followed in the preparation of fat emulsions suitable for intravenous nutrition. Such emulsions contain 10-15% oil (w/v) dispersed in particles less than one micron in diameter. They are made under nitrogen and subsequently autoclaved to ensure sterility.

Procedures are also given for screening each batch of emulsion by means of tests performed on rats, dogs, and rabbits. Emulsions of the type described have found extensive application in the clinic with a low incidence of unfavorable reactions.

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Synthetic Detergents from Animal Fats. V. Esters from Alpha-Sulfonated Fatty Acids and Sodium Isethionate[1]

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ISETHIONATE ESTERS of fatty acids, of the Igepon A type, particularly the ester of oleic acid, $CH_3(CH_2)_7CH = CH(CH_2)_7CO_2C_2H_4SO_3Na$, are well known surface active agents and detergents. The usefulness of this type has been somewhat limited because of instability to hydrolysis.

The presence of an α-sulfo group in esters, such as sodium methyl α-sulfopalmitate and sodium isopropyl α-sulfostearate, has been shown to retard hydrolysis, to a surprising degree, in acid and alkaline solutions (9). It was thus of interest to prepare and evaluate esters from α-sulfonated acids and hydroxyalkanesulfonates, such as sodium isethionate. The esters might be expected to have the desirable surface-active and detergent properties of sodium 2-sulfoethyl oleate and perhaps to be of greater potential usefulness because of greater resistance to hydrolysis.

Preparation of Esters

Esters were prepared from the diacid (α-sulfopalmitic, α-sulfostearic, or α-sulfobehenic acid) and sodium isethionate or sodium 2-hydroxypropanesulfonate, by a method previously described (10), without the use of an esterification catalyst.

α-Sulfopalmitic acid. Stabilized liquid sulfur trioxide, 1.25 moles, was added dropwise in 30 min. to a stirred slurry of 0.78 moles of purified palmitic acid in 500 ml. of carbon tetrachloride. The mixture was stirred and heated 1 hr. at 60-65°, cooled to —15°, and filtered. The diacid was washed with cold carbon tetrachloride and dried in a vacuum desiccator at room temperature to give a gray product in a yield of 85%. Analysis: calculated for $C_{16}H_{32}O_5S$, neutralization equivalent 168.2; found, 167.3.

α-Sulfostearic acid. A diacid was prepared from purified stearic acid in a similar manner in a yield of 88%. Analysis: calculated for $C_{18}H_{36}O_5S$, neutralization equivalent 182.3; found, 183.3.

α-Sulfobehenic acid. Commercial behenic acid was purified by two crystallizations from acetone to give behenic acid, m.p. 79.0-79.6°, neutralization equivalent 340.3 (calculated, 340.6). Reaction with sulfur trioxide gave α-sulfobehenic acid, yield 97%, neutralization equivalent 196.2 (calculated for $C_{22}H_{44}O_5S$, 210.3).

Disodium 2-sulfoethyl α-sulfostearate. A mixture of 0.2 mole of α-sulfostearic acid, 0.207 mole of sodium isethionate, and 250 ml. of toluene was stirred and heated at reflux temperature for 6 hrs., with azeotropic removal of water. The reaction mixture was cooled, diluted with 200 ml. of 95% ethanol and neutralized with 18 N sodium hydroxide. Solvent and water removal left 103 g. of light brown product, which was dissolved in hot water. The aqueous solution was cooled, and unesterified diacid was removed as the sparingly soluble sodium salt. Ethanol was added to give a 75% ethanol solution, which was decolorized with carbon. Two crystallizations from 75% ethanol at —15° gave $C_{16}H_{33}CH(SO_3Na)CO_2C_2H_4SO_3Na$ as a white product in a yield of 66%. Analysis: calculated for $C_{20}H_{38}Na_2O_8S_2$, 46.49% C, 7.41% H, 8.90% Na, 12.41% S; found, 46.36% C, 7.44% H, 8.82% Na, 11.95% S.

Disodium 2-sulfoethyl α-sulfopalmitate. Esterification of α-sulfopalmitic acid with sodium isethionate in a similar manner gave $C_{14}H_{29}CH(SO_3Na)CO_2C_2H_4SO_3Na$ as a white product. Analysis: calculated for $C_{18}H_{34}Na_2O_8S_2$, 44.25% C, 7.01% H, 9.41% Na, 13.13% S; found, 44.12% C, 6.90% H, 9.38% Na, 12.78% S.

Disodium 2-sulfoethyl α-sulfobehenate. Esterification of α-sulfobehenic acid with sodium isethionate gave

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TABLE I

Surface Active Properties of Disodium 2-Sulfoalkyl α-Sulfopalmitates, Stearates, and Behenates

	Surface and Interfacial Tension, 0.25% solutions in distilled water, 25°, dynes/cm.		Ca Stability, p.p.m., $CaCO_3$ (11)	Lime Soap Dispersing Power, % (2)	Foam Height, 0.25% solutions in 300 p.p.m., 60° immediate, mms. (7)	Sinking Time, 0.1% solutions in distilled water, 25°, secs. (8)
	S.T.	I.T.				
Disodium 2-sulfoethyl α-sulfopalmitate	35.2	9.8	>1800	5[a]	202	134
Disodium 2-sulfoethyl α-sulfostearate	35.8	11.6	>1800	5[a]	223	102
Disodium 2-sulfoethyl α-sulfobehenate	44.8	13.0	>1800	5[a]	123	201
Disodium 1-methyl-2-sulfoethyl α-sulfostearate	46.9	14.5	....	....	....	....

[a] 0.00125 g. dispersed the Ca soap formed from 0.025 g. of Na oleate.

$C_{20}H_{41}CH(SO_3Na)CO_2C_2H_4SO_3Na$ as a white product. Analysis: calculated for $C_{24}H_{46}Na_2O_8S_2$, 8.03% Na, 11.20% S; found, 7.95% Na, 11.30% S.

Disodium 1-methyl-2-sulfoethyl α-sulfostearate. A mixture of 0.156 mole of sodium 2-hydroxypropanesulfonate (m. p. 225°, prepared by the method of Lambert and Rose [6]), 0.146 mole of α-sulfostearic acid, and 300 ml. of xylene was heated and stirred 12 hrs. at reflux temperature; $C_{16}H_{33}CH(SO_3Na)CO_2CH(CH_3)CH_2SO_3Na$ was isolated as a white product. Analysis: calculated for $C_{21}H_{40}Na_2O_8S_2$, 47.53% C, 7.60% H, 8.67% Na, 12.09% S; found, 47.48% C, 7.60% H, 8.51% Na, 11.47% S.

Surface-Active Properties

Surface and interfacial tension, calcium stability, lime soap dispersing power, foaming and wetting properties, stability to metal ions, detergency, and stability to hydrolysis were measured. Values for some of these surface active properties are shown in Table I.

Solutions of the esters in distilled water did not give markedly low surface or interfacial tension values. High calcium stability values show the esters can be used in very hard water. Lime soap dispersion was excellent and about equal to that of sodium 2-sulfoethyl oleate and of sodium N-methyl-N-oleoyl taurate. This behavior suggests the possibility of favorable combinations with soap. The immediate foam height, fairly high for two of the esters, fell to about 50 mm. in 5 min. The esters were not very effective wetting agents in distilled water solutions.

Metallic ion stability measurements by the method of Harris (4) gave values of 100 for Mg^{++}, Al^{+++}, Ca^{++}, Fe^{++}, Ni^{++}, Cu^{++}, Zn^{++}, and Pb^{++} but values of 25-30 for Ba^{++} for disodium 2-sulfoethyl α-sulfopalmitate and disodium 2-sulfoethyl α-sulfostearate. The esters are therefore not precipitated under the test conditions except in the presence of Ba^{++}.

Disodium 2-sulfoethyl α-sulfopalmitate and disodium 2-sulfoethyl α-sulfostearate are easily soluble because of the presence of two sulfo groups and readily form solutions of about 20% concentration at 25°. Disodium 2-sulfoethyl α-sulfobehenate is soluble to the extent of about 0.5% at 25°.

Detergency

Detergency was measured in the Terg-O-Tometer, washing 10 swatches of A.C.H. No. 114[3] standard soiled cotton in 1 liter of detergent solution for 20 min. at 60°, 110 cycles per minute. Detergency was expressed as the increase in reflectance, △R, after washing. The results in 300 p.p.m. hard water are shown in Table II. A difference in △R values of 0.8 was significant with at least 95% probability.

The detergency of disodium 2-sulfoethyl α-sulfostearate was considerably improved by builder A, representative of that used in the formulation of Teepol (1), and by builder B, similar to that used in experiments with sulfated tallow alcohols (5). Disodium 2-sulfoethyl α-sulfopalmitate was improved by B, but not by A. Mixtures of the two esters (I and II), such as could be made from the saturated acids of tallow, responded favorably to building. Disodium 2-sulfoethyl α-sulfobehenate, and sodium 2-sulfoethyl oleate, were also improved detergents in the presence of builders.

TABLE II

Detergency of Disodium 2-Sulfoethyl α-Sulfopalmitates, Stearates, and Behenates

Terg-O-Tometer, 20 min. at 60°, 110 cycles/min., 10 swatches, A.C.H. No. 114 per l.; hard water of 300 p.p.m. (as $CaCO_3$)

	Detergency, △R		
Total detergent concn., %	0.05	0.10	0.25
Disodium 2-sulfoethyl α-sulfostearate (I)	27.1	29.2	29.7
0.10% I + 0.15% A[a]	......	......	34.1
0.10% I + 0.15% B[b]	......	......	37.9
0.05% I + 0.20% A	......	......	35.1
0.05% I + 0.20% B	......	......	34.2
Disodium 2-sulfoethyl α-sulfopalmitate (II)	24.4	26.9	29.8
0.05% II + 0.20% A	......	......	23.7
0.05% II + 0.20% B	......	......	27.2
0.05% I + 0.05% II	......	28.4	......
0.05% I + 0.05% II + 0.15% A	......	......	33.9
0.025% I + 0.025% II	27.1	......	......
0.025% I + 0.025% II + 0.20% A	......	......	34.0
Disodium 2-sulfoethyl α-sulfobehenate (III)	26.5	27.1	......
0.05% III + 0.20% B	......	......	35.4
Sodium 2-sulfoethyl oleate[c] (IV)	......	18.3	27.7
0.05% IV + 0.20% A	......	......	33.0
Sodium dodecyl sulfate	......	......	25.4

[a] Builder A: Na_2SO_4 71.11%, $Na_5P_3O_{10}$ 8.33, $Na_4P_2O_7$ 8.33, $NaBO_3.4H_2O$ 5.56, Na metasilicate 5.56, CMC 1.11.

[b] Builder B: $Na_5P_3O_{10}$ 55%, Na_2SO_4 24, $Na_4P_2O_7$, 10, Na metasilicate 10, CMC 1.

[c] Isolated active ingredient from a commercial product. Analysis: calculated for $C_{20}H_{37}NaO_5S$, saponification equivalent 412.6, iodine no. 61.5, 5.57% Na, 7.77% S; found, 413.0, 58.1, 5.69, 7.40, respectively.

The best detergent compositions of Table II were those containing disodium 2-sulfoethyl α-sulfostearate or disodium 2-sulfoethyl α-sulfobehenate as the active ingredient. The detergency of sodium dodecyl sulfate was measured for comparison.

Similar response to building was shown in washing experiments with G.D.C. No. 26 (3) standard soiled cotton.

Stability to Hydrolysis

The rate of acid hydrolysis of sodium methyl α-sulfopalmitate and disodium 2-sulfoethyl α-sulfopalmitate was measured by heating 0.01 mole of the ester in 100 ml. of N/3 sulfuric acid at 100° and by titrating 10-ml. samples at selected intervals (Table III). The rate was found to correspond to a first order reaction; the simple methyl ester was a little more

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[3] American Conditioning House Inc. Mention of a particular test cloth does not constitute recommendation by the U. S. Department of Agriculture over similar products not mentioned.

TABLE III

Rate of Hydrolysis[a] of Sulfonated Esters at 100°

	Acid Hydrolysis in N/3 H_2SO_4, k_1[b]	Alkaline Hydrolysis, k_2[c]
Disodium 1-methyl-2-sulfoethyl α-sulfostearate	....	0.13
Sodium methyl α-sulfopalmitate	0.0047	0.14
Disodium 2-sulfoethyl α-sulfopalmitate	0.0051	1.0
Sodium 2-sulfoethyl oleate[d]	Too rapid to measure accurately	4.3

[a] Rate constants shown are averages of 3 to 4 measurements made in the concentration range where x is 0 to 0.05.

[b] k_1 = first order rate constant = 1/t 1n a/a–x, in reciprocal minutes.

[c] k_2 = second order rate constant $= \frac{1}{t} \frac{x}{a(a-x)}$, in liters · moles^{-1} · minutes^{-1}.

[d] Isolated active ingredient from a commercial product.

stable to hydrolysis. The hydrolysis of sodium 2-sulfoethyl oleate was too rapid for accurate measurement under these conditions.

The rate of alkaline hydrolysis was measured by heating 0.01 mole of the ester in 100 ml. of 0.1 N sodium hydroxide at 100° and titrating 10 ml. samples at selected intervals. Alkaline hydrolysis was found to correspond to a second order reaction. Disodium 1-methyl-2-sulfoethyl α-sulfostearate, an ester of a secondary alcohol, was about as stable to hydrolysis as the simple methyl ester, which in turn was seven times as stable as disodium 2-sulfoethyl α-sulfopalmitate. The least stable ester, sodium 2-sulfoethyl oleate, was hydrolyzed about four times as fast as disodium 2-sulfoethyl α-sulfopalmitate. The isethionate esters of α-sulfo acids are therefore considerably more stable to hydrolysis, in acid and alkaline solutions, than isethionate esters of fat acids.

Summary

Disodium 2-sulfoethyl α-sulfopalmitate, disodium 2-sulfoethyl α-sulfostearate, and disodium 2-sulfoethyl α-sulfobehenate were prepared by esterification of the corresponding α-sulfonated acid with sodium isethionate. Disodium 1-methyl-2-sulfoethyl α-sulfostearate was made from sodium 2-hydroxypropanesulfonate. The esters were found to be readily soluble surface-active agents and detergents, very responsive to building with inorganic phosphates and sulfates.

Compared to sodium 2-sulfoethyl oleate the esters were readily prepared without the necessity of making the acid chloride; they were considerably more resistant to acid or alkaline hydrolysis; they were about equal in their excellent lime soap dispersing power, but inferior in foaming properties, producing a less permanent foam.

The esters were easily soluble because of the presence of two sulfo groups and were improved detergents in the presence of inorganic builders. Mixtures of the palmitic and stearic acid derivatives, such as might be obtained from the saturated acids of tallow, containing a total of 20% active ingredient, were effective detergents in hard water.

Disodium 1-methyl-2-sulfoethyl α-sulfostearate, an ester of a secondary alcohol, was even more resistant to alkaline hydrolysis than the esters from sodium isethionate.

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ABSTRACTS . . . . **R. A. Reiners, Editor**

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor
Sin'itiro Kawamura, Abstractor

Formation and structure of butter manufactured by Meleshin process. A. Zheltakov. *Molochnaya Prom.* **15**(6), 23–5(1954). The factors responsible for the emulsion reversal in Meleshin-made butter from fat-in-water to water-in-fat and the resulting structure of butter are discussed. (*C. A.* **49**, 529)

Spectrophotometric study of rancidity in oils. J. P. Wolff. *Parfumerie mod.* **46**, 53–61(1954). Spectrophotometry can be used to examine those oils whose rancidity causes formation of conjugated double bonds. This study is a review of such work done on linoleates, oleates, and olive, peanut, and almond oil. (*C. A.* **49**, 5004)

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Determination of summary tocopherols (vitamin E) in plant products. B. G. Savinov and G. M. Lushchevskaya. *Ukrain. Khim Zhur.* **18**, 540–6(1952). A method based on the reaction of 2,2′-dipyridyl with $FeCl_2$ is described. (*C. A.* **48**, 5257)

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