Disodium 2-Sulfohexadecyl and 2-Sulfoöctadecyl Sulfates[1]

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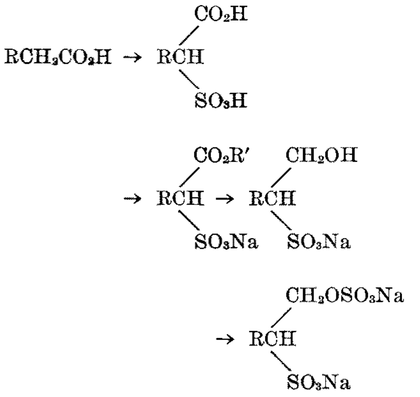
Abstract

Disodium 2-sulfoalkyl sulfates $RCH(SO_3Na)CH_2OSO_3Na$ were prepared from esters of α-sulfo acids by metal borohydride reduction of the ester group to a primary alcohol, and subsequent sulfation. Disodium 2-sulfoöctadecyl sulfate resembles disodium 2-sulfoethyl α-sulfostearate in general structure and properties, particularly in the fact that both are excellent lime soap dispersing agents.

Introduction

Reduction of sodium salts of esters of α-sulfopalmitic or α-sulfostearic acid with metal borohydrides had been found to give sodium 1-hydroxy-2-alkanesulfonates of high Krafft point and limited solubility, probably due to hydrogen bonding (9,10). Sulfation of the primary hydroxyl group, represented by the reaction scheme, gave disodium 2-sulfoalkyl sulfates with two adjacent strongly hydrophilic groups at the end of the molecule. The preparation and surface active properties are described.



Experimental

Sulfation. Chlorosulfonic acid was added dropwise in 1.5 molar ratio to a stirred solution of 2-sulfohexadecanol or 2-sulfoöctadecanol (9) in carbon tetrachloride at 25C. The mixture was heated to 50C to complete the reaction, cooled to −5C, neutralized with alcoholic NaOH and allowed to crystallize at 0C. Recrystallization from aqueous ethanol gave the disodium 2-sulfoalkyl sulfates in a yield of about 80%.

Analysis. Calculated for disodium 2-sulfohexadecyl sulfate $C_{16}H_{32}Na_2O_7S_2$, 10.30% Na, 43.03% C, 7.22% H, 14.36% S; found 10.17% Na, 43.19% C, 7.33% H, 14.35% S. Calculated for disodium 2-sulfoöctadecyl sulfate, 9.69% Na, 45.55% C, 7.65% H, 13.51% S; found 9.65% Na, 45.51% C, 7.61% H, 13.60%S.

Properties. Surface active and related properties are shown in Table I. Surface and interfacial tension was measured with duNoüy tensiometer, critical micelle concentration (cmc) by dye titration using Pinacyanole Chloride, foam ht by the Ross-Miles test (5), calcium stability by a modified Hart method (13) and lime soap dispersion properties by the method of Borghetty, reported as percentage or the number of g of the surface active agent required to disperse the calcium soap formed from 100 g of sodium oleate (1).

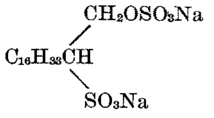
Wetting properties were measured by the Draves test (2) using a 5-g cotton skein and a 3-g hook. Detergency was measured as the increase in reflectance after washing ten swatches of standard soiled cotton, GDC No. 26 (3), in 1 liter 0.25% detergent solution, in the Terg-O-Tometer for 20 min at 60C and 120 cycles/min.

Metallic ion stability was measured by the method of Harris (4). Stability to acid hydrolysis was measured by heating a stirred 0.10 molar solution in 60% ethanol, 0.4 molar with respect to H_2SO_4, at 80C, titrating aliquots periodically.

Discussion

Comparing the properties of disodium 2-sulfohexadecyl sulfate and disodium 2-sulfoöoctadecyl sulfate (Table I) it is apparent that the shorter chain homolog has a higher cmc, is less surface active and has inferior wetting, detergent, foaming and lime soap dispersing properties. Likewise in the comparison of disodium 2-sulfoethyl α-sulfopalmitate and disodium 2-sulfoethyl α-sulfostearate (6,7,8,12) the shorter chain homolog has a higher cmc and is less surface active, but differences in properties are not as marked. Both the palmitate and stearate are excellent lime soap dispersing agents.

The 16 and 18 carbon 2-sulfoalkyl sulfates are similar to the isethionate esters of α-sulfopalmitic and α-sulfostearic acid, respectively, both in general structure and in surface active properties. In each case a long hydrophobic chain terminates in two bulky adjacent hydrophilic groups. This type of structure is evidently related to the excellent lime soap dispersing properties which both



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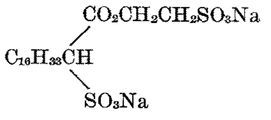

have in common.

Figure 1 shows in a general way how compounds of this structure might act in dispersing lime soaps. In the absence of a lime soap dispersing agent the typical soap micelle (B) formed from the oriented molecules (A), is changed by hard water to an inverted phase (C) which leads to separation of lime soap curds. In the presence of the lime soap dispersing agent inversion is prevented, possibly through formation of a mixed micelle in which the proper curvature is maintained by the bulky hydrophiles of the lime soap dispersing agent.

Disodium 2-sulfoöctadecyl sulfate, disodium 2-sulfoethyl α-sulfopalmitate, disodium 2-sulfoethyl α-sulfostearate and sodium dodecyl sulfate are about equal

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TABLE I

Surface Active Properties

	Approx solubility 25C %	Surface and interfacial tension 0.25%, 25C dynes/cm		cmc		Wetting time (6) 0.1%, 25C sec		Detergency 0.25%, 60C ΔR		Initial foam ht (3), 0.25%, 60C mm		Calcium stability (4) ppm $CaCO_3$	Lime soap dispersing power (5) %
		S.T.	I.T.	mmoles per liter	%	distd. water	300 ppm	distd. water	300 ppm	distd. water	300 ppm		
Disodium 2-sulfohexadecyl sulfate	30	48.5	21.5	8.9	0.40	184	84	13	16	125	155	>1800	84
Disodium 2-sulfoöctadecyl sulfate	15	41.3	11.3	3.6	0.17	28	42	27	22	155	200	>1800	5
Disodium 2-sulfoethyl α-sulfopalmitate	50	35.2	9.8	8.2	0.40	>300	>300	24	20	135	200	>1800	5
Disodium 2-sulfoethyl α-sulfostearate	30	35.8	11.6	1.9	0.10	>300	>300	29	26	175	225	>1800	5
Sodium dodecyl sulfate	45	34.3	11.5	6.8	0.20	7.5	88	26	22	205	225	720	30
Sodium octadecyl sulfate	0.02	......	......	0.11	0.004	....	....	33	31	185	20	....	

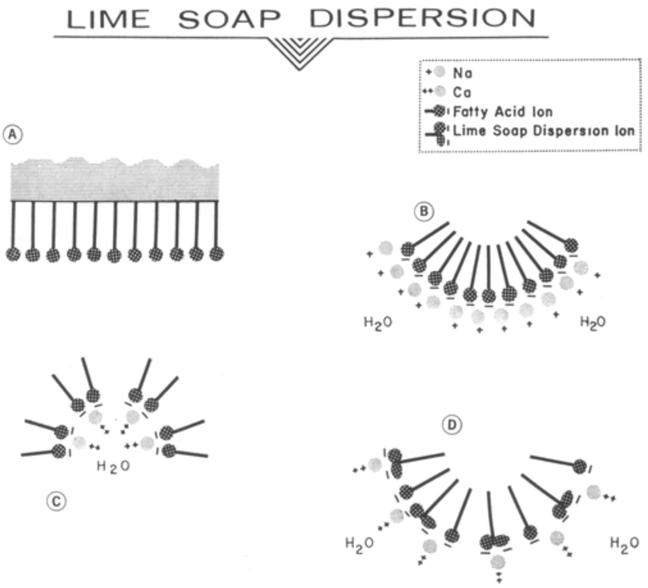

FIG. 1. Lime soap dispersion.

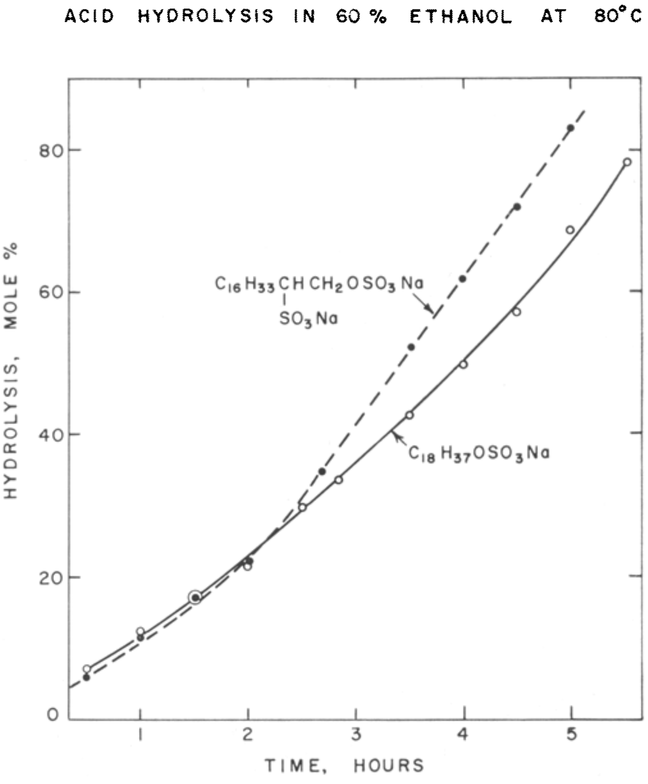

FIG. 2. Relative rate of acid catalyzed hydrolysis of disodium 2-sulfoöctadecyl sulfate and sodium octadecyl sulfate.

in detergency but there are some differences in wetting and foaming properties.

Sodium octadecyl sulfate is an excellent detergent but has limited solubility at room temp. Introduction of the α-sulfo group to form disodium 2-sulfoöctadecyl sulfate greatly increases solubility and cmc and results in excellent lime soap dispersing properties but detracts from detergency.

In the metallic ion stability test values of 100 representing excellent stability, clear solutions and no tendency to precipitate were obtained for Mg^{++}, Al^{+++}, Ca^{++}, Fe^{++}, Ni^{++}, Cu^{++}, Zn^{++} for both of the disodium 2-sulfoalkyl sulfates. Values for Ba^{++} and Pb^{++} were 15 and 75, respectively. The 2-sulfoalkyl sulfates are therefore not precipitated under the test conditions except in the presence of Ba^{++} and Pb^{++}. This stability to metal ions is similar to that of the isethionate esters of α-sulfo acids which are precipitated only by Ba^{++} (7).

Like the sodium alkyl sulfates the disodium 2-sulfoalkyl sulfates are stable to alkaline hydrolysis but can be hydrolyzed in acid solution. In a comparison of acid catalyzed hydrolysis of aqueous ethanol solutions (Fig. 2) disodium 2-sulfoöctadecyl sulfate was found to be hydrolyzed at a slightly faster rate than sodium octadecyl sulfate. No hydrolysis of disodium 2-sulfoethyl α-sulfostearate occurred under the same conditions.

Disodium 2-sulfoethyl esters of α-sulfo acids and disodium 2-sulfoalkyl sulfates are biodegradable in the River Water Die Away test (11) but not as readily as sodium alkyl sulfates, which lose all surface active properties on enzymatic hydrolysis.

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REFERENCES

1. Borghetty, H. D., and C. A. Bergman, JAOCS *27*, 88–90 (1950).
2. Draves, C. Z., and R. G. Clarkson, Am. Dyestuff Reptr. *20*, 201–208 (1931), A.A.T.C.C. Tech. Manual and Yearbook *33*, 154–155 (1957).
3. Draves, C. Z., and O. L. Sherburne, Am. Dyestuff Reptr. *39*, 771–772 (1950).
4. Harris, J. C., "Detergency Evaluation and Testing," Interscience, New York, 1954.
5. Ross, J., and G. D. Miles, Oil & Soap *18*, 99–102 (1941); Am. Soc. Testing Mater., "Book of ASTM Standards" *10*, 878–880 (1958).
6. Stirton, A. J., R. G. Bistline, Jr., J. K. Weil, Waldo C. Ault and E. W. Maurer, JAOCS *39*, 128–131 (1962).
7. Weil, J. K., R. G. Bistline, Jr. and A. J. Stirton, *Ibid. 32*, 370–372 (1955).
8. Weil, J. K., R. G. Bistline, Jr. and A. J. Stirton (Secretary of Agriculture), U.S. 2,806,044 (1957).
9. Weil, J. K., F. D. Smith and A. J. Stirton, J. Org. Chem. *27*, 2950–2952 (1962).
10. Weil, J. K., F. D. Smith, A. J. Stirton and R. G. Bistline, Jr., JAOCS *40*, 538–541 (1963).
11. Weil, J. K., and A. J. Stirton, *Ibid. 41*, 355–358 (1964).
12. Weil, J. K., and A. J. Stirton, J. Phys. Chem. *60*, 899–901 (1956).
13. Wilkes, B. G., and J. N. Wickert, Ind. Eng. Chem. *29*, 1234–1239 (1937).

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