initial foam in soft and hard water of 200–240 mm; esters of 19 carbon atoms had lower foam in hard water.
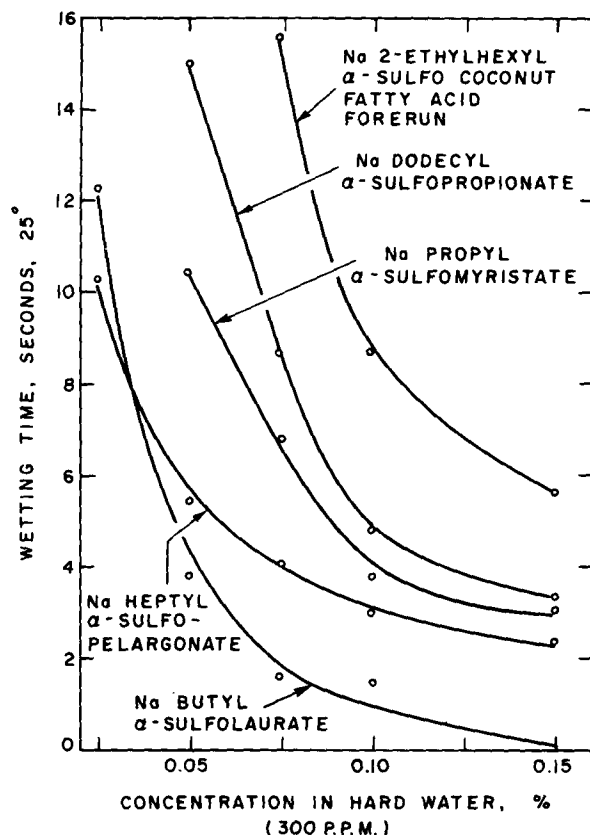

FIG. 2. Wetting time vs. concentration, hard water.

TABLE II
Wetting Agents

n-Alkyl esters RCH(SO₃Na)CO₂R'	Wetting time, seconds			
	Distilled water		300 ppm	
	0.05%	0.10%	0.05%	0.10%
Na hexyl α-sulfopelargonate	12.0	2.2	4.6	1.1
Na dodecyl α-sulfobutyrate	13.0	5.5	10.0	4.4
Na heptyl α-sulfopelargonate	2.8	0	5.5	3.0
Na butyl α-sulfolaurate	4.3	1.6	3.8	1.5
Na amyl α-sulfolaurate	4.2	1.6	8.9	4.9
Na propyl α-sulfomyristate	9.5	5.0	11.0	3.8

Esters with high stable foam in soft and hard water are shown in Table III.

Detergency. Detergency was measured as the increase in reflectance after washing G.D.C. No. 26 standard soiled cotton (6) in 0.25% solutions in the Launder-Ometer at 60C. The α-sulfomyristates, palmitates and stearates, and the tetradecyl and hexadecyl α-sulfopropionates were the best detergents.

TABLE III
Foaming Properties

0.25% Solutions, 60C	Foam height, mm	
	Distilled water	300 ppm
Na dodecyl α-sulfobutyrate	200	225
Na butyl α-sulfolaurate	220	230
Na tetradecyl α-sulfopropionate	220	240
Na amyl α-sulfolaurate	220	235
Na methyl α-sulfopalmitate	210	225
Na ethyl α-sulfopalmitate	210	215

The $\triangle$R values in soft and hard water are listed in Table IV for the best detergents in comparison with sodium dodecyl sulfate and sodium octadecyl sulfate as reference standards.

Lime Soap Dispersion Power. The per cent lime soap dispersion power was determined by the method of Borghetty and Bergman (3) as the number of g required to disperse the calcium soap formed from 100 g of sodium oleate. This value is recorded in Table I.

TABLE IV
Detergency

0.25% Solution, 60C	Detergency, △R	
	Distilled water	300 ppm
Na methyl α-sulfomyristate	32	16
Na ethyl α-sulfomyristate	32	15
Na tetradecyl α-sulfopropionate	32	16
Na methyl α-sulfopalmitate	31	17
K butyl α-sulfomyristate	32	16
Na ethyl α-sulfopalmitate	31	21
K hexadecyl α-sulfopropionate	34	23
Na methyl α-sulfostearate	31	21
Na dodecyl sulfate	28	24
Na octadecyl sulfate	38	32

Esters of 14 carbon atoms have no lime soap dispersion properties under these conditions. With esters of 15 to 17 carbon atoms the least symmetrical are the best agents; esters of 18 and 19 carbon atoms are about equal in lime soap dispersion. The best detergents listed above are also good lime soap dispersing agents.

Lime soap dispersion properties increase with the number of carbon atoms and the dissymmetry of the ester. They are also influenced by the length of the fatty acid chain since with the 15 and 16 carbon esters sodium methyl and ethyl α-sulfomyristates are better lime soap dispersion agents than sodium dodecyl α-sulfopropionate and butyrate.

For comparison, other α-sulfo compounds, disodium 2-sulfoethyl α-sulfopalmitate, disodium 2-sulfoethyl α-sulfostearate (11), sodium N-hydroxyethyl-α-sulfo-palmitamide, and sodium N-hydroxyethyl-α-sulfoste-

aramide are somewhat better agents with lime soap dispersion values of 5%.

Structure and Properties

The esters listed in Table I are divided into groups of position isomers of 14 to 19 carbon atoms. With minor exceptions, as the $-CH(SO_3M)CO_2-$ group which contains the hydrophilic portion is moved from the center position toward either end the cmc falls, surface and interfacial tension increase, calcium stability improves, wetting time increases, and lime soap dispersion power improves or remains about the same.

In each group of the same number of carbon atoms there are position isomers which are counterparts, with R and R' interchanged. A comparison shows such counterparts to be quite similar in properties.

The counterparts in the 15 carbon esters, sodium dodecyl α-sulfopropionate and sodium methyl α-sulfo-myristate have quite similar properties except that the myristate is a better detergent and lime soap dispersing agent. The counterparts in the 16 carbon esters, sodium dodecyl α-sulfobutyrate and sodium ethyl α-sulfomyristate are remarkably similar in properties except that again the myristate is a better detergent and lime soap dispersing agent.

With the 17, 18, and 19 carbon esters the similarity in the properties of counterparts, the first and the last ester of each group, continues but is not as marked. There is however a second pair of counterparts in the 19 carbon esters, sodium decyl α-sulfopelargonate and sodium heptyl α-sulfolaurate, and these are remarkably similar in the values for cmc, surface and interfacial tension, calcium stability, and foam height (240 mm in distilled water, 30 mm in hard water) but differ somewhat in wetting properties.

Acknowledgment

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