Surface-Active Properties of Salts of Alpha-Sulfonated Acids and Esters[1]

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SULFONATION of the saturated fat acids of tallow, palmitic, and stearic acids, with sulfur trioxide, has been shown to take place in the α-position and only monosulfonation occurs (15). The reaction appears to be as specific as α-bromination by the Hell-Volhard-Zelinskiĭ reaction. The preparation and the detergent properties of disodium α-sulfopalmitate, in particular, have been described (13). The simplicity and the inexpensive nature of the α-sulfonation process has encouraged a further step in synthesis, the esterification of the carboxyl group, and a study of the properties of the salts of α-sulfonated acids and esters which would indicate their possible use.

Salts of α-Sulfonated Acids

The properties of the mono- and disodium salts of α-sulfonated lauric, myristic, palmitic, and stearic acids have been further examined.

Solubility. The solubility of eight sodium salts is shown in Figure 1. Solubility was conveniently measured, using the Launder-Ometer as a constant temperature bath (13). Solubilities below room temperature were measured by storing samples in a refrigerator at selected temperatures. A considerable difference in the solubility of the eight salts is evident.

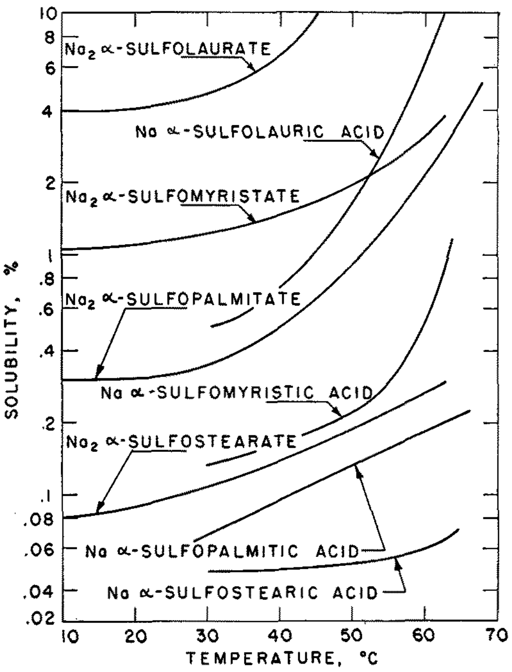

FIG. 1. Solubility of 8 sodium salts.

Detergency. The detergency of 0.25% solutions of each of the eight salts in distilled water and in hard water of 100 and 300 p.p.m., expressed as $CaCO_3$, was measured, using G.D.C. No. 26 standard soiled cotton (2). The conditions were as follows: Launder-Ometer, 30 minutes at 60°, 100 ml. of solution, 30¼-in. diameter stainless steel balls, one 2½ x 3¼-in. swatch per jar, 10 replicates; Terg-O-Tometer, 20 minutes at 60°, 550 ml. of solution, 110 cycles per minute, 6 swatches per beaker, load ratio 0.01 g./ml., 6 replicates.

Reflectance of the test cloth before and after washing, relative to MgO as 100, was measured with a Photovolt Reflection Meter, Model 610, using a green tristimulus filter. The percent detergency was calculated from the expression

$$D = \frac{\text{R after} - \text{R before}}{\text{R unsoiled} - \text{R before}} \times 100 = \frac{100\,\Delta\,\text{R}}{81.0 - 20.1}$$

The results are presented in Tables I and II. From calculations of the standard error and the value for t (8) it was found that the differences in D values were significant, with 95% probability, except in the comparisons bracketed.

TABLE I

Detergency of 8 Salts of α-Sulfonated Acids, Compared to Sodium Palmitate

Launder-Ometer: 0.25% concentration in distilled water, 30 minutes at 60°

	Abbreviation	D
Sodium palmitate		69.4
Disodium α-sulfostearate	$Na_2\alpha SS$	57.7
Sodium α-sulfomyristic acid	$Na\alpha SMA$	56.6
Sodium α-sulfopalmitic acid	$Na\alpha SPA$	55.6
Disodium α-sulfopalmitate	$Na_2\alpha SP$	49.5
Sodium α-sulfostearic acid	$Na\alpha SSA$	46.4
Disodium α-sulfomyristate	$Na_2\alpha SM$	26.1
Sodium α-sulfolauric acid	$Na\alpha SLA$	23.9
Disodium α-sulfolaurate	$Na_2\alpha SL$	19.2
Distilled water		11.8

TABLE II

Detergency of 8 Salts of α-Sulfonated Acids in Hard Water

Launder-Ometer: 0.25% concentration, 30 minutes at 60°

100 P.P.M.	D	300 P.P.M.	D
$Na_2\alpha SS$	64.3	$Na_2\alpha SS$	62.0
$Na\alpha SPA$	60.7	$Na_2\alpha SP$	57.1
$Na\alpha SSA$	60.0	$Na\alpha SPA$	53.5
$Na_2\alpha SP$	59.5	$Na\alpha SSA$	51.8
$Na\alpha SMA$	55.1	$Na\alpha SMA$	43.3
$Na_2\alpha SM$	24.6	$Na\alpha SLA$	23.9
$Na\alpha SLA$	23.1	$Na_2\alpha SM$	23.6
$Na_2\alpha SL$	11.8	$Na_2\alpha SL$	17.5

Terg-O-Tometer: 0.25% concentration, 20 minutes at 60°

100 P.P.M.	D	300 P.P.M.	D
$Na\alpha SPA$	65.9	$Na_2\alpha SS$	63.6
$Na_2\alpha SS$	63.6	$Na_2\alpha SP$	62.2
$Na_2\alpha SP$	60.2	$Na\alpha SSA$	58.7
$Na\alpha SSA$	57.9	$Na\alpha SPA$	55.8
$Na\alpha SMA$	57.7	$Na\alpha SMA$	47.7
$Na_2\alpha SM$	25.6	$Na_2\alpha SM$	28.9
$Na\alpha SLA$	16.2	$Na\alpha SLA$	26.4
$Na_2\alpha SL$	12.6	$Na_2\alpha SL$	21.2

Thus, in Table I, disodium α-sulfostearate, sodium α-sulfomyristic acid, and sodium α-sulfopalmitic acid were considered equal in detergency and the best of

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the eight salts; the next best detergents were disodium α-sulfopalmitate and sodium α-sulfostearic acid.

The Launder-Ometer and the Terg-O-Tometer methods did not place the salts in exactly the same order. Disodium α-sulfostearate was the best detergent in most cases, and, in general, the less soluble salts were the better detergents. Disodium α-sulfolaurate, the most soluble salt, in all cases had the least detergency. Sodium α-sulfolauric acid and disodium α-sulfomyristate were also easily soluble salts with poor detergency.

The surface active properties of 10 salts of α-sulfonated acids are summarized in Table III. Disodium α-sulfolaurate, and perhaps disodium α-sulfomyristate as well, resemble simple electrolytes with little evidence of surface active properties.

TABLE III

Surface-Active Properties of 10 Salts of α-Sulfonated Acids

	Solubility, 40° g./100 ml. water	Surface Tension dynes/cm. 0.1%, 25°	Sinking Time, secs., 0.1%, 30° (11)	Foam Height mm., .25%, 60° (9)	% Detergency 0.25% concn. in distilled water, 60°
NaαSLA	0.74	32.7	>1000	<10	23.9
NaαSMA	0.17	30.2	98	160	56.6
NaαSPA	0.096	......	176	......	55.6
NaαSSA	0.05	......	......	......	46.4
Na$_2$αSL	7.4	69.3	>1000	<10	19.2
Na$_2$αSM	1.5	62.8	349	<10	26.1
Na$_2$αSP	0.45	44.3	45	169	49.5
Na$_2$αSS	0.14	......	37	......	57.7
NH$_4$αSPA	0.5	40.4	100	185	56.1
TαSPA	130.0	42.4	77	215	55.4

Ammonium α-sulfopalmitic acid and triethanolammonium α-sulfopalmitic acid (NH$_4$αSPA and TαSPA of Table III) were prepared in a manner similar to that for the monosodium salts but were not as easily purified. The neutralization of the isolated diacid is an alternative method. Both salts appear to be good detergents. Triethanolammonium α-sulfopalmitic acid is exceptionally soluble in water and has the highest foam of the 10 salts.

At 0.1% concentration at 25° the pH of ammonium α-sulfopalmitic acid, triethanolammonium α-sulfopalmitic acid, sodium α-sulfolauric acid, and disodium α-sulfopalmitate was 3.8, 3.8, 3.4, and 7.7, respectively.

Ammonium α-sulfopalmitic acid. Stabilized sulfur trioxide in 1.5 molar ratio was added dropwise in 20 minutes to a stirred solution of 165 g. of palmitic acid in 1,200 ml. of tetrachloroethylene as the temperature rose from 25° to 45°. The mixture was heated to 70° to complete sulfonation, neutralized with aqueous ammonia to form the monoammonium salt, and distilled to recover tetrachloroethylene.

The crude product obtained by cooling the hot aqueous solution was heated with dilute sulfuric acid to convert ammonium palmitate and any diammonium α-sulfopalmitate which might possibly be present to palmitic acid and ammonium α-sulfopalmitic acid, respectively. The monoammonium salt is the salt of the α-sulfonic acid group, and there was no conversion to the diacid by heating ammonium α-sulfopalmitic acid with dilute sulfuric acid. After crystallization from ethanol, ammonium α-sulfopalmitic acid was obtained as a white powder in a yield of 68%, with the following analysis: N.E. 182.6, 3.89% N, 8.85% S; calculated for $C_{16}H_{35}NO_5S$, N.E. 176.8, 3.96% N, 9.07% S. A less pure tan-colored product was obtained in a yield of 85%.

Triethanolammonium α-sulfopalmitic acid. The monotriethanolammonium salt was prepared in a similar manner. A white product was obtained with the following analysis: N.E. 237.7, 3.27% N, 6.64% S; calculated for $C_{22}H_{47}NO_8S$, N.E. 242.8, 2.88% N, 6.60% S.

Sodium Salts of α-Sulfonated Esters

Several methods for the preparation of sodium salts of sulfonated esters have been disclosed in patents and reports. The methods include the esterification of the monosodium salt (3), the esterification of the diacid (4, 6, 7, 10), direct sulfonation of the ester (12), and the reaction of the carboxylic acid chloride of the diacid with an alcohol (1). The sulfonating agents used have been gaseous sulfur trioxide or chlorosulfonic acid.

Twenty-four esters, sodium salts of alkyl α-sulfonated palmitates and stearates, have been prepared in a pure state (14). Esterification of the isolated crude diacid, obtained by α-sulfonation of palmitic or stearic acid with liquid sulfur trioxide, was preferred to an alternative method, the esterification of the monosodium salt. The esters of alcohols of one to six carbon atoms were readily soluble in water and were selected for a study of their surface-active properties. A method of preparation, without extensive purification, is illustrated in the case of α-sulfostearic acid and sodium isopropyl α-sulfostearate.

α-Sulfostearic acid. Liquid sulfur trioxide, 44 g. (1.57 molar ratio), was added dropwise during one hour to a well-stirred slurry of 100 g. of stearic acid (N.E. 284.2, m.p. 69.4-69.8°) in 450 ml. of tetrachloroethylene as the temperature rose from 22° to 39°. The mixture was stirred and heated one hour at 50-63°, cooled to 0°, and filtered. The residue was washed with 100 ml. of cold chloroform and dried to constant weight in a vacuum desiccator over anhydrous calcium sulfate. α-Sulfostearic acid was obtained as a very hygroscopic light gray solid in a yield of 85% (N.E. 183.2; calculated for $C_{18}H_{36}O_5S$, N.E. 182.3). Diacids of this degree of purity are satisfactory for the preparation of esters and probably also for the preparation of numerous other derivatives.

Sodium isopropyl α-sulfostearate. A solution of 107 g. of crude α-sulfostearic acid in 200 ml. of isopropanol was stirred and refluxed for six hours, cooled, and neutralized with solid sodium carbonate. The mixture was decolorized with carbon, cooled to —10°, and filtered; the crystallized residue was washed with a small amount of methanol and dried in a vacuum oven at 65° to constant weight. Sodium isopropyl α-sulfostearate was obtained as a cream colored solid, m.p. 80-82°, in a yield of 68% based on stearic acid, 79% based on α-sulfostearic acid. Analysis gave 16.59% ash as Na_2SO_4; calculated for $C_{21}H_{41}NaO_5S$, 16.57.

Detergency. The detergency of six of the pure esters was compared with that of disodium α-sulfopalmitate in the Terg-O-Tometer under the conditions already described. The esters were sodium methyl α-sulfopalmitate, sodium methyl α-sulfostearate, sodium propyl α-sulfostearate, sodium isopropyl α-sulfostearate, sodium butyl α-sulfopalmitate, and sodium secondary butyl α-sulfopalmitate (abbreviated, in Tables, as NaMeαSP, NaMeαSS, NaPrαSS, Na iso PrαSS, NaBuαSP, and Na sec BuαSP, respectively). There was, on the whole, little difference in detergency in the six esters. They were equal to disodium α-sulfopalmitate in distilled water but somewhat inferior in hard water. The esters appear to lend themselves well to building because of their ease of solution and stability to hydrolysis. Further work is required to estimate their usefulness in detergent compositions.

Surface and interfacial tension. The surface tension and the interfacial tension against a refined mineral oil was measured for nine esters (Table IV). In this group of esters of the lower primary and secondary alcohols both surface and interfacial tension decreased with an increasing number of carbon atoms in the alkyl group.

TABLE IV

Surface and Interfacial Tension of Sodium Salts of Alkyl α-Sulfopalmitates and α-Sulfostearates, 0.1% Solutions at 25°.

	No. of Carbon Atoms		Dynes/cm.	
	per Alkyl Group	per Molecule	Surface Tension	Interfacial Tension
Na Me αSP	1	17	40.2	9.7
Na Me αSS	1	19	39.0	8.4
Na Et αSS	2	20	38.5	7.8
Na iso Pr αSS	3	21	37.6	7.1
Na Pr α SP	3	19	37.0	7.2
Na sec Bu αSP	4	20	36.0	7.5
Na Bu αSP	4	20	35.3	6.4
Na Am αSP	5	21	33.1	4.9
Na Am αSS	5	23	33.6	4.5

Stability to hydroylsis. The sodium salts of alkyl α-sulfopalmitates and α-sulfostearates were unexpectedly resistant to hydrolysis in hot acid or alkaline solutions. The saponification equivalent determination was not a suitable means of estimating purity because hydrolysis was in some cases not complete even after four hours of reflux with alcoholic potassium hydroxide.

Resistance to hydrolysis was shown in experiments to measure the rate constant for a second order reaction, by heating 0.01 mole of the ester with 0.01 mole of sodium hydroxide in 100 ml. of water at 100°. For comparison, 0.005 mole of sodium di-(2-ethylhexyl) sulfosuccinate, also an α-sulfonated compound, was likewise heated with 0.01 mole of sodium hydroxide and 100 ml. of water. The rate constants and the relative rates of hydrolysis are shown in Table V.

TABLE V

Rate of Hydrolysis of α-Sulfonated Esters

	k_{100} liters/mole x minutes	Relative Rate of Hydrolysis
Na di-(2-ethylhexyl) sulfosuccinate	0.9	100.0
Na Me αSP	0.14	16.0
Na Am αSS	0.053	6.0
Na iso Pr αSS	0.0047	0.5
Na sec Bu αSP	0.0021	0.2

Resistance to acid and alkaline hydrolysis was also shown by sinking time measurements before and after heating the surface-active agent, at 0.1% concentration, in boiling 5% sulfuric acid or 1% sodium hydroxide. Sinking time was measured at 25°, using a standardized binding tape (11). The results are shown in Table VI, compared to sodium dodecyl sulfate (NaDDS) and sodium tetradecyl sulfate (NaTDS). A further acid stability test (5) showed that the first four esters of Table VI (the methyl, propyl, and isopropyl esters) were also stable at 1% concentration in hot 10% sulfuric acid, but the butyl and secondary butyl esters were not.

The sodium salts of alkyl α-sulfopalmitates and α-sulfostearates were more resistant to hydrolysis than were several commercial surface-active agents in which the active ingredient was an ester or an amide. The presence of the α-sulfo group stabilizes the ester linkage to acid hydrolysis and to a lesser extent to alkaline hydrolysis; the nature of the alkyl group contributes additional stability to alkaline hydrolysis. α-Sulfonated esters of secondary alcohols were remarkably stable to both acid and alkaline hydrolysis. This behavior increases the range of possible application. Stability in acid solution suggests a possible use in acid-dyeing operations, in carbonizing baths, and in pickling or electroplating.

Foam height. Foam height was measured by the Ross-Miles method (9). The α-sulfonated esters had better foaming properties than disodium α-sulfopalmitate. The foam broke rapidly and was not as thick and persistent as that for sdoium oleyl sulfate. Foam height measurements for six esters are shown in Table VII.

TABLE VII

Foaming Properties of α-Sulfonated Esters. 0.25% Concentration in Distilled Water at 60°.

	Foam Height, mm.	
	Immediate	After 5 minutes
Na Me αSP	216	129
Na Me αSS	216	179
Na Pr αSS	164	134
Na iso Pr αSS	160	142
Na Bu αSP	202	133
Na sec Bu αSP	215	165

Calcium stability. Calcium stability was measured by a modified Hart method (16) with the results shown in Table VIII. Esters of primary alcohols of eight carbon atoms or more gave turbid solutions at 0.5% concentration, and the test could not be applied.

TABLE VI

Resistance to Acid and Alkaline Hydrolysis

	Distd. Water	Sinking Time, seconds, at 25°. 0.1% Concentration of Surface-Active Agent							
		5% H_2SO_4	Boiling 5% H_2SO_4			1% NaOH	Boiling 1% NaOH		
			0.5 hrs.	1.5 hrs.	4.0 hrs.		0.5 hrs.	1.5 hrs.	4.0 hrs.
Na Me αSP	22	16	22	25	31	24	>600	......	......
Na Me αSS	29	24	34	31	78	67	>600	......	......
Na Pr αSS	34	23	33	44	40	83	129	337	>600
Na iso Pr αSS	43	23	29	34	35	62	67	76	76
Na Bu αSP	18	18	23	29	26	41	91	>600	......
Na sec Bu αSP	18	16	18	21	22	26	27	30	31
Na DDS	18	20	88	>600	....	16	16	16	16
Na TDS	23	18	>600	....	....	15	128	150	138

TABLE VIII

Calcium Stability of α-Sulfonated Esters, p.p.m. $CaCO_3$

R	Palmitates $C_{14}H_{29}CH(SO_3Na)CO_2R$	Stearates $C_{16}H_{33}CH(SO_3Na)CO_2R$
CH_3	>1800	800
C_2H_5	>1800	540
n-C_3H_7	>1800	460
n-C_4H_9	590	620
n-C_5H_{11}	920	1060
n-C_6H_{13}	850	720
$(CH_3)_2CH$	......	>1800
$C_2H_5CHCH_3$	1500	......

There was no simple relation between calcium stability and molecular weight. Values for the α-sulfonated stearates were generally lower. Esters of secondary alcohols had higher calcium stability than esters of corresponding primary alcohols.

Metallic ion stability. Metallic ion stability (5) was measured for six esters with the results shown in Table IX. The esters were least stable to the trivalent ion, Al^{+++}.

TABLE IX

Metallic Ion Stability of α-Sulfonated Esters [a]

	Na Me αSP	Na Me αSS	Na Pr αSS	Na iso Pr αSS	Na Bu αSP	Na sec Bu αSP
Mg	100	100	100	100	100	100
Al	14	12	14	10	9	11
Ca	93	71	13	38	14	33
Fe	100	100	100	100	100	100
Ni	100	100	100	100	100	100
Cu	100	100	100	100	100	100
Zn	100	100	100	100	99	38
Ba	37	27	26	27	23	26
Pb	70	54	43	48	43	60

[a] Metallic ion stability (5) = 10 × no. of ml. of 1% metal salt solution, tolerated by 10 ml. of 1% surface active agent.

Summary

In a comparison of the solubility, detergency, and surface-active properties of the mono- and disodium salts of α-sulfonated lauric, myristic, palmitic, and stearic acids, it has been shown that the less soluble α-sulfopalmitates and α-sulfostearates, and sodium α-sulfomyristic acid as well, are the best detergents. The easily soluble disodium α-sulfolaurate resembles a simple electrolyte with little evidence of surface-active properties. Ammonium α-sulfopalmitic acid and triethanolammonium α-sulfopalmitic acid are more soluble surface-active agents and detergents than the sodium salts. Triethanolammonium α-sulfopalmitic acid is exceedingly soluble in water at room temperature.

The sodium salts of alkyl α-sulfopalmitates and α-sulfostearates are easily prepared from the isolated crude diacid. The esters of primary alcohols containing from one to six carbon atoms are readily soluble in water and quite stable to hydrolysis, especially in acid solution. Salts of α-sulfonated esters of secondary alcohols are stable both to acid and to alkaline hydrolysis. This behavior extends the range of possible application.

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Highly Unsaturated Fatty Acids. II. Fractionation by Urea Inclusion Compounds[1]

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THE phenomenon of the formation of crystalline urea inclusion compounds[4] with straight chain organic compounds was discovered by Bengen (2) in 1940. In the last three years the new technique has been the subject of several investigations. Schlenk (3), Zimmerschied *et al.* (4), and Schlenk and Holman (5, 6) confirmed Bengen's findings and extended his observations. The new reaction has offered many useful applications. Besides the main finding of Bengen that urea can be used to separate straight chain compounds from branched or cyclic compounds, numerous investigators have demonstrated that various straight chain compounds can be separated by this means. For example, the new technique has been applied for preparation of methyl oleate (6, 7, 8) and for the preparation of concentrates of linoleic and linolenic acids (9). Enrichment of the unsaturated fatty acids of soybean oil has been accomplished by this method (10). For detailed discussion of urea in-

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[4] The term "inclusion compounds," although somewhat clumsy, seems to be the most accurate generic term to describe the class of compounds to which urea and thiourea "complexes" and "adducts" belong (1).