Polyhydric Alcohol Esters of α-Sulfo Fatty Acids

T. MICICH, M. SUCHARSKI, J.K. WEIL and A.J. STIRTON,[1]
Eastern Regional Research Laboratory,[2] Philadelphia,
Pennsylvania 19118

ABSTRACT

Direct esterification of α-sulfopalmitic and α-sulfostearic acids with excess ethylene glycol, glycerol, pentaerythritol and 2-methoxyethanol was carried out in carbon tetrachloride to give products containing essentially monoesters. Surface active properties of these compounds were measured with emphasis on washing ability in combination with soap. The detergency of these esters was compared with those of hexitol and sucrose α-sulfo fatty acid esters. Although the esters had moderate lime soap dispersing ability, their detergency showed synergism when combined with soap.

INTRODUCTION

Fatty acid esters of carbohydrates and similar materials were reported to have desirable surfactant properties (1). Subsequently hexitol and sucrose esters of α-sulfo fatty acids were found to be effective detergents and lime soap dispersing agents (2). These esters are considerably more water soluble than the corresponding unsulfonated fatty acid esters and can tolerate polyester impurities without decreasing water solubility or surfactant properties. The present study was undertaken to prepare α-sulfo esters of polyhydric alcohols containing fewer than six carbon atoms and to determine their surfactant properties. The enhanced detergency of these esters in combination with soap was compared with detergency values obtained with hexitol and sucrose esters of α-sulfo fatty acids.

EXPERIMENTAL PROCEDURES

Materials

Palmitic and stearic acids were purified by standard distillation and crystallization methods. The purity of these acids was better than 99% by gas chromatography of the methyl esters. Ethylene glycol, glycerol, pentaerythritol and 2-methoxyethanol were of Eastman white label quality and used without further purification. Carbon tetrachloride, reagent grade, was dried by passage through silica gel prior to use. Dioxane was purified by Fiesers' method (3). Sulfur trioxide was distilled prior to use. Sucrose and hexitol sulfo fatty acid esters were prepared as given in reference (2).

Sulfonation

To a reaction flask equipped with a condenser, stirrer and dry N_2 sweep was added 145 ml carbon tetrachloride and 12.3 g (0.14 M) dioxane. The solution was cooled in an ice bath and 10.3 g (0.13 M) sulfur trioxide in 5 ml of carbon tetrachloride was added. After the slurry had been stirred for a few minutes, 33.2 g (0.12 M) of stearic acid in 50 ml of carbon tetrachloride was added and the mixture was heated 1 hr at 60 C. The resulting solution was evaporated to 150 ml for pentaerythritol esterification because of the low solubility of this alcohol but used

---

[1] Deceased.

[2] East. Market. Nutr. Res. Div., ARS, USDA.

TABLE I

Elemental Analysis of Polyhydric Alcohol Esters of α-Sulfo Acids

	Found				Theory[a]			
Sodium salt	C	H	S	Na	C	H	S	Na
Ethylene glycol α-sulfopalmitate	53.64	8.73	8.00	5.67	53.70	8.76	7.96	5.73
Glycerol α-sulfopalmitate	53.06	8.60	7.80	5.43	52.76	8.62	7.41	5.32
Pentaerythritol α-sulfopalmitate	52.56	8.64	7.56	5.03	52.91	8.67	6.72	4.83
2-Methoxyethyl α-sulfopalmitate	55.18	9.43	7.89	5.43	54.78	8.95	7.70	5.52
Ethyleneglycol α-sulfostearate	55.33	9.17	7.26	5.16	55.80	9.15	7.43	5.34
Glycerol α-sulfostearate	54.14	8.88	6.98	5.02	54.75	8.97	6.96	4.99
Pentaerythritol α-sulfostearate	54.38	8.98	6.48	4.55	54.73	8.99	6.36	4.56
2-Methoxyethyl α-sulfostearate	56.48	9.41	7.10	5.15	56.73	9.29	7.21	5.17

[a] Based on monoester content.

TABLE II

Surface Active Properties

α-Sulfoester[a]	Krafft point, C	Ca^{++} stability, ppm $CaCO_3$	Lime soap dispersing power, %	Surface and interfacial tension, 0.1% dynes/cm S.T. 25 C	I.T.	Foam height[b] 60 C, mm
Ethylene glycol α-sulfopalmitate	<1	>1800	10	43.1	13.2	180
Glycerol α-sulfopalmitate	<1	>1800	10	43.8	13.9	185
Pentaerythritol α-sulfopalmitate	<1	>1800	11	45.6	15.6	110
2-Methoxyethyl α-sulfopalmitate	<1	>1800	10	41.6	11.4	200
Ethylene glycol α-sulfostearate	<1	>1800	10	41.6	10.2	180
Glycerol α-sulfostearate	<1	>1800	10	42.8	11.3	170
Pentaerythritol α-sulfostearate	<1	>1800	6	46.2	14.8	135
2-Methoxyethyl α-sulfostearate	<1	>1800	9	40.5	9.0	150

[a] Essentially monoesters.

[b] Foam height was measured on 0.25% built solutions (0.05% active ingredient + 0.20% builder) in hard water 300 ppm.

directly for the remaining esterifications.

Esterification

The preparation of the pentaerythritol ester of α-sulfostearic acid is cited here as a typical example, representing the procedure used for the preparation of all esters. To the solution of 0.12 M sulfostearic acid in carbon tetrachloride was added 32.7 g (0.24 M) pentaerythritol. The mixture was stirred and gently refluxed until the theoretical amount of water was collected in a trap. The reaction mixture was diluted with 50 ml of hot carbon tetrachloride and filtered hot to remove excess pentaerythritol. The filtrate was diluted with an equal volume of 95% ethanol, neutralized with 5N NaOH, cooled to -30 C and filtered at this temperature. The filtrate was evaporated to 100 ml, cooled to -30 C and filtered to give 13.4 g (23% yield) of monoester, the elemental analysis of which is given in Table I.

Isolation and Analysis of Monoesters

Both sodium pentaerythritol esters and sodium glycerol α-sulfostearate were isolated as described above. The remaining esters, after initial removal of insoluble disodium salts and precipitation from the neutralized solution, were recrystallized two or three times from 95% ethanol. The composition of these esters was confirmed by elemental analysis for C, H and S as shown in Table I.

Disodium salt has been found previously to be a contaminant in this type of reaction mixture. Analysis of the present reaction products for disodium salt by a previously published method (2) indicated that the concentration of this impurity was less than 3.5%.

Saponification equivalents were determined by a standard method. The values were found to be within 10% of theory.

Surface Active Properties

Krafft point, calcium ion stability, lime soap dispersing power and surface and interfacial tension were measured by methods previously described (4). Foam height was measured by the Ross-Miles test and detergency was measured with the Terg-O-Tometer in hard water (300 ppm) at 60 C at 110 Cpm. The results are given in Tables II and III.

RESULTS AND DISCUSSION

Previous work (2,5,6) showed that several esterification procedures are applicable to polyhydric alcohols. Isomeric mixtures of partial esters were isolated from the products of such esterifications. The esterification of glycerol is complicated by the presence of two different hydroxyl groups. However acyl group migration should lead to a product containing mostly one substituted monoester.

Direct esterification was used in this program as it gave monoester products of acceptable color and purity. The products probably contained some higher ester components along with small amounts of disodium salt of sulfonated fatty acid. While yields ranged from 23-75% calculated on the initial quantity of fatty acid used, no attempt was made to optimize these yields of the esters. Carbon tetrachloride solvent was used after evaluation of other solvent systems showed it to be the best compromise for low reaction temperature, miscibility of components and azeotroping ability with water.

TABLE III

Detergency of Sulfoesters
With Soap[a] and With Builder

	Soap[b]		Builder[c]
Sodium salt	0.16%	0.19%	0.20%
		ΔR	
Ethylene glycol α-sulfopalmitate	33.9	32.6	31.8
Glycerol α-sulfopalmitate	33.7	31.5	31.7
Pentaerythritol αsulfopalmitate	33.0	33.0	30.6
2-Methoxyethyl α-sulfopalmitate	32.1	33.1	30.2
Ethylene glycol α-sulfostearate	35.4	31.2	30.7
Glycerol α-sulfostearate	36.8	31.9	31.0
Pentaerythritol α-sulfostearate	33.8	26.8	31.6
2-Methoxyethyl α-sulfostearate	32.5	32.2	30.5
Sucrose α-sulfostearate	34.9		
Mannitol α-sulfostearate	35.3		
Sorbitol α-sulfostearate	35.1		
2-Sulfoethyl α-sulfostearate	30.7		
Methyl α-sulfotallowate	34.2		

[a] Soap is purified sodium tallowate with ΔR = 28.8 at 0.20% level.

[b] Detergency measured with solutions containing 0.04% active ingredient + 0.16% soap and 0.01% active ingredient + 0.19% soap.

[c] Detergency measured with built solutions at 0.25% concentration containing 0.05% active ingredient + 0.20% builder. The builder contained 10% tetrasodium pyrophosphate, 55% sodium polyphosphate, 24% sodium sulfate, 1% cmc and 10% sodium silicate.

The surface active properties of the sulfo esters are summarized in Table II. All samples exhibit good solubility as shown by Krafft points below 1 C. Calcium ion stability is greater than 1800 ppm $CaCO_3$ for all samples. Lime soap dispersing power is moderate, while foam stability is fair in hard water (300 ppm). Surface and interfacial tension are high. Few differences are observed with any of the products studied. Detergency values for these sulfo esters are given in Table III in combination with soap (sodium tallowate) at 20% and 5% levels and with builder at the 20% level. By analysis of variance (7) a difference of 1.3 in ΔR was significant with 95% probability. Detergency for all samples listed is very good at the 80% soap level. The definite enhancement in detergency is seen in comparing the reflectance values for 80% soap and 80% builder. Little difference in detergency values is observed between the hexitol and sucrose esters and the esters of lower polyhydric alcohols. Further work is necessary to determine whether a relationship exists between the enhanced detergency and lime soap dispersing power of these esters.

ACKNOWLEDGMENT

Analysis for C, H and S was performed by L.H. Scroggins and A.S. Kravitz.

REFERENCES

1. Ames, G.R., Chem. Rev. 60:541 (1960).
2. Bistline, R.G., Jr., F.D. Smith, J.K. Weil and A.J. Stirton, Ibid. 46:549 (1969).
3. Fieser, L.F., and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, 1967.
4. Stirton, A.J., R.G. Bistline, Jr., E.A. Barr and M.V. Nuñez-Ponsoa, JAOCS 42:1078 (1965).
5. Osipow, L., F.D. Snell, W.C. York and A. Finchler, Ind. Eng. Chem. 48:1459 (1956).
6. Osipow, L., and W. Rosenblatt, JAOCS 44:307 (1967).
7. Stirton, A.J., R.J. Bistline, Jr., E.B. Leardi and M.V. Nuñez-Ponsoa, Ibid. 44:99 (1967).

[Received April 27, 1971]