

Sulfonated Branched Chain Fatty Acids and Esters¹T. J. MICICH, E. A. DIAMOND, R. G. BISTLINE, JR., A. J. STIRTON and W. C. AULT,
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Abstract

In continuation of work reported a year ago describing branched chain fatty acids, a series of monosodium methyl 2-sulfo-2-alkylalkanoates [RR'C(SO₃Na)CO₂CH₃] were synthesized. The surface active properties of these compounds were evaluated and compared with the corresponding disodium 2-sulfo-2-alkylalkanoates [RR'C(SO₃Na)CO₂Na]. Alkaline hydrolysis rates show that the sodium methyl esters are stable. Relative to the disodium salts, these compounds exhibit better wetting properties and more stable foams.

Introduction

TERMINAL DISODIUM 2-sulfoalkanoates (6) with 16-18 carbon atoms exhibit low solubility and good detergent properties. Esterification of the carboxyl group in these compounds with alcohols containing one to four carbon atoms yields products with improved foam stability, solubility, calcium ion stability and equivalent detergency. Extensive studies (4,7) of sodium alkyl 2-sulfo-alkanoates [R-CH(SO₃Na)CO₂R'] revealed that good wetting properties are observed if the hydrophilic group is centrally located in compounds containing 15-18 carbon atoms. When this group is one to four carbon atoms from the end of the chain (i.e., R or R' contains one to four carbon atoms) the compounds exhibit good detergent properties (7). A recent investigation (5) of the synthesis and surface active properties of sodium 2-alkylalkanoates and the corresponding disodium 2-sulfonate salts has reaffirmed these results. The present study extends this work in comparing surface active properties of sodium methyl 2-sulfo-2-alkylalkanoates with the corresponding disodium salts.

Experimental

Reagents

Reagent grade carbon tetrachloride was passed through a 12 in. column of silica gel and stored over anhydrous sodium sulfate. This solvent was used in sulfonation reactions for a period of two weeks after which time the purification procedure was repeated. Eastman yellow label dioxane was purified

according to the procedure by L. F. Fieser (8). The dry dioxane was then distilled through a 2-ft column of stainless steel protruded packing. The center cut, bp 102C, was taken and stored at 0C under a nitrogen atmosphere. Sulfur trioxide (Sulfam, Allied Chemical Corp.) was distilled (bp 45C) just prior to use. Di-*t*-butyl peroxide was obtained from Monomer-Polymer Corporation, Philadelphia, and used as received. The peroxide was stored at 0C. Eastman white label normal carboxylic acids and terminal olefins (Humphrey-Wilkinson, petroleum derived) were distilled through a 2-ft column of stainless steel protruded packing, the center cut being taken. The purified olefins were stored under dry nitrogen. Reagent grade methanol and acetone were used as received.

2-Alkylalkanoic Acids. These acids were prepared by di-*t*-butyl peroxide catalyzed addition of normal carboxylic acid to a terminal olefin at 140-155C in 60-65% yields (5). Propionic, octanoic and hexanoic acids were reacted with the appropriate 1-olefin to form 2-methylpentadecanoic acid, 2-hexadecanoic acid (neutral equivalent for both found 261, theory 256) and 2-butyldecanoic acid (neutral equivalent found 231, theory 228), respectively. Carbon-hydrogen analyses showed an average deviation from the calculated values of 0.06% and 0.13%, respectively. The remaining 2-alkylalkanoic acids used in this study were reported previously (5).

Disodium 2-Sulfo-2-Alkylalkanoates. These compounds were prepared by sulfonation of the 2-alkylalkanoic acids with SO₃·dioxane in carbon tetrachloride and neutralization with NaOH (5). Compounds 4, 5 and 6 in Table III were prepared for this study. The disodium salts were obtained as microcrystalline solids in 60-80% yields, the higher yields being achieved with those salts where the 2-alkyl group is a methyl group. These compounds showed no definite melting point but decomposed above 220C. With the exception of disodium 2-sulfo-2-methylpentadecanoate where low carbon and high sodium indicate the presence of sodium sulfate, the elemental analyses for these compounds (Table I) closely agree with the calculated values.

Sodium Methyl 2-Sulfo-2-Alkylalkanoates. These esters were prepared by the same procedure and quantities of reactants used in the preparation of the disodium salts (5). After filtration of insolubles

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TABLE I
Analysis of Disodium and Sodium Methyl 2-Sulfo-2-Alkylalkanoates
RR'C(CO₂Na)SO₃Na and RR'C(CO₂CH₃)SO₃Na

| Salt | Analysis | | | | | | | |
|------------------------|----------|------|------|-------|--------|------|------|-------|
| | Found | | | | Theory | | | |
| | C | H | S | Na | C | H | S | Na |
| Disodium 2-sulfo- | | | | | | | | |
| hexadecanoate | 50.51 | 8.08 | 8.17 | 11.96 | 50.53 | 7.90 | 8.42 | 12.10 |
| 2-methylpentadecanoate | 48.58 | 7.63 | 8.63 | 12.50 | 50.53 | 7.90 | 8.42 | 12.10 |
| 2-butyldecanoate | 47.76 | 7.48 | 8.74 | 13.30 | 47.73 | 7.39 | 9.09 | 13.07 |
| 2-hexyldecanoate | 50.80 | 8.13 | 8.40 | 12.02 | 50.53 | 7.90 | 8.42 | 12.10 |
| Sodium methyl 2-sulfo- | | | | | | | | |
| 2-methyleicosanoate | 59.83 | 9.83 | 7.40 | 5.14 | 59.72 | 9.73 | 7.24 | 5.20 |
| 2-methyloctadecanoate | 57.04 | 9.38 | 8.06 | 5.55 | 58.00 | 9.42 | 7.73 | 5.55 |
| 2-methylpentadecanoate | 55.13 | 9.14 | 8.41 | 6.02 | 54.84 | 8.87 | 8.60 | 6.18 |
| 2-butyldecanoate | 52.57 | 8.39 | 9.83 | 6.84 | 52.33 | 8.43 | 9.30 | 6.69 |
| 2-hexyldecanoate | 54.88 | 8.94 | 8.71 | 6.13 | 54.84 | 8.87 | 8.60 | 6.18 |
| 2-octyldecanoate | 57.27 | 9.28 | 8.10 | 5.63 | 57.00 | 9.25 | 8.00 | 5.75 |

from the sulfonation reaction mixture and prior to evaporation of the carbon tetrachloride solvent (0.2 mm/1 hr) the acidic mixture was treated with Darco Grade G-60 carbon black and filtered. The filtrate was evaporated at 0.2 mm/1 hr at 50C. The non-volatile acidic residue was refluxed with 5 moles of methanol for 24 hr. The methanol solution was treated with carbon black and filtered. The filtrate was neutralized with excess anhydrous sodium carbonate. The alkaline mixture was heated to boiling and filtered under vacuum. The sodium carbonate precipitate was washed with 25 ml of hot methanol and this filtrate was added to the solution of sodium methyl ester. The solution was cooled to precipitate the product as an amorphous white solid. The product was recrystallized 3-5 times from methanol. Any turbidity noted during dissolution of the product in methanol was removed by gravity filtration. For alkanooate esters containing 2-alkyl groups larger than methyl, acetone was used as the recrystallization solvent at 0 to -10C. The sodium methyl esters were obtained in 25-80% yield with the yield increasing with molecular weight and decreasing size of the 2-alkyl group. Elemental analyses for these compounds shown in Table I agree well with the calculated values.

Alkaline Hydrolysis of Sodium Methyl 2-Sulfo-2-Alkylalkanoates. Second order rate constants for the alkaline hydrolysis of these methyl esters (Table II) were obtained at 100C using 0.1 N NaOH solution by a previously reported procedure (4). Hydrolysis constants were not obtained for sodium methyl 2-sulfo-2-octyldecanoate because of its insolubility in the titration solvent and for sodium methyl 2-sulfo-2-butyldecanoate because of the low purity of the available sample.

Discussion

Esterification of 2-sulfo-2-alkylalkanoic acids with anhydrous methanol at alcohol to acid ratios ranging from 300:1 to 25:1 indicated that use of ratios higher than 50:1 did not substantially improve yields. All esterifications were performed at reflux temperatures for 24 hr. Lower temperatures and shorter reaction times reduced yields while longer reaction times increased the discoloration of the reaction mixtures. All sodium methyl esters are microcrystalline solids melting between 180-190C except that obtained from 2-sulfo-2-butyldecanoic acid (mp 166-167C).

Surface active properties of the sodium methyl 2-sulfo-2-alkylalkanoates and the corresponding disodium salts are shown in Table III. The linear salts, samples 1 and 8, are included for comparison purposes. The compounds are listed essentially in the order of increasing size of the 2-alkyl group. Krafft points for the disodium salts are generally higher than for sodium methyl esters. Minimum Krafft

TABLE II
Alkaline Hydrolysis Sodium Methyl 2-Sulfo-2-Alkylalkanoates

| Compound | Rate (k) lit/mole/min |
|---------------------------|--------------------------|
| Sodium Methyl 2-Sulfo- | |
| 1) hexadecanoate | 0.14 ^a |
| 2) 2-methylheptadecanoate | 0.005 |
| 3) 2-methyloctadecanoate | 0.004 |
| 4) 2-methylpentadecanoate | 0.005 |
| 5) 2-hexyldecanoate | 0.002 ^b |

^a Data from reference (6).

^b Sample percent deviation from calculated values for elemental analysis: carbon 0.19%, hydrogen 0.39%, sulfur 0.33%, sodium 0.11%.

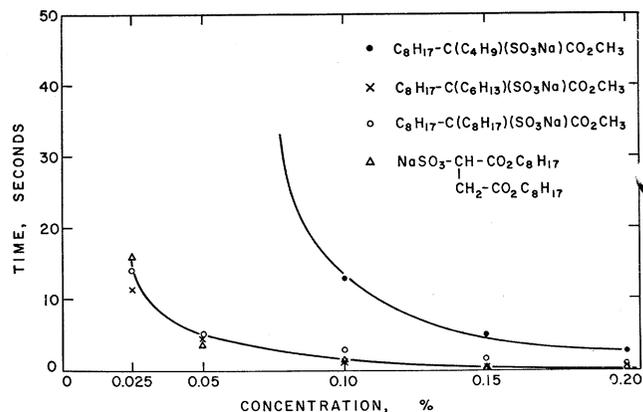


FIG. 1. Wetting ability versus concentration.

points appear to be associated with a low degree of molecular symmetry (5). Where comparisons can be made as in samples 1, 4 and 6, Krafft points decrease as the size of the 2-alkyl group increases. This behavior is not apparent with the corresponding sodium methyl esters.

Previous investigations (4,7) of sodium 2-sulfoalkylalkanoates and related studies (5) have shown that central location of the hydrophilic group generally results in good wetting properties and poor detergency while the reverse is observed when the hydrophilic group is at, or near, the end of the hydrocarbon chain. The data in Table III essentially confirm these observations for both the disodium salts and sodium methyl esters especially for the results obtained with distilled water. Of the disodium salts only that of 2-sulfo-2-octyldecanoate shows wetting properties in distilled water. Figure 1 illustrates the better wetting properties of the esters where wetting times are plotted as a function of concentration in distilled water. Sodium methyl 2-sulfo-2-hexyldecanoate and sodium methyl 2-sulfo-2-octyldecanoate are comparable to the control Aerosol OT at all concentrations. Sodium methyl 2-sulfo-2-butyldecanoate loses its wetting ability at concentrations less than 0.1%. In simulated hard water only sodium methyl 2-sulfo-2-hexyldecanoate (sample analysis given in footnote (b), Table II) is comparable to Aerosol OT at all concentrations.

Alkaline hydrolysis rate constants (4) (second order k) are given in Table II for the sodium methyl esters. These values are based on reaction times no greater than 10 hr (hydrolysis approx. 20% complete) since the rates become nonlinear in nearly every case beyond this reaction period. The 2-alkylated esters are at least 30 times more resistant to hydrolysis than is the linear sodium methyl 2-sulfohexadecanoate with stability tending to increase with increasing size of the 2-alkyl group. A similar tendency is observed with sodium 2-sulfoalkanoates [R-CH(SO₃Na)CO₂R'] when the size and degree of branching at R' is increased (4,6). The sodium methyl esters should exhibit greater resistance to acid hydrolysis than is noted under alkaline conditions since this is observed for esters (4) of the type R-CH(SO₃Na)CO₂R'.

Relative to the disodium salts, the foam stability of the esters is better in both distilled and hard water, the exception being sodium methyl 2-sulfo-2-butyldecanoate with very unstable foam properties. Calcium ion stabilities of the disodium salts are deficient. While the esters show greatly improved calcium ion stabilities, the values generally ranged be-

TABLE III
Surface Active Properties Disodium and Sodium Methyl 2-Sulfo-2-Alkylalkanoates

| Salt | Kraft point, °C | Tension ^g dynes/cm | | Wetting time (Sec) ^h | | Detergency ⁱ Terg-O-Tometer | | Foam height ^j | |
|---------------------------------------|-----------------|----------------------------------|-----------------|---------------------------------|---------------------------|---|---------------------------|--------------------------|---------------------------|
| | | Surface | Interfacial | Distilled water | 300 ppm CaCO ₃ | Distilled water | 300 ppm CaCO ₃ | Distilled water | 300 ppm CaCO ₃ |
| Disodium 2-Sulfo- | | | | | | | | | |
| 1. hexadecanoate | 63 | 41.5 ^d | 10 ^d | >300 | >300 | 22 ^d | 25 ^d | 175 | 125 |
| 2. 2-methyleicosanoate ^a | 53 | 41.4 | 9.5 | >300 | >300 | 22 | 16 | 193 | 0 |
| 3. 2-methyloctadecanoate ^a | 43.5 | 33.8 | 6.0 | >300 ^b | >300 | 22 | 17 | 200 | 45 |
| 4. 2-methylpentadecanoate | 44 | 45.8 | 24.3 | 41 | >300 | 12 | 16 | 85/40 | 140/20 |
| 5. 2-butyldecanoate | <1 | 61.7 | 35.2 | >300 | >300 | 9 | 9 | 20/0 | 0 |
| 6. 2-hexyldecanoate | <1 | 50.7 | 28.6 | 26 | >300 | 9 | 9 | 120/0 | 40 |
| 7. 2-octyldecanoate ^a | 67 | 35.5 | 15.7 | 5 | >300 | 8 | 8 | 0 | 95/25 |
| Sodium Methyl 2-Sulfo- | | | | | | | | | |
| 8. hexadecanoate ^c | 29 ^e | 39.0 | 9.7 | 25 | 16 | 16 ^d | 15 ^d | 210 | 225 |
| 9. 2-methyleicosanoate | 48 | 38.0 | 7.8 | >300 | >300 | 13 | 12 | 140 | 30 |
| 10. 2-methyloctadecanoate | 42 | 39.7 | 8.7 | 70 | >300 | 15 | 11 | 175 | 35 |
| 11. 2-methylpentadecanoate | 39 | 42.9 | 12.2 | 24 | >300 | 14 | 13 | 180/160 | 200 |
| 12. 2-butyldecanoate | <1 | 44.7 | 21.3 | 13.3 | 5.2 | 9 | 6 | 170/5 | 200/5 |
| 13. 2-hexyldecanoate | <1 | 36.3 | 9.7 | 1.3 | 3.7 | 11 | 12 | 204/190 | 213/200 |
| 14. 2-octyldecanoate | 22.5 | 29.1 | 5.9 | 2.8 | 38 | 12 | 10 | 210 | 215 |

^a Data from reference (5).

^b Value redetermined by (2).

^c Data from reference (7).

^d Lab. control samples.

^e Data from reference (9).

^f The temperature at which a 1% dispersion becomes a clear solution.

^g Determined at 0.1% solution at 25°C using a DuNoüy Tensiometer.

^h Determined using 0.1% solution at 25°C with a 5 g cotton skein and a 3 g hook (2).

ⁱ Determined by increase in reflectance after washing G.D.C. #26 standard soiled cotton in 0.25% solution at 60°C.

^j Measured using 0.25% solution by Ross-Miles test at 60°C (3). Initial foam height given as numerator while denominator indicates foam height after 5 min. Initial foam height given where change of <10 mm occurred after 5 min.

tween 250–550 ppm CaCO₃. Preliminary biodegradability studies of the sodium methyl esters by the River Water Die Away Method (1) indicate that the esters range from soft to moderately hard as the size of the 2-alkyl group is increased. Anomalous rates of biodegradation and values of ester concentration were observed with samples 9 and 14 in Table III.

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