AOS – An Anionic Surfactant System: Its Manufacture, Composition, Properties, and Potential Application

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ABSTRACT

Several sulfonation parameters, believed to be critical to the manufacture of good quality α-olefin sulfonate (AOS), are related to product color and conversion. The interfacial properties for single carbon number AOS and the major components comprising AOS are investigated. Results, based on surface activity, indicate that AOS in the molecular weight range from C_{14} through C_{18} should be of value in formulating efficient cleaning agents. The data show that AOS is more effective for lowering Crisco®/solution interfacial energy than the more commonly used surfactants. The alkene-1-sulfonate component of AOS was found to be most effective in lowering interfacial energy with the hydroxyalkane-1-sulfonate component being significantly less effective but still more effective than alcohol ether sulfate or linear alkylbenzene sulfonate of comparable molecular weight. Hand dishwashing efficacy was found greatest for the hydroxyalkane-1-sulfonate component of AOS, but combinations of hydroxyalkane-1-sulfonates and alkene-1-sulfonates were shown to be synergistic for laundering applications. The presence of the -OH group in the hydroxyalkane sulfonate structure was shown to increase solubility and lower surface activity significantly more than the presence of unsaturation in the alkene sulfonate. Long, single branching in the α-olefin sulfonate and random internal olefin sulfonate are shown to reduce drastically the surface activity. The hydroxyalkane and alkene-1-sulfonates were rapidly biodegraded. Disulfonates and long, singly branched sulfonate were more slowly degraded. Both 1,3-sultones and 1,4-sultones were found to biodegrade rapidly.

INTRODUCTION

Literature reference to the direct sulfonation of α-olefins with sulfur trioxide to form highly effective surface active agents can be found as early as nearly a half century ago (1). Only recently, the product of the direct sulfonation of α-olefins, AOS, attained an important commercial position in the detergent industry. Lion Fat and Oil of Japan first began extensive use of AOS in household detergent products 10 to 15 years ago. More recently, AOS has been gaining rapid acceptance as an important anionic surfactant in personal care, household, and industrial applications. α-Olefins of good quality are needed to satisfy the stringent requirements of low color and low unsulfonated matter demanded by these uses. Until the last decade, α-olefins of the necessary quality were not available at competitive prices and in sufficient quantity to get more than cursory attention within the detergent industry. Even then, it remained for recent innovative developments in hardware and technology for direct sulfonation before AOS could be considered a viable and economically competitive surfactant, useful in formulating personal care and household cleaning products.

The direct sulfonation of α-olefins with dilute SO_3, both complexed and free, has been extensively investigated (2-16). Much is reported in the literature concerning the mechanism of the reactions, intermediates formed, and the composition of the complex final product referred to simply as AOS (17-22). Numerous references (22-25) are also available demonstrating the usefulness of AOS in laundry products, dishwash liquids, and personal care products (26-29). However, much less has been reported on the functional properties of the individual structures namely, hydroxyalkane-1-sulfonate, alkene-1-sulfonate, and alkane disulfonate (30-32). The objective of this report is to highlight some critical manufacturing parameters, define some of the characteristics of AOS components, and define the properties of AOS components that may relate to their utility in commercial AOS applications.

EXPERIMENTAL PROCEDURES

Materials

The single carbon number α-olefin sulfonates used in this work were prepared from Ethyl Corporation's α-olefins using a laboratory falling film SO_3 unit operating with an 8% excess of SO_3 as a 2.5% solution in dry nitrogen. The branched chain α-olefin sulfonate was similarly produced in the laboratory using dimer olefin obtained from Jefferson Chemical Company. Internal olefin sulfonates were produced in the laboratory unit from linear internal olefins obtained from Humphrey Chemical Company. All experimental olefin sulfonates were de-salted by separation from 1/1 isopropanol/water solutions according to the procedure of Turbak (33) and de-oiled by petroleum ether extraction to eliminate effects of differing ionic strengths and free oil on the physical measurements.

The γ-sultones used in this work were obtained by fractional, low temperature crystallization from pentane solutions of sulfonic oils prepared in the laboratory unit using linear α-olefins obtained from Humphrey Chemical Company. Recrystallization gave essentially pure γ-sultones having sharp melting points.

The δ-sultones used were prepared by fractional crystallization of crude sulfonic oils previously heated to 100 C and held at this temperature for 1 hr to isomerize γ-sultones to δ-sultones (34).

Hydroxyalkane sulfonates were prepared by the anhydrous NaOH hydrolysis of γ-sultones in toluene solution at the temperature of reflux (~ 108 C) for 1 hr. After the reaction, the toluene and unreacted sultone were removed by ether extraction. The crude hydroxyalkane sulfonate was de-salted by separation from a 1/1 isopropanol/water solution, neutralized to a pH of 7-8 with dilute H_2SO_4, using Na_2CO_3 to effect phase separation. After discarding the aqueous phase, the isopropanol phase was evaporated to dryness to recover the hydroxyalkane sulfonate in purity of > 98% hydroxyalkane with <2% alkene sulfonate (34).

Alkene sulfonates were prepared by anhydrous NH_4Cl hydrolysis in tetradecane at 180 C for 3½ hr of crude sulfonic oils made in the laboratory sulfonation unit using Humphrey Chemical Company's linear α-olefins. An inert nitrogen atmosphere was maintained over the reaction mass

TABLE I

Properties of AOS Produced in Various Sulfonation Units[a]

Reactor type	Reactor length (ft)	Calculated peak temp. (F)	Color (Klett, 5%) Unbleached	Color (Klett, 5%) Bleached	K-value
Laboratory unit	2	131	125	30	0.5
Single-tube Pilot plant unit	20	159	180	40	5.0
Single-tube Pilot plant unit (4 Runs)	20	185	185	N.A.	5.0
		177	145	N.A.	5.0
		181	185	N.A.	5.0
		175	100	N.A.	5.0
Annular pilot Plant unit (4 Runs)	4	233	(240)	55	15.
		240	(320)	85	15.
		254	(180)	40	15.
		259	(400)	110	15.
Multi-tube Commercial unit	6	>300	(430)	115	30.
Annular Commercial unit	4	237	240	55	15.

[a]Values in parentheses were estimated.

during reaction. After completion of the HCl evolution, the reaction mass was cooled, and the unreacted material and tetradecane solvent were removed by extracting four times with ethyl ether. The dried product was dissolved in hot CCl_4 and filtered to remove the product from excess NH_4Cl. The clear hot CCl_4 filtrate was flashed off to give the ammonium alkene sulfonate in 99+% purity. Conversion to the sodium salt was achieved by refluxing the solution of the ammonium sulfonate in 1/1 isopropanol/water with a slight excess of Na_2CO_3 until NH_3 evolution ceased. The sodium alkene sulfonate was recovered by effecting phase separation with addition of more Na_2CO_3. The isopropanol phase, containing the sodium alkene sulfonate, was evaporated to recover the dry, white sodium alkene sulfonate (35).

Equipment

Surface tension values were obtained using the duNouy tensiometer or the Cahn electrobalance with the tensiometer accessory. Interfacial tension measurements were made using a spinning drop tensiometer purchased from the University of Texas, Austin, Texas.

RESULTS AND DISCUSSION

α-Olefin Sulfonation

The present state of technology dictates that α-olefins be sulfonated in reactors that provide thin olefin films and utilize dilute SO_3 to produce good quality AOS at a cost economically competitive with LAS or alcohol-based anionic surfactants.

Computer simulations of laboratory, pilot, and commercial scale falling-film sulfonation reactors indicate that the peak liquid film temperature reached within a reactor has a strong influence on the color of AOS produced. Such simulations also show that the configuration of the gas injection device at the reactor inlet has a strong influence on entrance effects and consequently on peak temperature and olefin conversion.

Large differences noted in product quality from various reactors operated at generally similar conditions (e.g., SO_3/olefin ratio or outlet temperature) prompted a computer simulation of falling-film sulfonators. The computer model developed divides a falling-film reactor into several hundred short segments. Heat and material balances are calculated for each segment starting at the inlet and working downward with outlet conditions for one segment becoming inlet conditions for the next (lower) segment until the bottom of the reactor is reached. A complete description of a very similar model may be found in an excellent article by Johnson and Crynes (36). Significant findings of computer simulations were:

1. The peak liquid film temperatures within various reactors can be very different, even though the outlet temperatures are identical.
2. Entrance effects can be very large in some commercial reactors.

Laboratory-scale and long (20 ft) sulfonation reactors are generally designed to have little turbulence at the gas inlet and consequently small entrance effects. These reactors depend on a small diameter (lab-scale) or long reaction zones to achieve high conversions.

Conversely, commercial reactors which are shorter than 10 ft (4 to 6 ft) are designed for significant turbulence, and entrance effects, at the gas inlet to allow high conversion in a short reaction zone. These reactors tend to develop high peak temperatures and produce relatively darker AOS. Sulfonic acids made from α-olefins are apparently more prone to darken at higher temperatures than are alkylbenzene sulfonic acids. This greater temperature sensitivity, coupled with a slightly higher heat of reaction for olefin sulfonic acids, explains why many commercial reactors have significantly lower capacities for olefin sulfonation than for alkylbenzene sulfonation. The more a reactor depends on entrance effects to achieve conversion, the greater the "derating" when changing from LAB to olefin feedstock.

The data represented in Table I illustrate performance for sulfonation of Ethyl Corporation's α-olefins in various types of reactors. The calculated peak temperatures in the reactors are included. The unbleached Klett color measurement was not available for all runs but, in these instances, it was estimated from bleach conditions and the final bleached color of the AOS. The unbleached Klett color is shown as a function of the peak temperature in Figure 1. This information has been helpful in determining the peak temperature allowable in a reactor for which a target unbleached Klett number has been set.

The interrelations between control variables such as feed rates, SO_3/olefin, or temperatures and reactor geometry such as the tube diameter or length are well covered in the above-mentioned Johnson and Crynes paper. Effects of the configuration of the gas injection device do need to be considered for many commercial units as discussed below. Entrance effects were quantified in the computer program using a correlation proposed by Boelter, Young, and Iverson (37). Quantities affected by entrance effects are the SO_3 mass transfer coefficient and the gas-liquid heat transfer coefficient. Empirically determined "K" values for each reactor type are included in Table I. A "K" value of 1.0 or less indicates essentially no entrance effect. A 90° bend

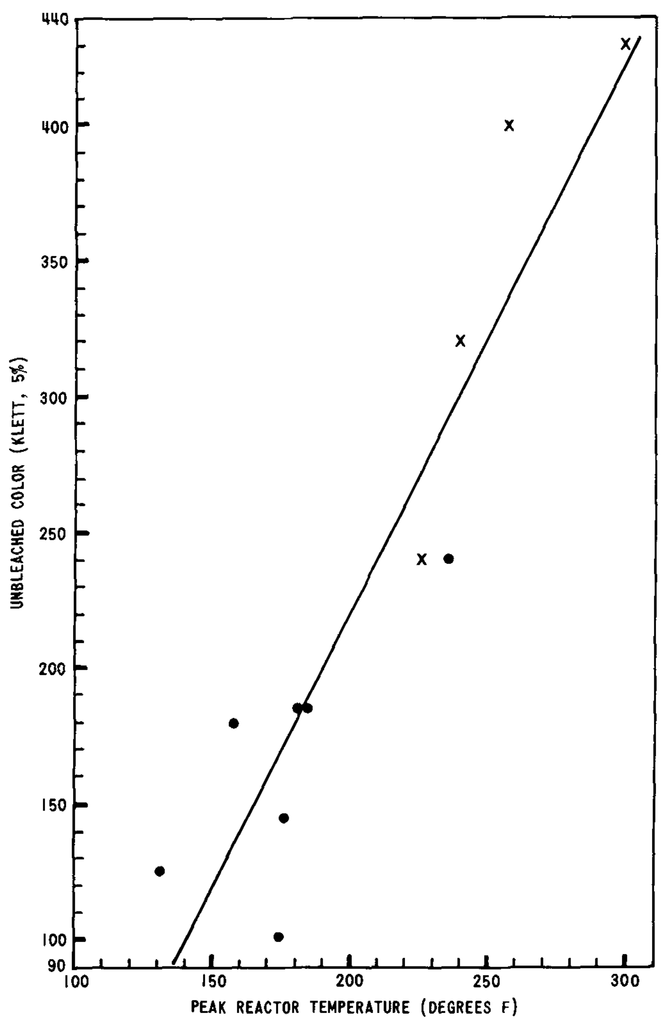

FIG. 1. Unbleached AOS color vs. temperature, 5% aqueous solutions. (●) Measured values; (x) estimated values.

before the entrance yields a "K" value of 7 and orifices yield "K" values of 7-30 depending on the orifice/tube area ratio.

AOS Surface Activity

Much about the potential functionality of a surfactant may be inferred from an inspection of the surface active properties in aqueous solutions (38). Performance evaluations in hand dishwashing and cotton laundering testing have resulted in selection of optimum average molecular weights for AOS (20, 24) under specific laboratory conditions. As an aid to better understanding the utility of AOS, the surface activity for C_{14}, C_{16}, C_{18}, and C_{20} AOS was measured as a function of concentration (Fig. 2-5) in 0 and 125 ppm water hardness.

The near linear portion of the plot for surface tension vs. logarithm of the concentration, $\partial \gamma/\partial \ln c$, just preceding the CMC was used to calculate σ, the area per molecule for the compressed state of the film. Being proportional to the equilibrium absorbtivity of the surfactant, σ will be taken for the purpose of this work as a convenient comparative measure of the relative surface activity for the structures studied. For instance, the greater the surface packing or the lower the surface area per molecule of surfactant, the higher will be the "surface activity" as arbitrarily defined by this concept. For comparative purposes, $\partial \gamma/\partial \ln c$ was determined using a low molecular weight LAS linear alkylbenzene sulfonate with a side chain of about C_{11}, widely used in formulating liquid dishwash products, and a high molecular weight LAS with a side chain of about C_{13} (Fig. 6), widely used in formulating heavy duty laundry products.

Through the information developed for the "surface activity" of LAS generally accepted as having good dishwashing performance (C_{11}) and for LAS similarly accepted as having good laundry performance (C_{13}) in a manner analogous with the HLB concept, it is instructive to compare "surface activities" of the AOS components as defined earlier (Table II). Presence of hard water ions exerts a significant effect by increasing adsorption of the surfactant at the air/solution interface as expected. This increase in surface activity by the hard water ions was greatest for the C_{16} AOS. Since hard water ions are normally present under practical use concentration, comparisons of additional olefin sulfonates were completed only in the presence of water hardness. Using the molecular area for the lower molecular weight LAS as an arbitrary lower limit of practical interest for selection of a dishwash detergent active, it is seen that the C_{14} AOS would represent the minimum

Surface Tension vs. Concentration at 23 C

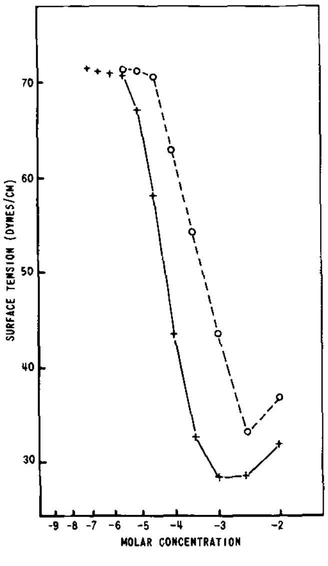

FIG. 2. C_{14} AOS.

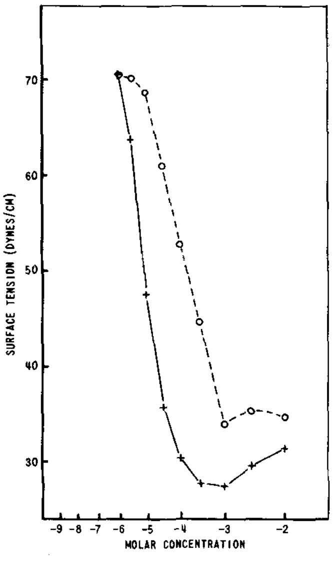

FIG. 3. C_{16} AOS.

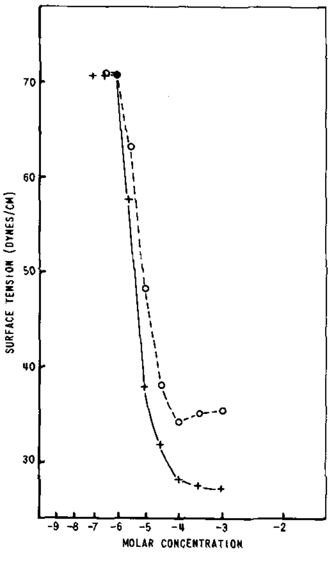

FIG. 4. C_{18} AOS.

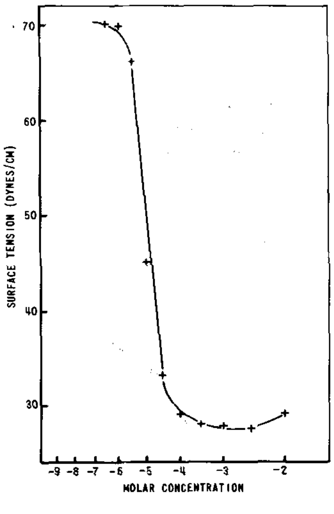

FIG. 5. C_{20} AOS.

+ = 125 ppm water hardness as $CaCO_3$ (Ca^{++}/Mg^{++}, 3/2). o = zero hardness.

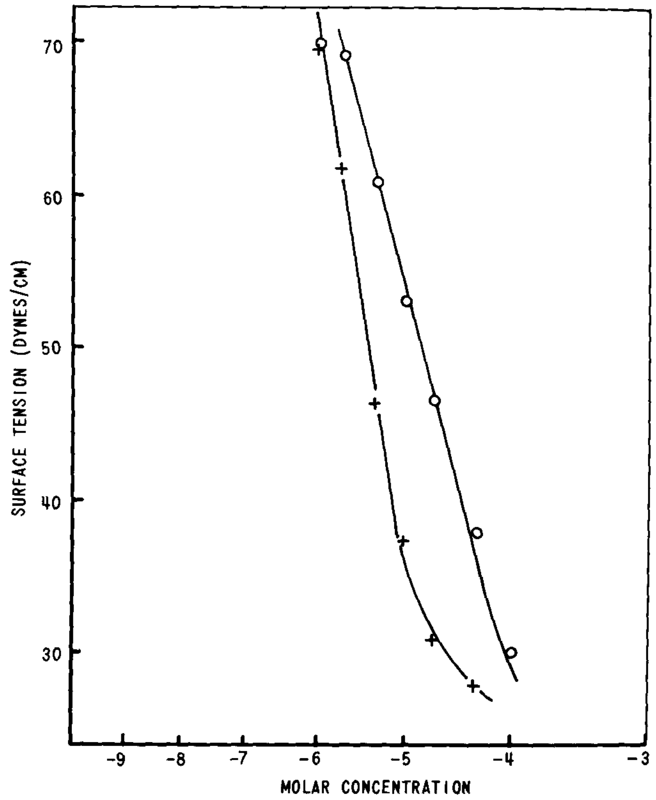

FIG. 6. Surface tension vs. concentration at 23 C. Water hardness-125 ppm as $CaCO_3$ (Ca^{++}/Mg^{++} of 3/2). (○) C_{11} LAS; (+) C_{13} LAS.

carbon length of interest. A C_{12} AOS would not likely represent an effective surfactant. At the other end of the spectrum, it is observed that the C_{20} AOS gives a film very close to the 20Å^2/molecule represented by a solid film at the Pockels point. Thus, it is likely that C_{20} AOS represents a surfactant beyond optimum surface activity under this hard water condition. The C_{18} AOS at the water hardness of 125 ppm has nearly the same σ as found for the C_{13} number chain LAS widely used as a laundry detergent active.

A branched chain C_{16} α-olefin sulfonate and an internal olefin C_{16} sulfonate were evaluated in a similar manner together with a commercial 2/1 blend of C_{14}/C_{16} AOS, a 1/1 blend of $C_{16/18}$ AOS, and a commercial paraffin sulfonate (Fig. 7-10). The data (Table II) indicate that neither the branched C_{16} α-olefin sulfonate nor the internal olefin sulfonate would be an appreciably effective surfactant for detergent use. Both were far less surface active than the C_{14} AOS in 125 ppm water hardness. This has been verified by practical evaluations (18, 30, 39).

Optimum performance in hand dishwashing is reported to be achieved with a 2/1 combination of C_{14}/C_{16} (20, 24). The surface activity of such a blend is found to be slightly above that for a paraffin sulfonate blend used in some dishwash liquid detergents. Similarly, a 1/1 blend of C_{16}/C_{18} AOS with surface acitivity slightly below that for the C_{13} LAS has been suggested as an effective laundry detergent active (20, 24).

Composition of AOS

Formulators of cleaning products utilizing surface active agents generally are accustomed to working with homologous series encompassing relatively low spreads of molecular weight, such as LAS, with the various isomers determined by the position of attachment of the phenyl group along the alkyl chain or, as another example, paraffin sulfonates with the isomers determined by the random points of attachment for the sulfonate groups along the alkyl chain. Other common "building blocks" of the formulator of surface active products are even more specific in chemical structure and are imparted variant properties only by altering molecular weight or structural configuration of the hydrophobe as for the case of the alcohol sulfates or by altering molecular weight of both the hydrophobe and hydrophile as in the case for alcohol ethylene oxide condensates. Optimum performance for any given class of surfactants in any given cleaning, wetting, or emulsifying operation is achieved by proper selection of molecular weight and, where possible, isomeric content. Formulation

TABLE II

Surfactant Area/Molecule, σ (Å^2) at the Air/Water Interface

	Water hardness as $CaCO_3$ – 3/2 Ca^{++}/Mg^{++}		
Sulfonate type	0 ppm	50 ppm	125 ppm
C_{14} AOS	42.8	---	39.9
C_{16} AOS	34.9	---	28.7
C_{18} AOS	28.5	---	24.4
C_{20} AOS	---	---	21.5
2/1 – C_{14}/C_{16} AOS	---	40.7	31.6
1/1 – C_{16}/C_{18} AOS	---	31.7	25.5
C_{16} Branched AOS	---	---	51.5
C_{16} Internal olefin sulfonate	---	---	45.2
Commercial C_{11} LAS	---	---	38.8
Commercial C_{13} LAS	---	---	24.7
Commercial paraffin sulfonate	---	41.3	32.8

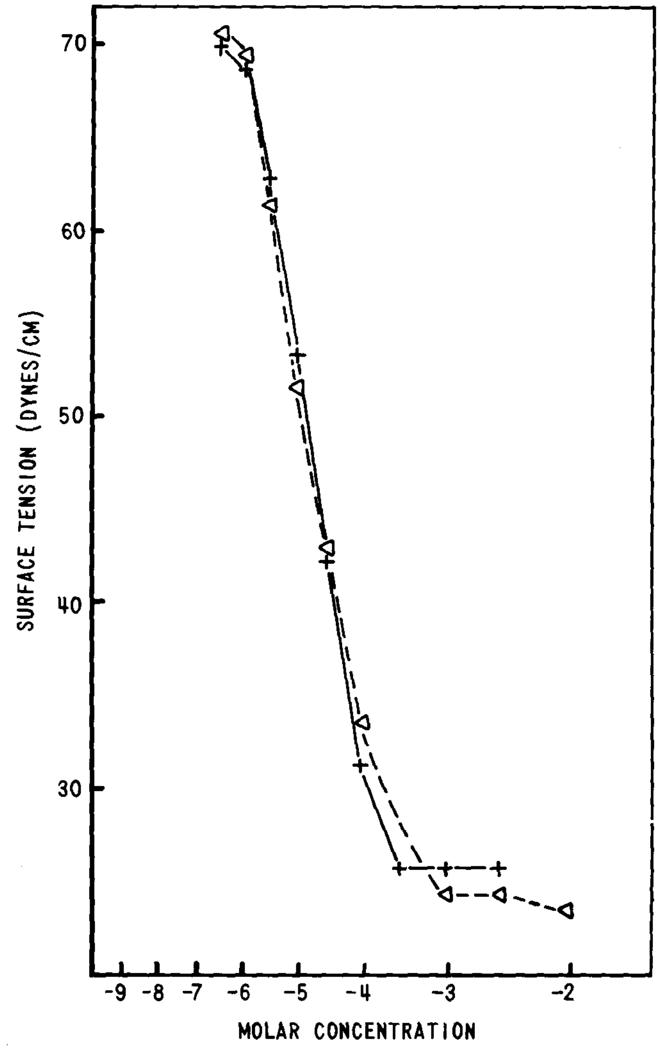

FIG. 7. Surface tension vs. concentration at 23 C. Water hardness-125 ppm as $CaCO_3$ (Ca^{++}/Mg^{++} of 3/2). (△) Branched chain C_{16} AOS; (+) internal C_{16} sulfonate.

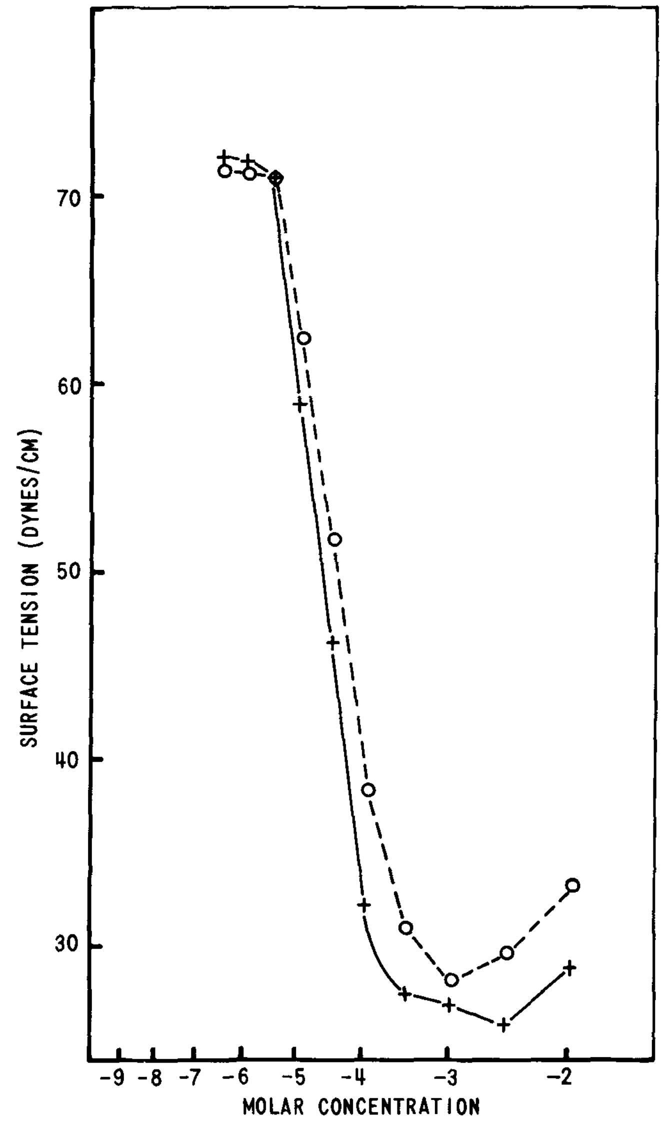

FIG. 8. 2/1 By weight of C_{14}/C_{16} AOS. Surface tension vs. concentration at 23 C. Water hardness $CaCO_3$ (Ca^{++}/Mg^{++} of 3/2). (○) 50 ppm; (+) 125 ppm.

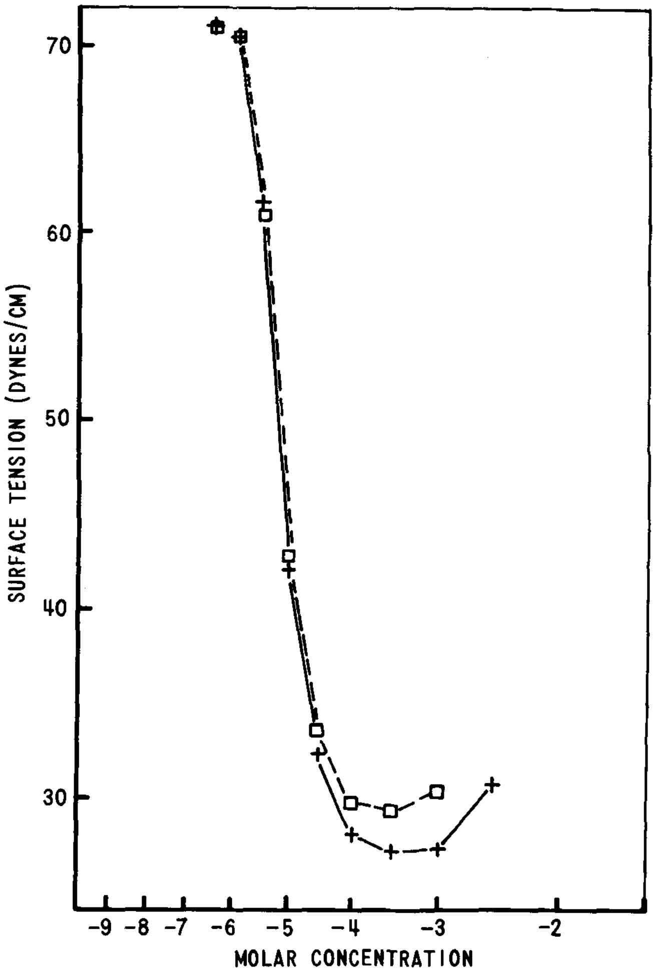

FIG. 9. 1/1 By weight of C_{16}/C_{18} AOS. Surface tension vs. concentration at 23 C. Water hardness as $CaCO_3$. (Ca^{++}/Mg^{++} of 3/2). (□) 50 ppm; (+) 125 ppm.

optimization is achieved through proper selection of several surfactants such that each complements the functionality of the others. As a consequence, highly efficient cleaning products normally contain a blend of surfactants.

α-Olefin sulfonates are unique among the numerous surfactants available to the formulator of detergent products today in that their commercial production results naturally in a blend consisting primarily of two distinct chemical entities, hydroxyalkane-1-sulfonate and alkene-1-sulfonate (22). A minor third component of AOS, alkane disulfonate, will not be considered in this presentation since it is far less surface active than the two major structures comprising AOS. As produced commercially in the U.S. by numerous sulfonators using Allied, Chemithon, and Stepan units, the composition of high quality AOS differs little in the alkene, hydroxyalkane, and disulfonate content. A recent study of AOS composition gave compositions ranging from 64 to 72% alkene, 21 to 26% hydroxyalkane, and 7 to 11% disulfonate irrespective of the type of falling film reactor or whether hydrolysis was conducted batch-wise at atmospheric pressure and temperatures of about 100 C or continuously under pressure at 150-160 C.

As an aid to understanding performance of AOS, the surface active properties of the major components, hydroxyalkane-1-sulfonate and alkene-1-sulfonate were investigated under relatively more practical conditions. The alkane disulfonate again was not investigated as a surfactant component of AOS since it is only a minor and much less surface active component of AOS.

Surface Activity of Hydroxyalkane -1-sulfonate vs. Alkene-1-sulfonate

The surface tensions of sodium hydroxydodecane-1-sulfonate, sodium dodecene-1-sulfonate, and sodium dodecane-1-sulfonate were measured as a function of concentration in 0 and 150 ppm water hardness using both the spinning drop and the duNuoy ring tensiometer attachment for the Cahn electrobalance (Fig. 11-13). Good agreement was found using both methods. Surprisingly, the surface tension of the hydroxyalkane-1-sulfonate required approximately an hour to reach equilibrium at ambient temperatures for concentrations below the CMC. Using the spinning drop tensiometer, it was found that increasing the temperature reduced the time to attain equilibrium (Fig. 14). No significant dependence upon time was observed for attaining equilibrium surface tension values for the sodium dodecene-1-sulfonate.

A comparison of the equilibrium surface areas per molecule for dodecane-1-sulfonate, hydroxydodecane-1-sulfonate, and dodecene-1-sulfonate at 150 ppm water hardness (Ca^{++}/Mg^{++} of 3/2) illustrates again the effect of introducing the -OH or unsaturation into the molecule (Table III). Regarding surface activity again as proportional to σ, as done earlier, we can qualitatively estimate the effect. The introduction of the -OH group into the sodium dodecane-1-sulfonate reduces surface activity to relatively

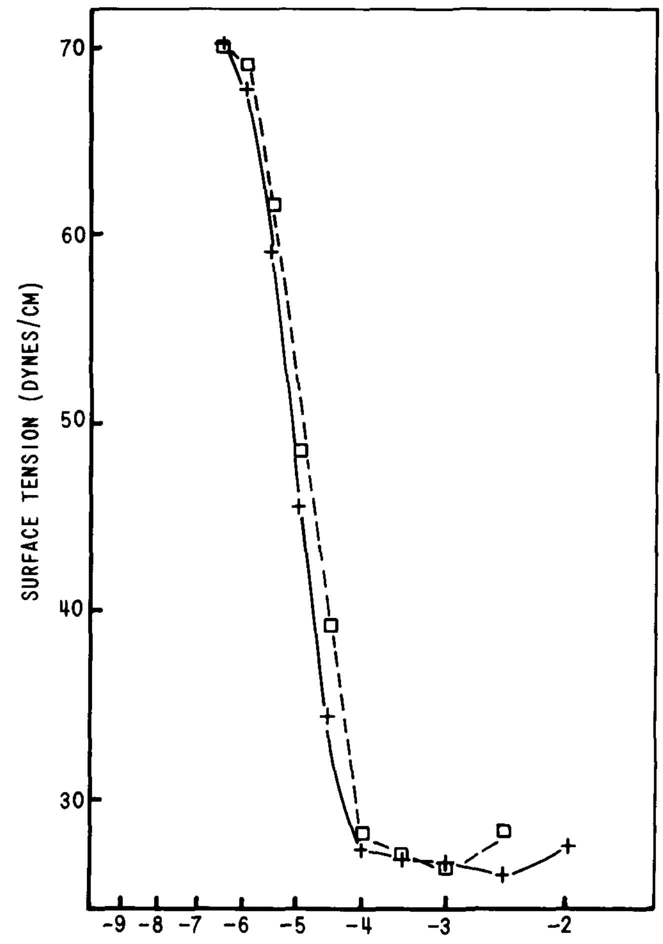

FIG. 10. Commercial paraffin sulfonate. Surface tension vs. concentration at 23 C. Water hardness as $CaCO_3$ (Ca^{++}/Mg^{++} of 3/2). (□) zero ppm; (+) 125 ppm.

ineffective levels in both 0 ppm and 150 ppm water hardness compared to sodium dodecane-1-sulfonate. Only in 300 ppm water does the sodium hydroxydodecane-1-sulfonate have sufficient surface activity to warrant interest.

Introduction of unsaturation into sodium dodecane-1-sulfonate has much less of an effect than introduction of an -OH group. Although the sodium dodecane-1-sulfonate has limited solubility at room temperature in 300 ppm water, the sodium dodecene-1-sulfonate is quite soluble and exhibits good surface activity.

The respective CMC for the sodium dodecane-1-sulfonate, sodium dodecene-1-sulfonate, and sodium hydroxydodecane-1-sulfonate were determined from the surface tension vs. concentration curves to be about 5 x 10^{-4}, 1 x 10^{-2}, and 3 x 10^{-2}, respectively.

Solubility of Calcium Hydroxy and Alkene Sulfonates

An estimate of the contribution to solubility of the hydroxy or unsaturated moiety in the structures comprising AOS may also be inferred from an inspection of the relative solubilities for the respective calcium salts (Table IV). Three techniques, calcium ion activity by specific ion electrode determination, nephelometric end-point, and conductance were used at a constant ionic strength of 10^{-3}. All three methods gave consistent results. As expected, solubility decreased with increasing molecular weight. The hydroxyalkane sulfonates were consistently more soluble than the alkene sulfonate of the same carbon number. This effect is very much pronounced for the lower carbon numbers.

Interfacial Properties of AOS Components

The interfacial tensions of 0.045% active solutions of C_{12} sodium alkene-1-sulfonate and sodium hydroxy alkane-1-sulfonates against Crisco were determined in water of 0, 150, and 300 ppm hardness as 3/2 Ca^{++}/Mg^{++} (Table V). This concentration was selected to simulate the use concentration of 0.15% for a hand dishwash detergent containing 30% active. The spinning drop tensiometer was used

Surface Tension vs. Concentration at 23 C

Water Hardness as $CaCO_3$ (Ca^{++}/Mg^{++} of 3/2)

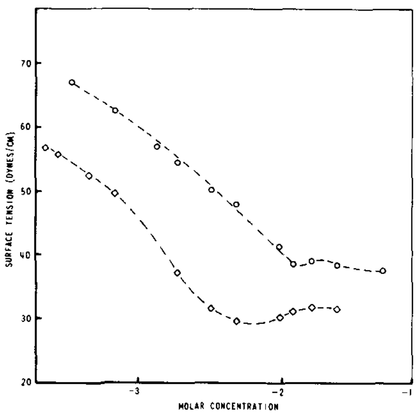

FIG. 11. C_{12} hydroxyalkane-1-sulfonate.
o = zero ppm
◇ = 150 ppm

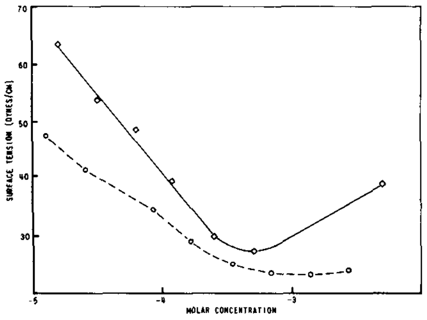

FIG. 12. C_{12} hydroxyalkene-1-sulfonate.
◇ = zero ppm
o = 150 ppm

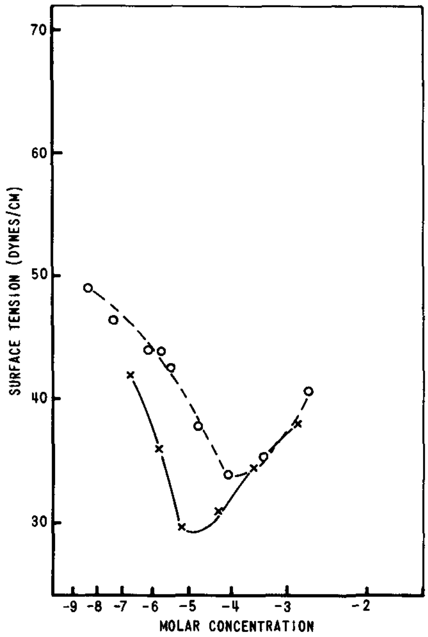

FIG. 13. C_{12} alkane-1-sulfonate.
o = zero ppm
x = 150 ppm

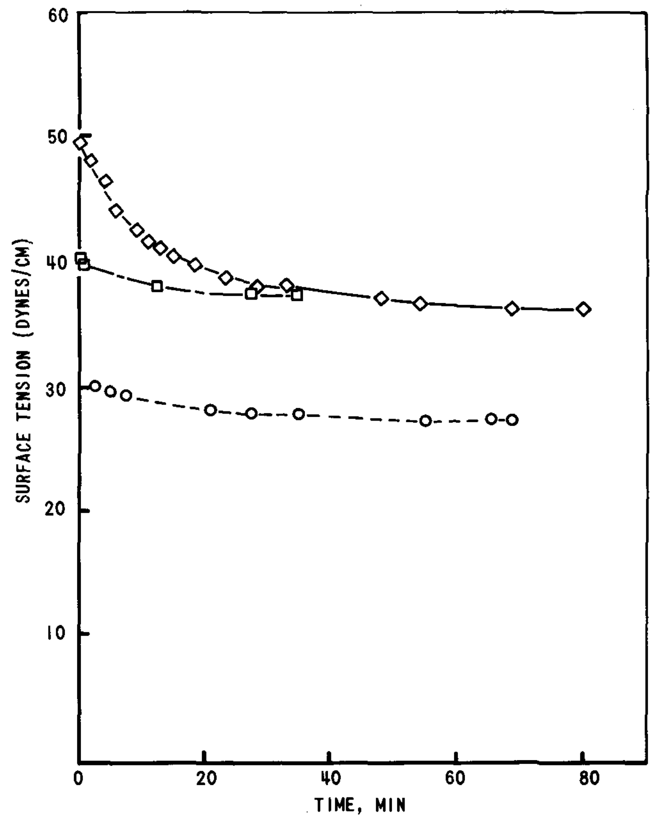

FIG. 14. Surface tension of AOS components vs. time. Zero ppm water hardness. (◇) C_{12} hydroxyalkane-1-sulfonate at 23 C; (□) C_{12} hydroxyalkane-1-sulfonate at 60 C; (○) C_{12} alkene-1-sulfonate at 23 C.

TABLE III

Surfactant Area/Molecule, σ ($Å^2$) at the Air/Water Interface

	Water hardness as $CaCO_3$ — 3/2 Ca^{++}/Mg^{++}		
Sufonate type	0 ppm	150 ppm	300 ppm
Dodecane-1-sulfonate (Na)	59.1	35.1	insol.
Hydroxyalkane-1-sulfonate (Na)	113	80.3	54.8
Dodecene-1-sulfonate (Na)	51.5	40.0	33.2

TABLE IV

Solubility of AOS Components as Calcium Salts -Ksp

Carbon number	Alkene-1-sulfonate	Hydroxyalkane-1-sulfonate
C_{14}	2.7×10^{-12}	3.2×10^{-10}
C_{16}	9.6×10^{-13}	3.2×10^{-12}
C_{18}	7.8×10^{-13}	5.5×10^{-13}

TABLE V

Interfacial Tension of 0.045% Aqueous Solutions of C_{12} Sulfonates vs. Crisco at 60 C — Dynes/cm

Parts by weight	Water hardness[b]		
C_{12} components[a]	0 ppm	150 ppm	300 ppm
1 HA + 0 A	5.32	1.15	0.85
3 HA + 1 A	---	0.87	0.83
1 HA + 1 A	---	0.86	0.81
1 HA + 3 A	---	0.82	0.77
0 HA + 1 A	5.27	0.75	0.57

[a] A = alkene-1-sulfonate; HA = hydroxyalkane-1-sulfonate.

[b] Ca^{++}/Mg^{++} = 3/2 as $CaCO_3$.

TABLE VI

Interfacial Tension of 0.045% Solutions of Surfactants vs. Crisco at 60 C — Dynes/cm

Surfactant	300 ppm Water hardness
LAS — avg. C_{11} side chain	0.57
Lauryl alcohol ether sulfate	0.25
Commercial paraffin sulfonate	0.56
C_{14} alkene-1-sulfonate	0.06
C_{14} hydroxyalkane-1-sulfonate	0.14

TABLE VII

Dishwash Performance of AOS Components — Plates Washed (40)

	Water hardness as $CaCO_3$ — 3/2 Ca^{++}/Mg^{++}		
Olefin component	0 ppm	50 ppm	150 ppm
C_{16} alkene-1-sodium sulfonate	28	33	25
C_{16} hydroxyalkane-1-sulfonate	27	43	33
C_{14} alkene-1-sulfonate	27	35	31
C_{14} hydroxyalkane-1-sulfonate	26	35	31
LAS instead of AOS component	25	33	35

for these measurements. A temperature of 60 C was selected to ensure drop fluidity at all times. No significant difference was found between the interfacial energy of the hydroxyalkane-1-sulfonate and alkene-1-sulfonate interfaces in water of zero hardness. However, presence of water hardness had a pronounced effect on the interfacial energy. In every case, when hard water ions were present, alkene-1-sulfonate lowered interfacial tension against Crisco more than the hydroxyalkane-1-sulfonate. Combinations of hydroxyalkane and alkene-1-sulfonates gave intermediate interfacial tensions, increasing as hydroxyalkane-1-sulfonate content increased.

The interfacial energies of the C_{14} hydroxyalkane and alkene-1-sulfonates against Crisco in water of 300 ppm hardness are surprisingly low (Table VI). Again, the alkene-1-sulfonate is most efficient in lowering Crisco interfacial tension. Both the hydroxyalkane and alkene-1-sulfonates were more effective in reducing interfacial energy than a typical alcohol ether sulfate. In return, the alcohol ether sulfate is more effective than either LAS or sodium alkane sulfonate for lowering solution/Crisco interfacial energy.

These interfacial tension data suggest that AOS would be a more effective emulsifier of Crisco than either LAS or ether sulfate.

Dishwash Performance of AOS Components

The above Crisco interfacial energy results, indicating the potential for unusual effectiveness of AOS as an emulsifier of oils typified by Crisco, a soil used extensively for laboratory evaluation of hand dishwashing formulations (40), could have a negative effect on foam persistence in water of high hardness due to rapid consumption and depletion of the active in solution.

Each C_{14} and C_{16} component was evaluated in a formulation consisting of 6 parts of the AOS component, 3 parts of alcohol ether sulfate, and 1 part lauric/myristic monoethanolamide to give 30% total organic active with the balance being 7% ethanol and 63% water to total 100%. A concentration of 0.15% was used for dishwash evaluation using the miniplate technique (40). The data (Table VII) show that addition of a small amount of hardness, 50 ppm, increases performance of all the surfactants dramatically. This is consistent with data reported earlier showing increasing surface activity with addition of water hardness. However, as water hardness is increased further to 150 ppm, the dishwash performance falls significantly for all the

TABLE VIII

Detersive Efficiency-Washed Cloth Reflectance[a] – 300 ppm Water Hardness as $CaCO_3$ – 3/2 Ca^{++}/Mg^{++}

AOS component carbon number	Alkene/hydroxyalkane 1/0	3/1	1/1	1/3	1/9	0/1
C_{16}	36.8	43.4	43.7	43.4	41.9	33.6
C_{18}	36.6	39.9	43.2	42.5	32.9	30.1

[a] Gardner color difference meter Rd value – 101 EMPA synthetic soil – Tergitometer at at 120 F – 1.5 g/liter detergent. Least significant difference is 1.5 at 95% confidence level.

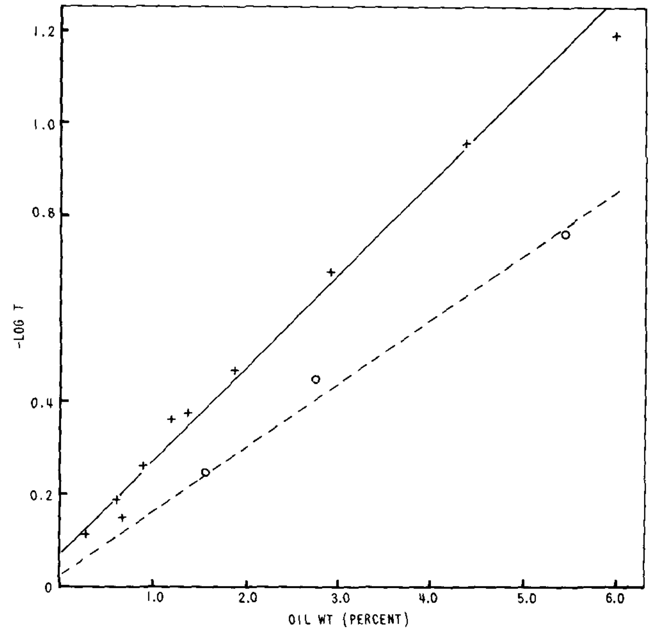

FIG. 15. Transmittance of Crisco emulsions vs. concentration of emulsified Crisco at 55 C. 0.05% Active in aqueous phase. (+) 2/1 By weight of C_{14}/C_{16} AOS; (○) C_{11} LAS.

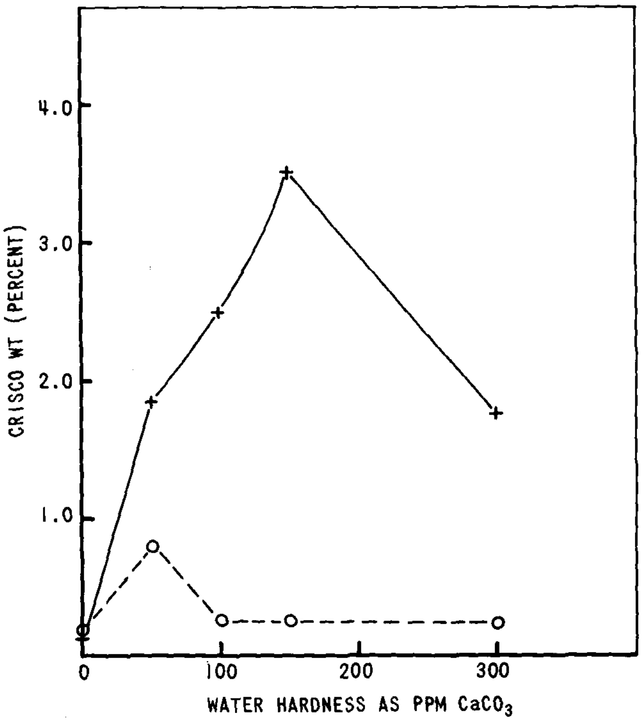

FIG. 16. Emulsion capacity as a function of water hardness at 55 C. Water hardness as ppm $CaCO_3$ (Ca^{++}/Mg^{++} of 3/2). (+) 2/1 By weight of C_{14}/C_{16} AOS; (○) C_{11} LAS.

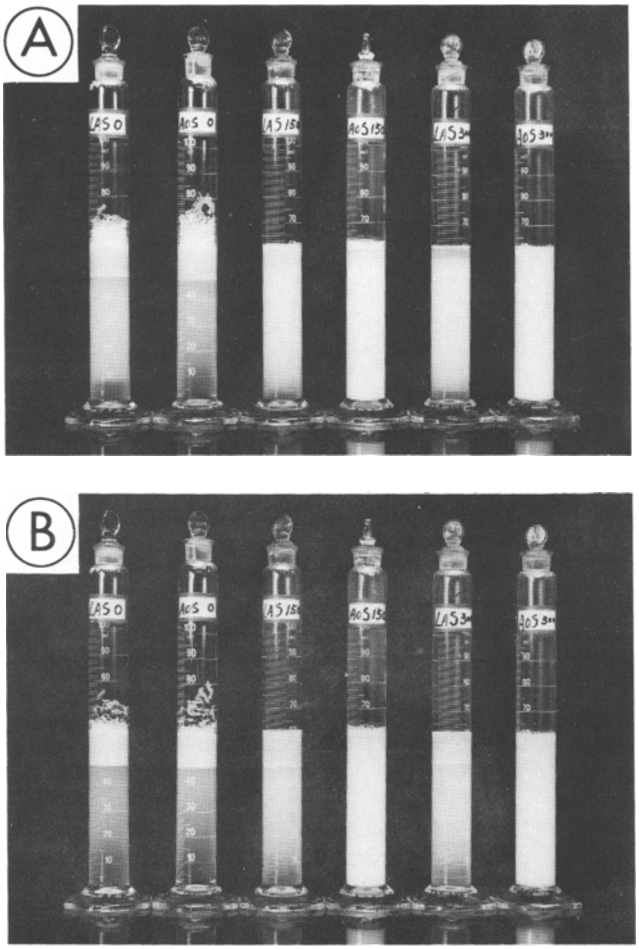

FIG. 17. Emulsion stability of 2/1 C_{14}/C_{16} AOS vs. commercial C_{11} LAS. 50 ml of 0.05% active aqueous solutions plus 10 ml Crisco; (A) after 30 min and (B) after 90 min standing; 0, 150, and 300 ppm water hardness as $CaCO_3$ with 3/2 Ca^{++}/Mg^{++}.

AOS components. Both the C_{14} and C_{16} hydroxyalkane sulfonates were superior to the alkene sulfonates in the hardest water tested. These observations would be consistent with the postulation that the AOS components produce significantly more Crisco/solution interface than LAS under the same conditions of high hard water ion concentration because of their ability to lower the interfacial energy much more effectively. As a possible consequence, the solutions of AOS could be more rapidly depleted in surfactant with a corresponding lowering of the foam persistence. Assuming such a phenomenon does occur, one would then expect the AOS components to be inferior to LAS in foam persistence under the higher hard water conditions since the AOS interfacial energies are much lower than for the corresponding LAS. As shown in Table VII, this appears indeed to be the case.

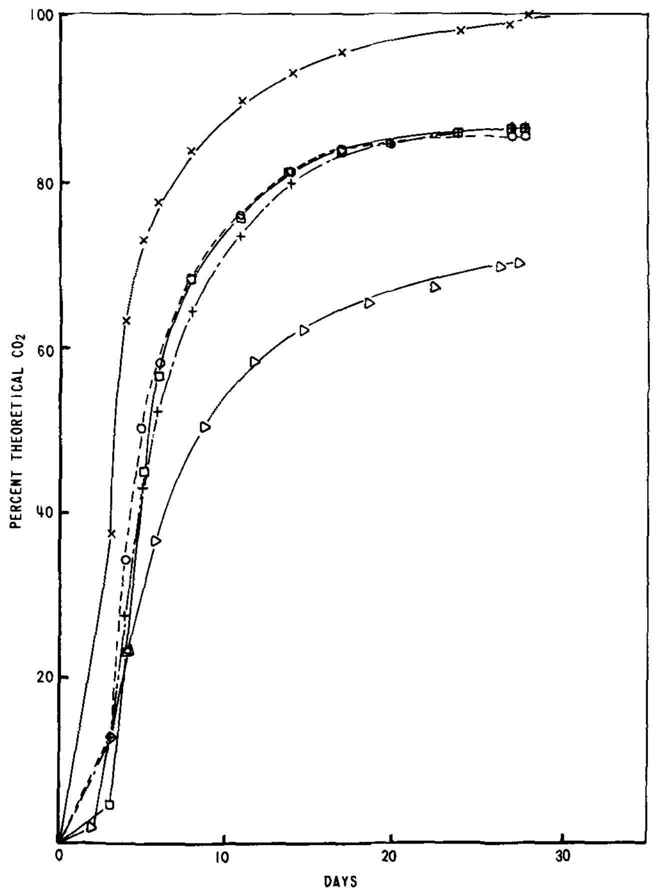

FIG. 18. Rates of ultimate biodegradation. (x) Dextrose standard; (□) C_{14} hydroxyalkane-1-sulfonate; (+) C_{16} hydroxyalkane-1-sulfonate; (○) C_{18} hydroxyalkane-1-sulfonate; (△) commercial soft C_{11} LAS.

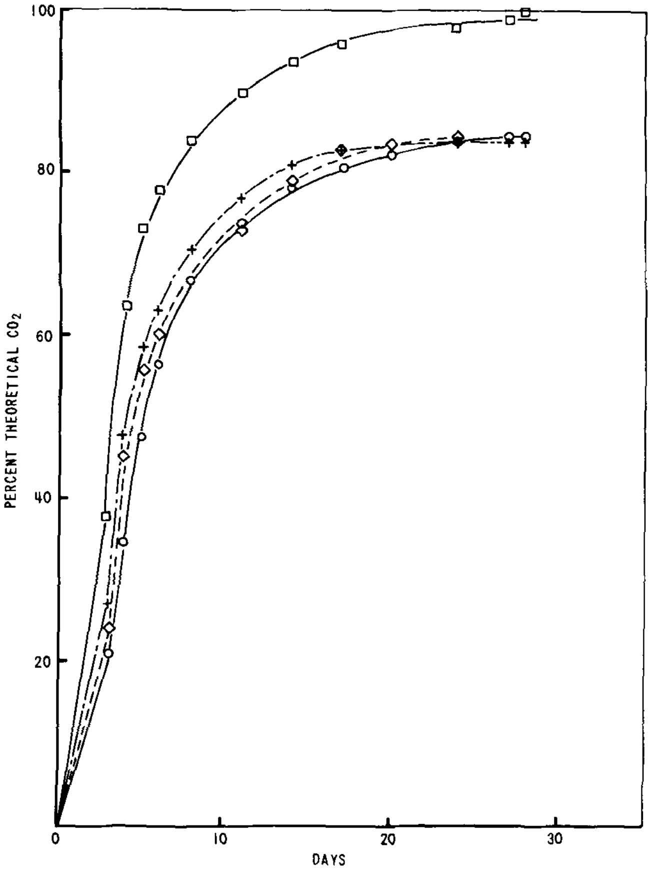

FIG. 19. Rates of ultimate biodegradation. (□) Dextrose standard; (x) C_{14} alkene-1-sulfonate; (○) C_{16} alkene-1-sulfonate; (◇) C_{18} alkene-1-sulfonate.

Crisco Emulsification Properties of AOS Components

The quantity of solid material in a colloidal suspension can be determined by measurement of the transmitted light. The transmittance of a solid suspension is given approximately by the equation (41):

$$-\log T = Kbcd^3/(d^4 + \alpha\lambda^4).$$

Where T is the transmittance, b is the thickness of the colloidal suspension, c is the concentration, d is the average diameter of the particles, λ is the wavelength, K is a proportionality constant which depends on the nature of the suspension and on the method of measurement (turbidimetry or nephelometry), and α is a constant depending on the method only. The equation shows that, for a given colloidal suspension measured with monochromatic radiation in a given apparatus so that α, K, d, and λ are fixed, -log T is proportional (ideally) to bc. This is analogous to Beer's Law for adsorption and indicates that similar apparatus can be employed for its observation and also that the results can be computed by comparable mathematical procedures.

In order to establish the validity of the equation for our emulsion studies, the calibration curves for both the systems Crisco/AOS and Crisco/LAS were first constructed. A known amount of Crisco oil was added into a 100 ml graduated cylinder containing 50 ml of 0.05% active detergent with water hardness of 150 ppm as $CaCO_3$. The Crisco, the detergent solution, and the graduated cylinder were thermostated at 55 C prior to mixing. Agitation was provided by inverting the capped graduated cylinder at 20 rpm for 2 min. The amount of Crisco added was carefully adjusted so that not only a complete emulsification was achieved but also a reasonably stable emulsion was formed. The emulsified Crisco/detergent system was then allowed to cool to room temperature. The transmittances of the series of diluted Crisco/detergent systems were then measured with a Bausch and Lomb photometer at 575 μm wavelength.

The linear relationships obtained from the -log T vs. c plots of both Crisco/AOS and Crisco/LAS systems (Fig. 15) indicate that the Crisco suspensions are reasonably stable, and dilution with deionized water does not seriously alter either the shape or the size of the suspended solid Crisco particles. Therefore the above equation is valid for the systems of interest.

The emulsion capacities of both AOS and LAS were obtained, essentially, by following the same procedures described above. However, instead of a small amount of Crisco added, a fixed amount of Crisco (10 ml) was added to each of the 50 ml detergents. Due to the excessive amount of Crisco added, phase separation was observed. The upper one appeared to be a solid Crisco phase, and the lower one was a reasonably stable uniform solid suspension colloidal phase. After a 4-hr cool down period, the lower phase was then pipetted out for transmittance measurements. No deviation greater than 5% was noted for two different extents of dilutions of each emulsion system studied.

The emulsion capacities, in oil wt % for both AOS and LAS detergents at various water hardnesses, are shown in Figure 16. In the water hardness range (0-300 ppm) examined, AOS performed superior to LAS, except probably at 0 ppm water hardness. AOS's better hard water tolerance is also shown in Figure 16. Our calibration curves show that at constant c, the corresponding -log T value of AOS is larger than the -log T value of LAS. This difference in -log T values would suggest that the Crisco/AOS emulsion system is made up of a smaller average particle size. The

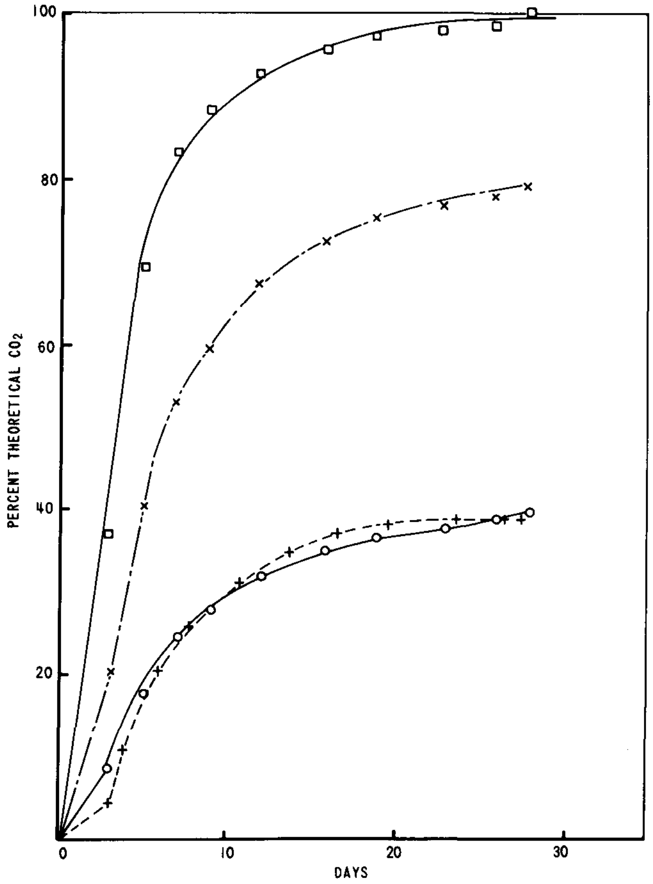

FIG. 20. Rates of ultimate biodegradation. (□) Dextrose standard; (x) internal olefin sulfonate; (○) branched chain α-olefin sulfonate; (+) disulfonate.

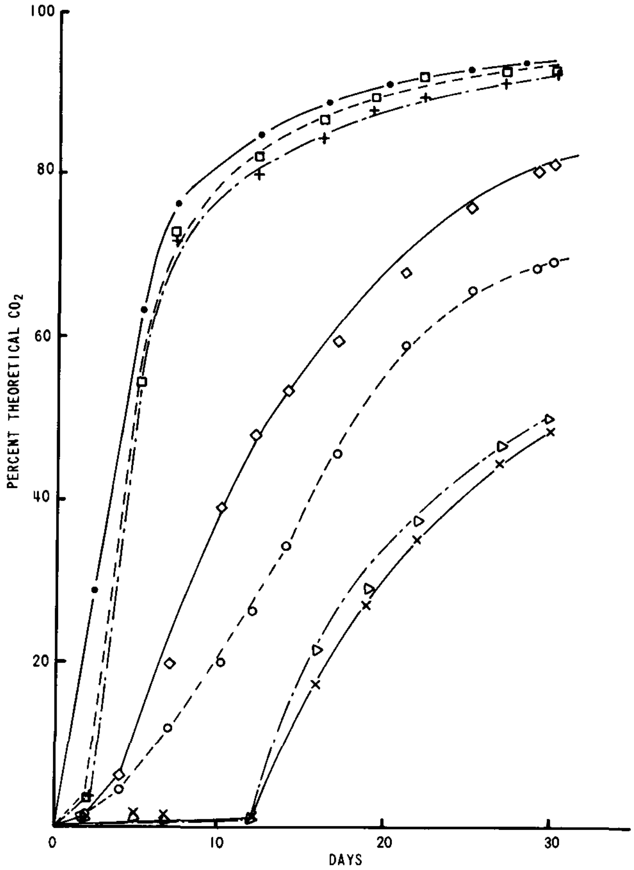

FIG. 21. Rates of ultimate biodegradation. (●) Dextrose standard; (△ and x) 1,4-butane sultone; (□ and +) 1,3-butane sultone; (◇) 1,4-hexadecane sultone; (○) 1,3-hexadecane sultone.

conclusion of finer particle size for the Crisco/AOS system not only correlates well with our emulsion capacity results but also is in good agreement with our interfacial tension measurements. The extent of detergent depletion by oil is also evidenced by the foaming characteristics. Stable foam is associated with systems of small emulsion capacity (both AOS and LAS at 0 ppm), as illustrated in Figure 17.

Detersive Efficiency of AOS Components

Sodium hexadecene-1-sulfonate, sodium octadecene-1-sulfonate, sodium hydroxyhexadecane-1-sulfonate, and sodium hydroxyoctadecane-1-sulfonate were evaluated singly and in combination as the sole active in the following formulation:

Active	20%
Sodium tripolyphosphate	35%
"RU" silicate (solids)	6%
Sodium sulfate	29%
Water	10%

The alkene sulfonates are significantly more efficient as a laundry detergent active than the hydroxyalkane sulfonates (Table VIII). Combinations of alkene with hydroxyalkane sulfonates were found to be synergistic over a wide range. Since laundry detergency is a much more complicated function than dishwash detergency, no attempt will be made to correlate performance with fundamental physical measurements.

Biodegradation of AOS Components

The technique of Sturm (42) was used to estimate the ultimate biodegradation of the components of AOS by measuring the quantity of CO_2 evolved compared with that calculated from the theoretical conversion of all carbon in the molecule to CO_2 (Fig. 18 and 19). No difference in biodegradation rate was observed between hydroxyalkane and alkene sulfonates. Also, no significant difference in the rate of biodegradation was observed that was dependent upon molecular weight for any structure between C_{14} and C_{18} inclusive. All the above structures biodegraded ultimately at a rate appreciably faster than the LAS.

A comparison of the ultimate biodegradation rate for minor additional C_{16} components which may be present in AOS shows that the disulfonate and a long chain (C_{16}) single branched vinylidene olefin sulfonate degrade at about the same rate and significantly slower than that for LAS (Fig. 20). The sulfonate of an internal hexadecene sulfonate biodegraded at a rate only slightly slower than that for the corresponding sodium hydroxyhexadecene-1-sulfonate or sodium hexadecene-1-sulfonate.

Although no 1,3-sultones and little 1,4-sultone (usually less than 5 ppm) are detectable in commercial AOS slurries, it is of interest to establish the fate of these intermediates in the environment. The hexadecane 1,4-sultone and the hexadecane 1,3-sultone were evaluated using the above ultimate biodegradation test procedure. Both structures biodegraded rapidly with only a slight induction period (Fig. 21). Completeness of degradation was at least equivalent to that of LAS for the 1,3-sultone and definitely superior to LAS for the 1,4-sultone.

The completeness of the degradation of the 1,3- and 1,4-sultones was sufficiently below that for the dextrose standard to permit theoretically existence of low molecular weight sultone degradation products. Slopes of the rate curves would, however, indicate continued degradation beyond the 30 days of observation. It was considered important to attempt to establish that degradation of the ring does indeed occur in the ultimate biodegradation test. To accomplish this objective, pure 1,3-propane sultone and pure 1,4-butane sultone were used to establish biodegradation of the ring structures. Since all carbon atoms for these compounds exist as a member of the ring, any CO_2 evolution must indicate degradation of the ring. Under these conditions, the biodegradation of the 1,3-propane sultone proceeded rapidly, with only a slight hesitation for induction. The 1,4-butane sultone required about 12 days before biodegradation started and, afterwards, proceeded at a rapid rate. The test was terminated, as dictated by protocol, after 30 days but, at this time, the rate was continuing rapidly and appeared to indicate that satisfactory biodegradation of the ring structure would occur in nature.

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