

Salts of Alkyl Esters of α -Sulfopalmitic and α -Sulfostearic Acids¹

A. J. STIRTON, R. G. BISTLINE, JR., ELIZABETH A. BARR and M. V. NUNÉZ-PONZOA, Eastern Regional Research Laboratory,² Philadelphia, Pennsylvania

Abstract

Lithium, ammonium, sodium, potassium, magnesium, and calcium salts of methyl, ethyl, propyl, isopropyl, butyl, isobutyl and secondary butyl esters of α -sulfopalmitic and α -sulfostearic acids were prepared for a study of structure-property relations. The esters are easily biodegradable, have good foaming, detergent and lime soap dispersing properties and resist acid and alkaline hydrolysis. The α -sulfopalmitates are more soluble.

Differences in the cation and the alcohol influence melting point, aqueous solubility, solubility in organic solvents, surface and interfacial tension, critical micelle concentration and emulsifying properties.

Introduction

ESTERS OF α -SULFO ACIDS are of current interest as biodegradable detergents, lime soap dispersing agents and wetting agents (1,3,8-10,12,13). Variations in the structure $\text{RCH}(\text{SO}_3\text{M})\text{CO}_2\text{R}'$ or $[\text{RCH}(\text{CO}_2\text{R}')\text{SO}_3]_2\text{M}$ are easily possible by choice of the particular fatty acid, aliphatic alcohol, or salt. The present investigation is a systematic survey of 84 esters to better relate structure and properties.

Commercial α -sulfopalmitic acid and α -sulfostearic acid (Armosul-16 and Armosul-18, Armour Industrial Chemical Company) estimated to contain about 3-8% of impurities in the form of unsulfonated fatty acid and the homologous 16 or 18 C α -sulfo acid, were esterified with methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and secondary butyl alcohols and neutralized to form lithium, ammonium, sodium, potassium, magnesium, and calcium salts. The properties measured included melting point, Krafft point, solubility in water and organic solvents, surface and interfacial

tension, critical micelle concentration (cmc), calcium stability, metal ion stability, detergent, foaming, wetting, lime soap dispersing, and emulsifying properties, rate of hydrolysis, and relative ease of biodegradation.

Experimental

Preparation of the Esters

α -Sulfopalmitic acid, 0.6 mole (200 g), was dissolved in 250 ml of the selected alcohol and esterified by heating 6 hr at the reflux temperature. The reaction mixture was divided into 6 equal parts and the salts were formed by neutralization or double decomposition with calculated amounts of lithium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, magnesium chloride or calcium chloride. The precipitated salts were dried, dissolved in absolute ethanol, decolorized, and recrystallized from aqueous ethanol at -20C . The same procedure was used for esters of α -sulfostearic acid. The esters were obtained in a pure state as white powders with an overall average for metal analysis within 0.1% of the theoretical value. The average purity of the ammonium salt, estimated from neutralization equivalent, was 98%.

Properties

Melting points were determined with the Fisher-Johns apparatus, surface and interfacial tension was measured with the du Noüy tensiometer, critical micelle concentration by the pinacyanole chloride method, and biodegradability by the river water test (13). Krafft point, detergency, foam height, wetting time, calcium stability, stability to metal ions, and lime soap dispersing power were measured as in previous publications (12). Emulsifying properties were measured by the method of Griffin and Behrens (6).

Rate of hydrolysis under acid catalysis, a first order reaction, was measured by heating 0.01 mole of the sodium salt of the ester in 100 ml $\text{N}/3 \text{H}_2\text{SO}_4$ at 100C , withdrawing 10 ml aliquots for titration at selected time intervals. Rate of hydrolysis under al-

¹ Presented at the AOCs Meeting in Houston, 1965.
² Eastern Util. Res. and Dev. Div., ARS, USDA.

TABLE I
 Melting Points, Krafft Points, and Aqueous Solubilities of Salts of Esters of α -Sulfopalmitates^a

Alkyl Ester	α -Sulfopalmitates						α -Sulfostearates					
	Li	NH ₄	Na	K	Mg	Ca	Li	NH ₄	Na	K	Mg	Ca
CH ₃	143-6	>200	181-3	194-6	>200	198-200	151-2	>200	175-6	186-8	>200	190-5
	vs	30.5	29	59.5	53.5	39	vs	41.5	39	68	62	gel
CaH ₅	132-3	198-200	92-5	186-7	>200	130-2	133-4	190-3	98-100	181-3	198-200	130-2
	vs	19.5	vs	55.5	57.5	gel	vs	22.5	22	63	64	gel
C ₂ H ₇	128-9	167-71	58-61	168-9	176-8	122-3	123-5	164.6	67-70	165-6	167-9	121-3
	vs	vs	vs	38	37	gel	vs	vs	42	42	gel	ss
(CH ₃) ₂ CH	142-4	>200	71-2	129-31	>200	111-14	140-1	>200	76-80	126-7	189-92	125-8
	vs	vs	vs	vs	66	gel	vs	vs	12	12	gel	gel
C ₄ H ₉	124-6	120-2	56-9	170-3	79-83	54-6	124-5	120-2	63-5	167-9	72-5	61-3
	vs	vs	vs	34	gel	ss	vs	vs	40	40	ss	ss
(CH ₃) ₂ CHCH ₂	146-7	111-12	145-7	160-2	42-4	71-3	142-5	113-16	113-15	159-62	64-5	63-5
	vs	vs	vs	vs	gel	gel	vs	vs	12	12	ss	ss
CH ₃ CHC ₂ H ₅	132-4	190-2	119-21	117-19	73-4	113-16	127-8	188-90	113-17	117-19	82-4	115-17
	vs	vs	vs	vs	vs	ss	vs	vs	vs	16	gel	ss

^a Melting point (upper line) and Krafft point (lower line), °C; vs = very soluble, clear 1% solution at 1C; ss = slightly soluble, turbid 1% aqueous dispersion at 100C.

kaline catalysis, a second order reaction, was measured by heating 0.01 mole of the sodium salt of the ester in 100 ml N/10 NaOH at 40, 60, 80, and 100C, withdrawing 10 ml aliquots for titration. Energy of activation was calculated from rate of hydrolysis at different temperatures.

Results and Discussion

Melting Point

As shown in Table I melting points range from 42 to >200C. Only certain of the sodium, magnesium, and calcium salts melt below 100C. The melting points of esters of normal primary alcohols decrease with increase in molecular weight of the alcohol; esters of secondary alcohols usually have higher melting points.

Krafft Point and Aqueous Solubility

The Krafft point, the temperature at which a 1% aqueous dispersion changes sharply to a clear solution on gradual heating, is a convenient measure of aqueous solubility. Twenty-five esters have measurable Krafft points, which range from 12C to 68C. Krafft point generally decreases with increase in molecular weight of the alcohol.

The melting point and the Krafft point parallel one another in the case of the potassium salts. Most

of the lithium, ammonium, and sodium salts are too soluble to have measurable Krafft points and form clear 1% solutions even at 1C. A number of the calcium and magnesium salts, particularly the alkyl α -sulfostearates, form clear gels at 1% concentration, or else turbid 1% dispersions which do not clarify even at 100C.

Solubility in Organic Solvents

Data on solubility in organic solvents is pertinent to the possible application of surface active agents in nonaqueous systems.

The esters dissolve in a variety of organic solvents listed in order of decreasing solvent power as follows: chloroform, ethanol, petroleum ether, diethyl ether, and mineral oil. Most of the esters, with the exception of the potassium salts, are soluble to the extent of 10% or more in chloroform and ethanol. Magnesium and calcium salts of the n-butyl, isobutyl, and secondary butyl esters, which have relatively low melting points, are soluble to the extent of 10% or more in each of the five solvents.

In general, alkyl α -sulfopalmitates are more soluble in organic solvents than alkyl α -sulfostearates, the solubility of esters of primary alcohols increases with molecular weight, and esters of secondary and branched chain alcohols are more soluble than esters of normal primary alcohols.

 TABLE II
 Surface Active Properties of Sodium Alkyl α -Sulfopalmitates and α -Sulfostearates, RCH(SO₃Na)CO₂R'

R'	Total number of C atoms	Surface and interfacial tension 0.1%, 25C dynes/cm		cmc ^a millimoles per liter	Detergency ^b 0.25%, 60C ΔR		Foam height ^c 0.25%, 60C distilled water mm	Wetting time ^d 0.1%, 25C seconds	Calcium stability ^e ppm Ca CO ₃	Lime soap dispersing power ^f %	Biodegradability ^g time in hr for 80% degradation
		S.T.	I.T.		distilled water	300 ppm					
		α -Sulfopalmitates									
CH ₃	17	40.4	10.4	0.37	31	26	205	21 ^h	9	100
C ₂ H ₅	18	39.0	9.1	0.31	29	195	19 ^h	8	115
C ₂ H ₇	19	37.4	8.4	0.24	29	195	16 ^h	8	140
(CH ₃) ₂ CH	19	38.0	8.8	0.31	30	23	205	17 ^h	9	120
C ₄ H ₉	20	35.0	6.4	0.16	20	200	20	590	9	165
(CH ₃) ₂ CHCH ₂	20	35.8	7.0	0.16	21	190	16	275	6	165
C ₂ H ₅ CHCH ₃	20	36.8	7.7	0.18	21	205	18	530	7	150
α -Sulfostearates											
CH ₃	19	39.7	8.4	0.16	28	23	190	65	800	9	90
C ₂ H ₅	20	38.7	7.8	0.13	27	180	44	540	11	110
C ₂ H ₇	21	37.6	6.9	0.072	26	160	69	460	12	110
(CH ₃) ₂ CH	21	37.6	7.1	0.08	25	20	175	58 ^h	12	130
C ₄ H ₉	22	36.4	5.6	0.06	25	155	150	620	10	95
(CH ₃) ₂ CHCH ₂	22	35.8	6.1	0.05	25	160	142	220	12	90
C ₂ H ₅ CHCH ₃	22	36.9	6.5	0.065	25	160	128	345	10	140

^a Critical micelle concentration, pinacyanole chloride method.

^b ΔR = increase in reflectance after washing standard soiled cotton (5). For comparison ΔR for 0.25% Na dodecyl sulfate in distilled water = 29.

^c Ross-Miles test (11); stable foam.

^d Draves test (4).

^e Modified Hart method (14).

^f Borghetty method (2).

^g River water methylene blue method (13).

^h Greater than 1800 ppm.

TABLE III

Surface Tension, Salts of Alkyl Esters of α -Sulfostearic Acid, 0.1% Solutions, 25°C $C_{12}H_{25}CH(SO_3M)CO_2R'$

R'	Li	Na	K
CH ₃	42.2	39.7	^a
C ₂ H ₅	41.0	38.7	^a
C ₃ H ₇	40.0	37.6	35.6
(CH ₃) ₂ CH	40.1	37.9	35.8
C ₄ H ₉	38.8	36.4	33.4
(CH ₃) ₂ CHCH ₂	36.9	35.8	32.8
C ₂ H ₅ CHCH ₃	36.8	36.9	35.1

^a Insufficiently soluble.**Surface Active Properties**

The properties most directly related to use as surface active agents or detergents were examined and are recorded in Table II for the sodium salts. Other metal salts have similar foaming, wetting, and detergent properties.

Surface and Interfacial Tension

Surface and interfacial tension values of esters of normal primary alcohols decrease with increase in molecular weight of the alcohol. Surface tension values depend also upon the cation as shown in Table III and decrease for the alkali metal salts from lithium to sodium to potassium.

Critical Micelle Concentration

The cmc of esters of normal primary alcohols decreases with increasing molecular weight in the expected manner. Esters of secondary alcohols have higher values. All the metal salts have the same critical micelle concentration.

Detergency

Best detergency is shown by esters of 17-19 carbon atoms with the hydrophilic group near the end of the molecule.

Foam

Esters of 17-20C atoms have the best foaming properties and the foam remains stable for 5 min or more. Foam height of the alkyl α -sulfostearates decreases with increasing molecular weight.

Wetting Time

The α -sulfopalmitates have better wetting properties. The three butyl α -sulfostearates are the least efficient wetting agents.

Lime Soap Dispersing Power

All of the esters of Table II are lime soap dispersing agents. Sodium methyl α -sulfostearate and all of the sodium alkyl α -sulfopalmitates, particularly the isobutyl ester, are the most effective under the test

TABLE IV

Emulsifying Properties of Salts of Esters of α -Sulfofatty Acids

Emulsifying Agent	Time in hours for 10% phase separation ^a	
	C ₄ H ₉ OH - H ₂ O	CCl ₄ - H ₂ O
Li propyl α -sulfopalmitate	4
Li butyl α -sulfopalmitate	4
Li isobutyl α -sulfopalmitate	4
Mg methyl α -sulfopalmitate	...	1.5
Mg propyl α -sulfopalmitate	2	1
Mg sec. butyl α -sulfopalmitate	3.5	3
Mg methyl α -sulfostearate	2.5
Mg propyl α -sulfostearate	1
Ca methyl α -sulfopalmitate	2.5
Ca isopropyl α -sulfopalmitate	1
Ca ethyl α -sulfostearate	5
Ca propyl α -sulfostearate	...	1

^a 1% solution of the ester in 25 ml C₄H₉OH or CCl₄ shaken mechanically for 3 min with 25 ml H₂O.

TABLE V

Salts of Esters of α -Sulfofatty Acids. Rate Constants, Acid and Alkaline Hydrolysis, 100°C

	N/3 H ₂ SO ₄	N/10 NaOH
	k ^a	k ^b
Na methyl α -sulfopalmitate	0.0062	0.14 ^c
Na methyl α -sulfostearate	0.0068	0.10 ^c
Na ethyl α -sulfopalmitate	0.0050	0.048
Na propyl α -sulfopalmitate	0.0038	0.032
Na isopropyl α -sulfopalmitate	0.0024	0.006
Na butyl α -sulfopalmitate	0.0042	0.028
Na isobutyl α -sulfopalmitate	0.0039	0.020
Na secondary butyl α -sulfopalmitate	0.0025	0.002

^a First order reaction, $k = 1/t \ln a/(a-x)$.^b Second order reaction, $k = 1/t x/(a-x)$.^c Values at 60°C and 80°C, and energy of activation (kcal/mole) from $E_a = 2.3 R (T_2/T_1 - T_2 - T_1) \log k_2/k_1$ are as follows, resp.:
Na methyl α -sulfopalmitate, 0.010, 0.034, 16.5;
Na methyl α -sulfostearate, 0.007, 0.026, 16.6.

conditions. Calcium and magnesium salts of the α -sulfo esters are also lime soap dispersing agents (8,9).

Calcium Stability

Most of the esters of Table II have good or excellent calcium stability. Only the isobutyl esters have values less than 300 ppm.

Metal Ion Stability

Metal ion stability was measured as 10 x number of ml of 1% metal salt solution tolerated by 10 ml of 1% sodium alkyl α -sulfopalmitate or stearate (7). Most of the esters have excellent stability to Mg⁺⁺, Fe⁺⁺, Ni⁺⁺, Cu⁺⁺, and Zn⁺⁺ (expressed by a value of 100), but are sensitive to Al⁺⁺⁺, Ba⁺⁺, and Pb⁺⁺ with average values of 10, 28, and 52, respectively. Two esters, sodium butyl and isobutyl α -sulfostearate, are also sensitive to Ni⁺⁺, Cu⁺⁺, and Zn⁺⁺, with average values of 30 for these metals.

Emulsifying Properties

The esters have no significant emulsifying properties with the organic solvents used to measure solubility (chloroform, ethanol, petroleum ether, diethyl ether, mineral oil). Stable aqueous emulsions were formed, however, with lithium, magnesium, and calcium salts in butanol or carbon tetrachloride. A 1% solution of the ester in butanol or carbon tetrachloride was shaken mechanically for 3 min with an equal volume of water using the Atlab Emulsion Test Apparatus, following the method of Griffin and Behrens (6). The time in hours for 10% phase separation is shown in Table IV.

Lithium salts form stable emulsions with butanol but not with carbon tetrachloride, magnesium salts form stable emulsions with either solvent, and calcium salts form stable emulsions only with carbon tetrachloride. The results suggest a possible use of lithium, magnesium and calcium salts of α -sulfo esters in more complex emulsions designed for specific applications.

Biodegradability

All of the esters were biodegradable in the river water test (13) from an initial concentration of 5 ppm to 1 ppm (80% degradation) within 4-7 days. For comparison the time required for sodium dodecylsulfonate was 94 hr: for branched chain sodium alkylbenzenesulfonate >700 hr.

Sodium methyl and isopropyl α -sulfostearates have been found to be easily degraded in a laboratory scale activated sludge sewage system (3). Under anaerobic conditions these esters did not degrade but

unlike linear or branched chain alkylbenzenesulfonates had no adverse effect on the digestion process (10).

Rate of Hydrolysis and Energy of Activation

Esters of α -sulfo fatty acids are surprisingly resistant to hydrolysis, possibly because the presence of the bulky sulfo group retards attack at the carboxylate linkage.

The rate for acid catalyzed hydrolysis, as shown in Table V, generally decreases with increase in molecular weight of the primary alcohol and is significantly less for esters of secondary alcohols.

The rate for alkaline hydrolysis again decreases with the number of methylene groups in the primary alcohol and is markedly less for esters of secondary alcohols. Apart from any other considerations this suggests that the isopropyl or secondary butyl esters would be the most suitable in the formulation of esters spray-dried in the presence of alkaline builders.

The rate of alkaline hydrolysis for sodium methyl α -sulfopalmitate and sodium methyl α -sulfostearate,

at 60, 80, and 100C, plotted as $\log k$ vs. $1/T$ gave straight lines consistent with the Arrhenius equation. Calculation of the energy of activation gave values of 16.5 and 16.6 kcal per mole, respectively.

REFERENCES

1. Bistline, R. G., Jr., and A. J. Stirton, *JAACS* **41**, 654-656 (1964).
2. Borghetty, H. C., and C. A. Bergman, *JAACS* **27**, 88-90 (1950).
3. Cordon, T. C., E. W. Mauer, J. K. Weil and A. J. Stirton, *Develop. Ind. Microbiol.* **6**, 3-15 (1964).
4. Draves, C. Z., *Am. Dyestuff Repr.* **28**, 425-428 (1939); A.A.T. C.C. Tech. Manual and Yearbook 1960, 161-163, Test Method 17-52.
5. Draves, C. Z., and O. L. Sherburne, *Am. Dyestuff Repr.* **39**, 771-772 (1950).
6. Griffin, W. C., and R. W. Behrens, *Agr. Chem.* **7**, No. 3, 63, 65 (1952); *Anal. Chem.* **24**, 1076-1077 (1952).
7. Harris, J. C., *A.S.T.M. Bull.* No. 141, 49-53 (1946).
8. Knaggs, E. A., and E. Fischer, *Technical Bulletin*, Stepan Chemical Co., December 3, 1962.
9. Knaggs, E. A., J. A. Yeager, L. Varenzi and E. Fischer, *JAACS* **42**, 805-810 (1965).
10. Maurer, E. W., T. C. Cordon, J. K. Weil, M. V. Nunéz-Ponzoa, W. C. Ault and A. J. Stirton, *JAACS* **42**, 189-192 (1965).
11. Ross, J., and G. D. Miles, *Oil & Soap* **18**, 99-102 (1941); A.S.T.M. Method D-1173-53.
12. Stirton, A. J., *JAACS* **39**, 490-496 (1962).
13. Weil, J. K., and A. J. Stirton, *JAACS* **41**, 355-358 (1964).
14. Wilkes, B. G., and J. N. Wickert, *Ind. Eng. Chem.* **29**, 1234-1239 (1937).

[Received July 26, 1965—Accepted October 18, 1965]