

Conditions during Phase 5 (July 30 to August 14) did not appear to reach a steady state. Continued loss of solids occurred and it was noted that the mixed liquor dissolved oxygen remained at zero until August 10, when trace concentrations were found. It may have been advantageous to continue under these operating conditions until a steady state had been reached; however, the schedule made it necessary to terminate the use of LAS at this point, in order to acquire additional information on ABS removal at mixed liquor solids conditions similar to those prevailing during Period 4.

Removal of MBAS during Phase 6 (August 15 to September 4) returned to levels poorer than previously experienced during Phase 2. The average mixed liquor suspended solids during Phase 6 was 2,578 mg/liter as compared with 8,430 mg/liter during Phase 2. Per cent removal of MBAS during Phase 6 was 65.2% as compared with 89.9% during Phase 2. This difference could have been due to the higher solids levels present during Phase 2 or it is possible that further acclimation of the sludge and continued operation at these conditions would have resulted in improved removals of the ABS materials.

C. Correlation Between BOD and LAS Removal

Phases 3, 4-A, 4-B, and 5 provided results for comparing BOD removal with LAS removal. The BOD and MBAS average removals for these periods are

plotted in Figure 8. The data indicate that a good relationship exists between the two with a slope of approximately 45 degrees.

Although the few points suggest a good one-to-one relationship, it would, of course, be necessary to verify these data before any firm conclusion could be made, recalling that the conditions during Phase 5 were essentially anaerobic, and that solids were being lost in the effluent during this phase. However, the data in Figure 8 do lend support to the hypothesis that LAS removal is correlated with BOD removal with a slope of approximately 1.

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Sulfonation of Hexadecene-1 and Octadecene-1¹

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Abstract

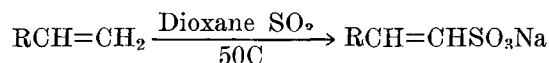
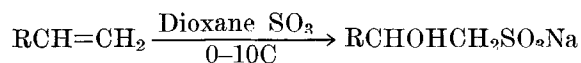
The reaction of dioxane-sulfur trioxide with hexadecene-1 and octadecene-1 carried out below 10C gave difficultly soluble sodium 2-hydroxy-1-alkanesulfonates containing smaller amounts of other vicinal position isomers.

Sulfonation of the olefins at 50C gave a mixture of isomeric vicinal sodium alkenesulfonates containing also small amounts of hydroxyalkanesulfonates, sulfo-sulfates and sultones. This higher temperature reaction product was readily soluble with good foaming and detergent properties.

Introduction

Fat-based α -olefins of 16 and 18 carbon atoms, from the dehydration of hexadecanol and octadecanol, are possible intermediates for detergents and surface active agents. The sulfonation of the olefins and properties of the reaction products was therefore explored.

Products which are mixtures of hydroxyalkanesulfonates and alkenesulfonates have been reported in similar investigations (1,7), the former favored by lower and the latter by higher reaction temperatures.



Dioxane-sulfur trioxide was selected as the sulfonating agent, since it appeared to have the right degree of reactivity, was convenient to work with, and dioxane was easily removed from the product. Markownikoff addition of sulfur trioxide or a sulfur trioxide adduct to an α -olefin would be expected to give products hydrolyzable to 2-hydroxy-1-alkanesulfonates. Comparison of these with 1-hydroxy-2-alkanesulfonates from the sodium borohydride reduction of methyl esters of α -sulfo esters (8), showed that, in contrast to the alkenesulfonates, both the 1-hydroxy and 2-hydroxy sulfonates were difficultly soluble, probably due to hydrogen bonding. Sulfo-sulfates from 1-hydroxy-2-alkanesulfonates, however, are readily soluble detergents and lime soap dispersing agents (6).

Experimental

α -Olefins. The commercial high purity α -olefins from Archer-Daniels-Midland Co. were further purified by crystallization from acetone at -20C , and

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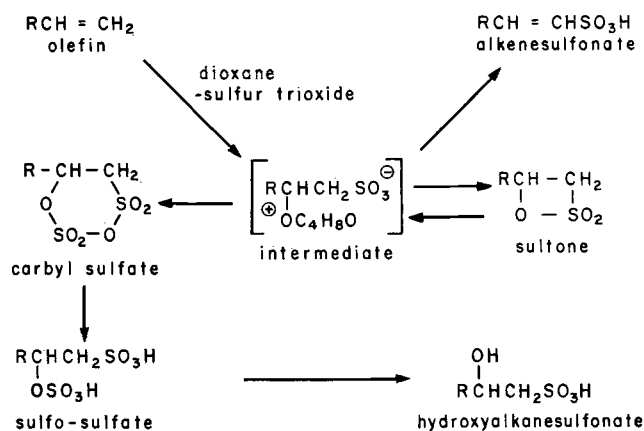


FIG. 1. Reaction of dioxane-sulfur trioxide with α -olefins.

then distilled through a 2-foot column containing Cannon extruded packing. Distillation range, f.p. and n_D^{20} were as follows: hexadecene-1, 181C/40 mm, 5.2–4.0C, 1.4413; octadecene-1, 201C/32 mm, 18C, 1.4448. Infrared analyses in the 10.6 μ region showed that nonterminal trans olefin content was 1–2%. Since the lower melting nonterminal cis olefin would be preferentially lost on crystallization, the terminal olefin content of all of these hydrocarbons is at least 97%.

Dioxane-Sulfur Trioxide. The sulfonation complex was prepared by adding 20 ml (0.5 mole) of liquid sulfur trioxide dropwise to a stirred solution of 45 g (0.5 mole) of purified dioxane in carbon tetrachloride while cooling in an ice bath. (Dioxane may be treated with potassium hydroxide and distilled or passed through activated alumina to remove stabilizer and trace quantities of peroxides and water.) The freshly prepared white slurry of dioxane-sulfur trioxide was used to react with the olefin at the appropriate temperature.

Low Temperature Sulfonation

Sodium Hydroxyhexadecanesulfonate. Hexadecene-1, 0.25 mole, was added to a cold, stirred, slurry of 0.50 mole dioxane-sulfur trioxide in carbon tetrachloride. The mixture was stirred 3 hr at 0–10C, then diluted with 95% ethanol, neutralized with 18 N sodium hydroxide, and filtered. The solid product was heated in constant boiling hydrochloric acid for 4 hr at reflux temperature to destroy sultone and sulfate structures. The acid mixture was neutralized with sodium hydroxide and filtered. Recrystallization of the solid product from aqueous ethanol gave 26% sodium hydroxyhexadecanesulfonate.

Analysis Calculated for $\text{C}_{16}\text{H}_{33}\text{NaO}_4\text{S}$: C, 55.78%; H, 9.66%; Na, 6.68%; S, 9.31%.

Found: C, 56.07%; H, 9.85%; Na, 6.58%; S, 9.31%.

As will be shown more particularly for the 18 carbon compound, this product is a mixture of vicinal position isomers and is predominantly sodium 2-hydroxy-1-hexadecanesulfonate.

Sodium Hydroxyoctadecanesulfonate. Low temperature sulfonation of octadecene-1 carried out as described for hexadecene-1 gave a 75% yield of crude product after hydrolysis with constant boiling hydrochloric acid and neutralization, and 41% yield of purified sodium hydroxyoctadecanesulfonate after recrystallization.

Analysis Calculated for $\text{C}_{18}\text{H}_{37}\text{NaO}_4\text{S}$: C, 58.03%; H, 10.01%; Na, 6.17%; S, 8.61%.

Found: C, 57.81%; H, 10.06%; Na, 6.28%; S, 8.27%.

Vicinal Position Isomer Composition by Oxidative Degradation. A stirred mixture of 2 g of sodium hydroxyoctadecanesulfonate and 50 ml of concentrated nitric acid was heated slowly until brown fumes began to evolve at 43C, then poured on ice and diluted with 95% ethanol. Crystallization from aqueous ethanol gave 80% yield of fatty acids. Gas-liquid chromatographic analysis of the methyl esters showed the presence of methyl heptadecanoate, hexadecanoate and pentadecanoate, and traces of lower esters, corresponding to the presence of 64% sodium 2-hydroxy-1-octadecanesulfonate with 33% of the 3-hydroxy-2-sulfo and 3% of the 4-hydroxy-3-sulfo isomers.

Chromic acid oxidation instead of nitric acid oxidation showed the same proportion of the three isomers.

High Temperature Sulfonation

Sodium Hexadecenesulfonate. The reaction which favored alkenesulfonate formation was carried out by adding the olefin to a stirred slurry of dioxane-sulfur trioxide at 40–50C, and stirring the mixture for 2 hr at 50–55C. Neutralization of the reaction mixture gave 87% yield of crude product. Treatment with ethanol, removal of insoluble matter, and crystallization of the filtrate at –20C, gave 55% yield of sodium hexadecenesulfonate as a white solid.

Analysis Calculated for $\text{C}_{16}\text{H}_{31}\text{NaO}_3\text{S}$: C, 58.86%; H, 9.57%; Na, 7.04; S, 9.82%; iodine value, 77.7.

Found: C, 56.19%; H, 9.52%; Na, 6.97%; S, 9.99%; iodine value (by hydrogenation), 41.6.

This analysis corresponds to a mixture of 55% sodium hexadecenesulfonate, 35% sodium hydroxyhexadecanesulfonate, 8% sulfated hydroxyhexadecanesulfonate ($\text{C}_{16}\text{H}_{32}\text{Na}_2\text{O}_7\text{S}_2$), and 2% sultone ($\text{C}_{16}\text{H}_{32}\text{O}_3\text{S}$). This composition was indicated also by thin-layer chromatography, with 5% acetic acid in methanol as the mobile phase and hydrated silica gel for the stationary phase. The presence of hydroxy compounds was shown by characteristic infrared absorption.

Sodium Octadecenesulfonate. High temperature sulfonation of octadecene-1 carried out as described for hexadecene-1 gave a 55% yield of sodium octadecenesulfonate as a white solid, after recrystallization.

Analysis Calculated for $\text{C}_{18}\text{H}_{35}\text{NaO}_3\text{S}$: C, 60.98%; H, 9.95%; Na, 6.49%; S, 9.04%; iodine value, 71.6.

Found: C, 57.47%; H, 9.43%; Na, 6.49%; S, 9.64%; iodine value (by hydrogenation), 36.9.

This analysis corresponds to a mixture of 52% sodium octadecenesulfonate, 28.5% sodium hydroxyoctadecanesulfonate, 15.5% sulfated hydroxyoctadecanesulfonate ($\text{C}_{18}\text{H}_{36}\text{Na}_2\text{O}_7\text{S}_2$), and 4% sultone ($\text{C}_{18}\text{H}_{36}\text{O}_3\text{S}$).

Sodium octadecenesulfonate was also prepared by bringing the sulfonating agent and the α -olefin together at 0–10C and later raising the temperature to 50–55C for 2 hr. Sodium hydroxyoctadecanesulfonate was isolated from the cold reaction mixture; and a predominance of sodium octadecenesulfonate along with its usual impurities was recovered from the reaction after heating.

Vicinal Position Isomer Composition by Oxidative Degradation. The fatty acid mixture formed by oxidation of 2 g of sodium octadecenesulfonate with aqueous chromic acid was converted to methyl esters and analyzed by gas-liquid chromatography. Methyl heptadecanoate, hexadecanoate, pentadecano-

TABLE I
 Surface Active Properties of α -Olefin Sulfonation Products, and Related Compounds

	Krafft point ^a °C	Calcium stability ^b 0.5%, 25°C ppm CaCO ₃	Foam height ^c 0.25%, 60C mm.		Detergency 60C, ΔR^d		
			Distilled water	300 ppm	Distilled water	300 ppm	0.05% + 0.20%
							builder ^e
Na Hexadecenesulfonate ^f	38 ^g	720	210	240	19	16	23
Na Octadecenesulfonate ^f	36	340	200	185	21	20	22
Na Hydroxyhexadecanesulfonate ^h	88 ⁱ ⁱ ⁱ	12	9	9
Na Hydroxyoctadecanesulfonate ^h	97 ⁱ ⁱ ⁱ	10	12	10
Na 1-Hydroxy-2-hexadecanesulfonate ^j	84 ⁱ ⁱ ⁱ	16	5	12
Na 1-Hydroxy-2-octadecanesulfonate ^j	93 ⁱ ⁱ ⁱ	15	6	12
Na Oleyl Sulfate.....	clear at zero	920	240	230	25	15	29
Na Octadecyl Sulfate.....	56 ⁱ ⁱ ⁱ	31	29	30
Na Dodecyl Sulfate.....	16	650	175	195	16	19	12

^a Temperature at which a 1% dispersion became a clear solution on gradual heating.

^b Modified Hart method (11).

^c Stable foam, Ross-Miles test (5).

^d Increase in reflectance after washing standard soiled cotton (3) 20 mins. in the Terg-O-Tometer.

^e Builder composition 55% Na₅P₃O₁₀, 24% Na₂SO₄, 10% Na₄P₂O₇, 10% Na metasilicate, 1% CMC.

^f Partially purified product from high temperature sulfonation.

^g Hexadecenesulfonate, further purified, has a Krafft Point of 22C.

^h Mainly RCHOHCH₂SO₃Na from low temperature sulfonation.

ⁱ Not sufficiently soluble.

^j Borohydride reduction of RCH(SO₃Na)CO₂CH₃ (8).

ate, tetradecanoate, tridecanoate and dodecanoate were found to be present in amounts corresponding to the presence of 30% sodium 1-octadecenesulfonate, C₁₆H₃₃CH=CHSO₃Na, and 45%, 15%, 7%, 2% and 1% of the corresponding 2, 3, 4, 5 and 6-isomers, respectively.

Surface Active Properties

The Krafft point, calcium stability and foaming and detergent properties of the low and high temperature sulfonation products were measured and are recorded in Table I in comparison with values for sodium 1-hydroxy-2-alkanesulfonates (8) and sodium alkyl and alkenyl sulfates (10).

Discussion

The formation of intermediates in the reaction of an α -olefin with sulfur trioxide or a sulfur trioxide adduct is shown in Figure 1. Nielsen (4) has isolated a sultone as the principal intermediate in the reaction with sulfur trioxide and proved this structure by nuclear magnetic resonance and infrared spectroscopy. Bordwell (1,2) has proposed that a monosulfonate formed from a sulfur trioxide adduct can further react to produce carbyl sulfate.

The neutralized product could therefore contain a mixture of hydroxyalkanesulfonates, alkenesulfonates, sulfo-sulfates and intermediary unhydrolyzed sultones and carbyl sulfates. Analysis of the reaction product from high temperature sulfonation indicates such a mixture. The data of thin-layer chromatography suggests that chromatographic separation of products is possible, but we found ordinary separations based on solubility, such as those suggested by Turbak (7), to be satisfactory.

The reaction mixture from low temperature sulfonation may have as many components but the limited solubility of the sodium hydroxyalkanesulfonates in aqueous ethanol permits their removal and purification, except for the separation of the vicinal position isomers from each other.

Isomerization of the α -olefin may take place through a carbanion ion mechanism prior to reaction with sulfur trioxide and give isomeric hydroxyalkanesulfonates and alkenesulfonates. High temperature sulfonation causes a greater degree of isomerization.

The Krafft point data of Table I shows that the hydroxyalkanesulfonates from low temperature sul-

fonation, primarily 2-hydroxy-1-alkanesulfonates, like the 1-hydroxy-2-alkanesulfonates, are difficultly soluble, probably because of hydrogen bonding. The Krafft point for the low temperature sulfonation products is not sharp because they are mixtures of isomers. The values recorded (88C and 97C) were the temperatures at which all of the sample went into solution and are likely to be the Krafft points of the least soluble isomers.

The Krafft points for the sodium alkenesulfonates depend upon the degree of purification and would be considerably lower for pure compounds or simple mixtures of vicinal isomers.

The hydroxyalkanesulfonates listed in Table I have poor detergency, regardless of origin. The sodium alkenesulfonates have good foaming and detergent properties and resemble sodium oleyl sulfate in this respect. They are better detergents than sodium dodecyl sulfate but inferior to sodium octadecyl sulfate.

Biodegradability. Comparison of sodium hydroxyhexadecanesulfonate (from low temperature sulfonation) with sodium 1-hydroxy-2-hexadecanesulfonate (from borohydride reduction) and sodium octadecenesulfonate (from high temperature sulfonation) in the river water methylene blue test (9) showed they were "soft" detergents; 80% of each detergent was degraded in less than 4 days. Sodium dodecenesulfonate, used as a control, required 5 days for 80% degradation.

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