TABLE II

Prediction Equations for SFI Values and Per Cent Solids by NMR

Prediction equation
For all values
SFI value = 3.8550 + 0.6216 (% solids by NMR)
Per cent solids by NMR = 2.6542 + 1.4001 (SFI value)
For values less than 10
SFI value = 1.2454 + 0.6198 (% solids by NMR)
Per cent solids by NMR = 4.2963 + 0.5145 (SFI value)
For values 10 and higher
SFI value = 7.826 + 0.5206 (% solids by NMR)
Per cent solids by NMR = −10.1137 + 1.6990 (SFI value)

more valuable than SFI in the study of the solids content of fats and shortenings..

In addition to the advantages of NMR measurements given here, it is possible to condition separate samples at selected temperatures at the same time and then measure all at the end of the conditioning period instead of conditioning and reading at successively higher temperatures as in the SFI method. This appreciably reduces the elapsed time for a test. It also appears that it will be possible to extend the measurements to lower temperatures to gain information on products like winterized oils. The application of this technique to investigations of hydrogenation, interesterfication, processing, final formulations and similar phases of fat and oil research may be expected to extend the basic knowledge in this area.

REFERENCES

1. Official and Tentative Methods of the AOCS Solid Fat Index Method Cd 10-57.
2. Taylor, J. R., W. D. Pohle and R. L. Gregory, JAOCS *41*, 177–180 (1964).
3. Chapman, D., R. E. Richards and R. W. Yorke, JAOCS *37*, 243 (1960).
4. Ferren, W. P., and R. E. Morse, Food Tech. *17*, 1066–1068 (1963).

[Received May 11, 1965—Accepted October 1, 1965]

Salts of Alkyl Esters of α-Sulfopalmitic and α-Sulfostearic Acids[1]

A. J. STIRTON, R. G. BISTLINE, JR., ELIZABETH A. BARR and M. V. NUÑEZ-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 $RCH(SO_3M)CO_2R'$ or $[RCH(CO_2R')SO_3]_2M$ 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, isoproypl, butyl, isobutyl, and secondary butyl alcohols and neutralized to form lithium, ammonium, sodium, potassium, magnesium, and calciun 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 N/3 H_2SO_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-Sulfofatty Acids[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 vs	>200 30.5	181–3 29	194–6 59.5	>200 53.5	198–200 39	151–2 vs	>200 41.5	175–6 39	186–8 68	>200 62	190–5 gel
C_2H_5	132–3 vs	198–200 19.5	92–5 vs	186–7 55.5	>200 57.5	130–2 gel	133–4 vs	190–3 22.5	98–100 22	181–3 63	198–200 64	130–2 gel
C_3H_7	128–9 vs	167–71 vs	58–61 vs	168–9 38	176–8 37	122–3 gel	123–5 vs	164.6 vs	67–70 vs	165–6 42	167–9 gel	121–3 ss
$(CH_3)_2CH$	142–4 vs	>200 vs	71–2 vs	129–31 vs	>200 66	111–14 gel	140–1 vs	>200 vs	76–80 vs	126–7 12	189–92 gel	125–8 gel
C_4H_9	124–6 vs	120–2 vs	56–9 vs	170–3 34	79–83 gel	54–6 ss	124–5 vs	120–2 vs	63–5 vs	167–9 40	72–5 ss	61–3 ss
$(CH_3)_2CHCH_2$	146-7 vs	111–12 vs	145–7 vs	160–2 vs	42–4 gel	71–3 gel	142–5 vs	113–16 vs	113–15 vs	159–62 12	64–5 ss	63–5 ss
$CH_3CHC_2H_5$	132–4 vs	190–2 vs	119–21 vs	117–19 vs	73–4 vs	113–16 ss	127–8 vs	188–90 vs	113–17 vs	117–19 16	82–4 gel	115–17 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, $RCH(SO_3Na)CO_2R'$

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 CO₃	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_2H_5	18	39.0	9.1	0.31	29	....	195	19	.....[h]	8	115
C_3H_7	19	37.4	8.4	0.24	29	....	195	16	......[h]	8	140
$(CH_3)_2CH$	19	38.0	8.8	0.31	30	23	205	17	...[h]	9	120
C_4H_9	20	35.0	6.4	0.16	20	....	200	20	590	9	165
$(CH_3)_2CHCH_2$	20	35.8	7.0	0.16	21	....	190	16	275	6	165
$C_2H_5CHCH_3$	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_2H_5	20	38.7	7.8	0.13	27	....	180	44	540	11	110
C_3H_7	21	37.6	6.9	0.072	26	...	160	69	460	12	110
$(CH_3)_2CH$	21	37.6	7.1	0.08	25	20	175	58	......[h]	12	130
C_4H_9	22	36.4	5.6	0.06	25	....	155	150	620	10	95
$(CH_3)_2CHCH_2$	22	35.8	6.1	0.05	25	....	160	142	220	12	90
$C_2H_5CHCH_3$	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, 25C $C_{16}H_{33}CH(SO_3M)CO_2R'$

R'	Li	Na	K
CH_3	42.2	39.7	[a]
C_2H_5	41.0	38.7	[a]
C_2H_7	40.0	37.6	35.6
$(CH_3)_2CH$	40.1	37.9	35.8
C_4H_9	38.8	36.4	33.4
$(CH_3)_2CHCH_2$	36.9	35.8	32.8
$C_2H_5CHCH_3$	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 conditions. Calcium and magnesium salts of the α-sulfo esters are also lime soap dispersing agents (8,9).

TABLE IV

Emulsifying Properties of Salts of Esters of α-Sulfofatty Acids

Emulsifying Agent	Time in hours for 10% phase separation[a]	
	$C_4H_9OH - H_2O$	$CCl_4 - H_2O$
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 C_4H_9OH or CCl_4 shaken mechanically for 3 min with 25 ml H_2O.

TABLE V

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

	N/3 H_2SO_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, $k = 1/t\ x/a(a{-}x)$.

[c] Values at 60C and 80C, and energy of activation (kcal/mole) from $E_a = 2.3\ R\ (T_1T_2/\ T_2{-}T_1) \log k_2/k_1$ are as follows, resp.:
Na methyl α-sulfopalmitate, 0.010, 0.034, 16.5;
Na methyl α-sulfostearate, 0.007, 0.026, 16.6.

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 dodecanesulfonate 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, JAOCS *41*, 654–656 (1964).
2. Borghetty, H. C., and C. A. Bergman, JAOCS *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 Reptr. *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 Reptr. *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. Varenyi and E. Fischer, JAOCS *42*, 805–810 (1965).
10. Maurer, E. W., T. C. Cordon, J. K. Weil, M. V. Nunẽz-Ponzoa, W. C. Ault and A. J. Stirton, JAOCS *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., JAOCS *39*, 490–496 (1962).
13. Weil, J. K., and A. J. Stirton, JAOCS *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]

Ultraviolet Spectroscopic Analysis for Following the Biodegradation of Hydrotropes[1]

E. A. SETZKORN and R. L. HUDDLESTON, Research and Development Department, Continental Oil Company, Ponca City, Oklahoma

Abstract

The standard methylene blue colorimetric method for the analysis of ppm concentrations of anionic detergents is sensitive to the chain length of the hydrophobic portion of the molecule. The response to this method is not quantitative among alkylbenzene sulfonates when the alkyl chain is shorter than about eight carbon atoms, and becomes essentially zero with the sulfonates of benzene, toluene and xylene.

Although these low molecular weight aromatic sulfonates have few detergency properties, their function and substantial commercial use as solubilizers in detergent formulations lend some importance to a study of their biodegradability.

Ultraviolet spectroscopic analysis was successfully applied to the study of the biodegradation of these compounds both in a synthetic medium-sewage *inoculated* system and in the well-known river die-away procedure.

Sensitivity to below 1 ppm was obtained from absorption bands between about 220 and 230 mμ. Bands were also utilized near 260–270 mμ for those compounds having significant absorption in this region. Information concerning changes in functional group substitution and aromatic degradation was obtained from monitoring these two band systems during the biodegradation period.

Introduction

DURING THE PAST few years much attention has been focused on the problems of detergent biodegradation. In the search for more biodegradable detergent materials it was, of course, necessary to develop suitable biological test methods and the necessary analytical techniques to assay the results of the biological tests.

The river die-away, semicontinuous activated sludge, and shake flask systems are the most common biological test methods employed in detergent biodegradation studies. Warburg manometry and biochemical oxygen demand (BOD) tests are less frequently used in such studies.

The methylene blue colorimetric analysis (1) is by far the most common method of analysis for anionic detergents in the various biological test systems. The cobaltothiocyanate method (2) appears to be a satisfactory test for nonionic detergents in the various test systems. Surface tension and foam measurement methods also have been used to monitor detergent degradation, though these measurements do not provide sufficient sensitivity to detect small changes in detergent concentration.

However, with the exception of Warburg manometry and BOD tests, none of the analytical techniques mentioned above are suitable for monitoring the biodegradation of benzene, toluene and the xylene sulfonates. These compounds do not respond to the methylene blue test, and since they also neither foam nor significantly affect surface tension, these methods of analysis cannot be applied.

Warburg manometry could be used with these compounds, but the technique is somewhat difficult to apply, requires special equipment, and as normally occurs with such compounds, considerably less than 100% of the theoretical oxygen requirement for complete oxidation of the compound is obtained—which complicates a proper interpretation of the test result. BOD tests could be used; however, as ordinarily applied, the analysis method is slow and tedious and

---

[1] Presented at the AOCS Meeting, Houston, April 1965.