

TABLE VI  
Dry Rendering of Lard

Antioxidant	AOM Stability	Initial P.V.	F.F.A.
	Hrs.	me./kg.	%
None.....	5	<0.1	0.25
0.05% APC (after rendering).....	37	<0.1	0.26
0.05% APC (before rendering).....	30	<0.1	0.24
None.....	9	<0.1	0.28
0.05% APC (after rendering).....	60	<0.1	0.28
0.05% APC (before rendering).....	40	<0.1	0.29
None.....	4	<0.1	0.26
0.05% AT (after rendering).....	60	<0.1	0.26
0.05% AT (before rendering).....	70	<0.1	0.26
None.....	2	<0.1	0.35
0.05% AT (after rendering).....	36	<0.1	0.31
0.05% AT (before rendering).....	35	0.4	0.28

APC still showed somewhat better stabilization, when added after rendering, than it did when added before rendering. With the less water-soluble mixture AT, results before rendering were as good as, or slightly better than, those obtained on adding the stabilizer after rendering.

**Effect of Deodorization.** It was of interest to determine to what extent the antioxidants added before or shortly after rendering are removed by distillation during steam deodorization. Batches of lard rendered from cutting fats and containing added BHA or BHT were deodorized in all-glass laboratory equipment for 4 hrs. at 220°C. and 1-mm. pressure. BHA was determined in the deodorized oils by the method of Mahon and Chapman (5) and BHT by the method of Austin (6).

Results of this test are recorded in Table VII. Both BHA and BHT are removed almost quantitatively during deodorization.

### Discussion of Results

The laboratory- and plant-scale rendering tests described here demonstrate that lard and edible beef

TABLE VII  
Effect of Deodorization

Antioxidant	Initial P.V.	AOM Stability	Anti-oxidant Found	Lovibond Color	
	me./kg.	Hrs.	%	Y	R
None.....	0.3	1	0.000	7	— 1.2
0.01% BHA (before deodorization).....	0.7	1	0.0007	7	— 1.1
0.01% BHT (before deodorization).....	0.5	1	0.0001	7	— 1.3
0.01% BHA (after deodorization).....	0.4	20	0.01	7	— 1.0
0.01% BHT (after deodorization).....	0.5	13	0.01	7	— 1.0

fats can be stabilized effectively by incorporating phenolic antioxidants during pressure steam-rendering. The individual phenolics, such as BHA and BHT, provide relatively more protection for a given stabilizer level than do the mixtures containing BHA and BHT in cottonseed oil (AT), propyl gallate and citric acid in propylene glycol (PC), or BHA, propyl gallate, and citric acid in propylene glycol (APC).

The ineffectiveness of the combinations in propylene glycol such as PC or APC can be explained in part by their relatively high solubility in the aqueous phase. The fact that AT did not produce maximum stability when incorporated before rendering has no obvious explanation. The unusually high stability found when BHA was added to beef fats prior to pressure steam-rendering (Table IV) parallels a similar observation made by Dugan *et al.* (1) with dry rendering.

From the results given in Table VII it is apparent that the stabilizing effects of BHA and BHT are lost completely during steam-deodorization. Obviously then there is little to be gained by adding these antioxidants during or shortly after the rendering step if the fat is to be processed promptly into finished shortening.

However a large proportion of the lard and edible beef fats produced in this country is stored for variable periods and at times under adverse conditions. It is therefore most important to protect these raw materials from the time they are rendered in order to assure the production of shortening of maximum shelf-life.

### Summary

Studies have shown that lard and edible beef fats can be stabilized effectively with phenolic antioxidants during pressure steam-rendering. Best results were obtained for a given stabilizer level with the individual phenolics butylated hydroxyanisole and butylated hydroxytoluene. Poorer results were obtained with the mixtures in propylene glycol.

### REFERENCES

1. Dugan, L. R. Jr., Marx, L., Ostby, P., and Wilder, O. H. M., *J. Am. Oil Chemists' Soc.*, **31**, 46 (1954).
2. Gearhart, W. M., and Stuckey, B. N., *J. Am. Oil Chemists' Soc.*, **32**, 287-290 (1955).
3. Paschke, R. F., and Wheeler, D. H., *Oil and Soap*, **21**, 52-57 (1944).
4. Wheeler, D. H., *Oil and Soap*, **9**, 89-97 (1932).
5. Mahon, J. H., and Chapman, R. A., *Anal. Chem.*, **23**, 8, 1116-1120 (1951).
6. Austin, J. J., "Quantitative Analysis of Butylated Hydroxytoluene (BHT) in Fats and Oils," private communication.

[Received March 26, 1956]

## Effect of Free Carboxylic Groups on the Course of Sulfur Trioxide Sulfonation of Unsaturated Fatty Acids<sup>1</sup>

THOMAS W. SAULS and WALTER H. C. RUEGGERBERG, Tennessee Corporation Research Laboratories, College Park, Georgia

IT HAS RECENTLY BEEN SHOWN (1) that the presence of small amounts of simple carboxylic acids, both aliphatic and aromatic, exhibits profound effects on the mechanism of sulfonation of aromatic hydrocarbons with sulfur trioxide in liquid sulfur dioxide. Presumably carboxylic acids destroy intermediate or-

<sup>1</sup> Patent covering the reaction products and their preparation has been applied for.

ganic pyrosulfonic acids to produce acylsulfonic acids. This results in pronounced reduction in the formation of sulfones which are postulated to form through the reaction between such pyrosulfonic acids and aromatic hydrocarbons. In a more recent disclosure (2) Gilbert and Giolito describe similar results for sulfur trioxide sulfonations of aromatic hydrocarbon conducted in the presence of slightly larger amounts of

low molecular weight aliphatic carboxylic acids in the absence of liquid sulfur dioxide.

### Object

Thus it was of interest to extend this principle of the carboxylic acid group effect to the aliphatic series and, specifically, to the sulfonation of long chain unsaturated fatty acids and their esters, where the effect of the free carboxyl group on the course of the sulfonation reaction should be readily discernible. From previous data mentioned (1, 2) it was suspected that, when sulfur trioxide is allowed to react with such substances as oleic acid or undecylenic acid, the carboxyl group could materially affect the manner of sulfonation, which with these types of materials is usually thought of as proceeding through a carboxyl sulfate intermediate. Also it could be expected that an ester of oleic acid, where no free carboxylic group is encountered, should undergo the anticipated carboxyl sulfate type sulfonation. The object of this paper is to show that such differences can be demonstrated to exist. Another object is to explain some aspects of mechanism of sulfonation of fatty materials, an art which has been largely practiced in a rather unscientific way for a long time. To this end oleic acid and its *n*-propyl ester were reacted at  $-10^{\circ}\text{C}$ . with sulfur trioxide in liquid dioxide at atmospheric pressure, and the resulting products were studied.

It should be noted that monosulfonated oleic acid and monosulfonated oleic acid esters are of considerable commercial importance as surface-active agents. They are often preferred over the monosulfated products, the sulfuric acid adducts to the carbon-carbon double bond, because of the sulfonate's greater thermal and chemical stability. Alpha-sulfo substituted fatty acid esters, made by the reaction of sulfur trioxide with saturated fatty acid esters, have been recently described as useful products by Weil, Bistline, and Stirton (3). Numerous other references (4) describing the direct or modified action of sulfur trioxide on fats and oils appear in the literature.

### Experimental

#### Materials

*Oleic Acid*, Emery Industries Inc., Cincinnati 2, O., "Emersol 233 LL Elaine," commercial high-grade, low linoleic content.

Polyunsaturates, 5% max.

Titer,  $3-7^{\circ}\text{C}$ .

Iodine Value, Wijs, 86-90

Free Fatty Acid, as oleic 100-102%

Acid Value, 199-203, mg. KOH

Saponification Value 197-203, mg. KOH

Unsaponifiable content, 1.5% max.

*n*-Propyl Oleate, Emery Industries Inc., Cincinnati 2, O.

Free Fatty Acid, 3.0%

Saponification Value 174-178, mg. KOH

Iodine Value, Wijs, 76-81

Acid Value, 6, mg. KOH, max.

*Undecylenic Acid* (10-undecene-1-oic acid), Distillation Products Industries, Eastman Kodak Company, Rochester 3, N. Y., white label grade.

*Crotonic Acid*, Tennessee Eastman Company, Kingsport, Tenn.

*Sulfur Dioxide*, Tennessee Corporation, Copperhill, Tenn., "highest quality" grade.

*Sulfur Trioxide*, freshly distilled from 20% oleum, Tennessee Corporation, Copperhill, Tenn.

### Procedure

*Sulfonation of Oleic Acid*. Into a two-liter ground glass three-neck flask, equipped with stirrer, thermometer, dropping funnel, and exhaust tube ending in a  $\text{CaCl}_2$  trap were charged 280 g. (0.99 mole) of high grade commercial oleic acid. Over a 15-min. period a mixture containing 91 g. (1.14 mole) of liquid  $\text{SO}_3$  dissolved in 1,200 ml. of liquid  $\text{SO}_2$  was added; the temperature dropped rapidly from  $25^{\circ}\text{C}$ . to  $-9^{\circ}\text{C}$ . during this time. The  $\text{SO}_2$  was evaporated from the product over a period of 1.5 hrs. by stripping and use of a warm water bath. When the temperature reached  $7^{\circ}\text{C}$ ., 310 ml. of water at  $50^{\circ}\text{C}$ . were added with stirring, and subsequently 86 g. of 50.0% aqueous NaOH solution were added as the temperature rose to  $70^{\circ}\text{C}$ . After stirring for 1 hr. and 20 min. at  $60-70^{\circ}\text{C}$ ., with air sweeping through the flask, over its contents, to remove residual  $\text{SO}_2$ , an additional 50 g. of 50.0% NaOH were added to bring the pH to approximately 6.5. The clear amber solution was boiled gently, with stirring, for 1 hr. to hydrolyze any unstable linkages present. Presumably labile complexes of the sulfonation product and excess sulfur trioxide are formed which require this treatment to liberate the desired product. The amount of sodium hydroxide required to neutralize the product is a measure of the amount of sulfonic and sulfuric acids present. For practical reasons however an amount of sodium hydroxide approximately 30% in excess over that required to neutralize the sulfonic and sulfuric acids is used since this results in a more soluble and homogeneous reaction product at 40-50% concentrations of the neutralized sulfonated product in water.

The sulfonation product was analyzed in the following manner: Total solids were determined by drying to constant weight in an oven at  $110^{\circ}\text{C}$ . The amount of unreacted oil was determined by diluting a 50-g. sample with 100 ml. of water, reducing the pH to 2 with dilute  $\text{H}_2\text{SO}_4$ , cooling and extracting with three 100-ml. portions of petroleum ether (boiling range  $30-65^{\circ}\text{C}$ .). These combined ether extracts, after washing with 50 ml. of distilled water, were evaporated to constant weight at  $110^{\circ}\text{C}$ . Sodium sulfate in the products was determined by adding 22 ml. of water and 250 ml. of anhydrous methanol to precipitate the inorganic salt from a 5-g. sample. The precipitated salt was filtered on a tared filter paper or Gooch crucible, washed with 95% methanol and dried to constant weight at  $110^{\circ}\text{C}$ .

More than 30 separate runs, including a large number on a pilot plant scale, were made, yielding the following average compositions of the product:

Mole % Excess $\text{SO}_3$	Composition of Product, Wt. % on a Dry Basis		
	Unsulfonated	Sodium Salt of Sulfonated Oleic Acid	$\text{Na}_2\text{SO}_4$
—1.....	27.0	66.2	5.7
0.....	14.2	80.4	5.7
5.....	13.6	80.9	6.0
10.....	12.4	80.2	7.4
15.....	8.2	83.6	8.2

For practical reasons 15 mole % excess of sulfur trioxide was considered to be the upper limit for obtaining a product with a high monosulfonate content.

Oil-free and salt-free samples of the sulfonated products were obtainable either as the monosodium salt of the sulfonate, neutralized to pH 5, or as the di-sodium salt of the product completely neutralized to pH 9.5, by the analytical procedure, given above. The degree of unsaturation, hydroxyl content, sulfur, carbon, and hydrogen determinations were usually made on the disodium salt because of its comparatively greater ease of handling. Carbon, hydrogen, and sulfur analyses are given in Table III.

Unsaturation determinations, using standard methods of iodine mono-chloride in glacial acetic acid, hydrogenation, and bromine addition, although definitely indicating the presence of the double bond, produced neither consistent nor quantitative results. The hydrogenation was carried out with glacial acetic acid as solvent, using Adams' catalyst (platinum oxide) at atmospheric pressure and room temperature in an apparatus which was proved to be satisfactory for the hydrogenation of maleic acid.

Oleic acid was selected as a compound most nearly resembling the sulfonated product for comparison. Two samples consumed, respectively, 1.08 and 1.16 moles of hydrogen per mole of oleic acid. Since the absolute purity of the oleic acid is unknown, little significance was attached to these values except to show that the catalyst was sufficiently active to hydrogenate the fatty acid. The hydrogenation of oleic acid was fairly rapid at first, about 80–85% having reacted within 10 min. The final 15–20% required 20–30 min. additional.

To show that no catalyst poisons were present in the sample, oleic acid was added to a mixture of catalyst and the di-sodium salt of sulfonated oleic acid after completion of a run. The oleic acid was then hydrogenated with the same catalyst and in the presence of the sulfonation product. No significant decrease in the rate of hydrogenation of oleic acid occurred.

The sulfonated oleic acid is hydrogenated from the start at a somewhat slower rate than oleic acid. The last amounts of hydrogen are absorbed so slowly that it is difficult to determine exactly when the reaction is ended. There is also an indication of a point of inflection in the rate curve, suggesting a stepwise process of some sort. The rate curve (volume of hydrogen absorbed *vs.* time) has approximately the shape of a titration curve involving two equilibria except that the initial absorption of hydrogen is much more rapid than at the end.

The two runs which appeared to be best gave 0.25 and 0.24 moles of hydrogen per mole of compound. One of these samples was the original 50% aqueous solution (calculated to dry basis of the salt- and oil-free product), and the other was the solid di-sodium salt of the sulfonated oleic acid prepared by drying to constant weight at 105°C. The molecular weight was taken as 433, the average molecular weight for the composition given in Table III. Several other runs were unsatisfactory because the slowly decreasing rate of absorption of hydrogen made it impossible to fix the end of the reaction. The hydrogenation reaction is therefore inconclusive, at this stage, as a measure of degree of unsaturation.

Bromination, carried out by the method of Lucas and Pressman (5), using mercuric sulfate as a catalyst, is equally incomplete. Several experiments indicated that the amount of bromine absorbed is dependent on concentration of bromine, time of mixing, concentration of sample, and perhaps other factors. The following values were obtained with different combinations of the above mentioned variables: 0.37, 0.39, 0.40, 0.16, 0.24, 0.26 moles bromine per mole of compound.

The hydroxy content was determined by acetylation with acetic anhydride in pyridine. Both the monosodium salt of the sulfonate and the di-sodium salt are freely soluble in water but are insoluble in non-polar solvents, such as benzene or toluene. Alcohols exhibit considerable solubility for these materials; the mono-sodium salt is soluble to the extent of 13+ % in *n*-butanol at 60°C.

Surface-tension measurements against air were made on aqueous solutions of the sulfonated oleic acid at room temperature (26–27°C.), and sulfuric acid and sodium hydroxide were used to adjust pH. A Cenco du Nouy interfacial tensiometer was used. Wetting times were measured according to the method of Clarkson and Draves (7).

*Sulfonation of *n*-Propyl Oleate.* In a manner similar to that described for the sulfonation of oleic acid, 50.7 g. of liquid SO<sub>3</sub> dissolved in 475 ml. of liquid SO<sub>2</sub> were added to 138.9 g. of commercial *n*-propyl oleate. The SO<sub>2</sub> was evaporated, and 40 ml. of water were added while keeping the temperature under 45°C. with a cooling bath. Residual SO<sub>2</sub> was removed by aspirator suction before neutralizing to pH 7 with 26 g. of NaOH in 120 ml. of H<sub>2</sub>O, keeping the temperature under 45°C. with an ice bath. Other esters, from methyl to octyl, can be sulfonated in the same manner.

Analyses of the sulfonated product were carried out in the same manner as described for the oleic acid sulfonation product. The resulting compounds are essentially saturated materials.

*Sulfonation of Undecylenic Acid.* In a manner similar to that described for the sulfonation of oleic acid, 53.6 g. of liquid SO<sub>3</sub> dissolved in 300 ml. of liquid SO<sub>2</sub> were added to 112 g. of undecylenic acid mixed with 200 ml. of liquid SO<sub>2</sub>. After the bulk of the SO<sub>2</sub> had been evaporated, the mass solidified; 200 ml. water were added and the mixture was brought to a gentle boil for five minutes to dissolve the solids and expel residual SO<sub>2</sub>. After cooling to 25°C., the total product was extracted with three 100-ml. portions of petroleum ether, which after evaporation left 6.2 g. of unsulfonated oil. The extracted aqueous solution was then filtered to remove 1.5 g. of a rubbery material before neutralizing to pH 5 with 26.3 g. of NaOH and then to pH 9.5 with 21.7 g. of additional NaOH. The completely neutralized solution was evaporated to dryness overnight in an oven at 110°C. The final weight of the crude di-sodium salt was 190.5 g.

A sample of this de-oiled di-sodium salt was found to contain 0.73% Na<sub>2</sub>SO<sub>4</sub> by dissolving the organic salt from the inorganic salt with hot glacial acetic acid.

An unsaturation determination, using the Wijs method of iodine-monochloride in acetic acid and back-titrating with standard sodium thiosulfate, indicated that this di-sodium salt contained 0.00086 mole

of carbon-carbon double bond per gram. Acetylation with acetic anhydride in pyridine showed a maximum hydroxyl content of 0.000266 mole hydroxy per gram of disodium salt. A total sulfur trioxide content of 27.1% was found by a Parr bomb fusion, as compared with a theoretical value of 25.9% for the unsaturated monosulfonate. With these results the composition of the sulfonated undecylenic acid was calculated to be:

monosulfonate.....	80%
hydroxy-sulfonate.....	9-10%
sulfonate-sulfate.....	9-10%
Na <sub>2</sub> SO <sub>4</sub> .....	0.7-0.8%

One gram of this product was dissolved in 80 ml. of water together with 4 g. of KMnO<sub>4</sub> and 1 ml. of 10% NaOH and boiled for 2 hrs. Upon acidification with dilute H<sub>2</sub>SO<sub>4</sub> there resulted a vigorous evolution of gaseous oxides of carbon, indicating the formation of formic acid and the terminal position of the olefinic bond in the sulfonated undecylenic acid.

**Sulfonation of Crotonic Acid.** In a manner similar to that described above, 98.8 g. of liquid SO<sub>3</sub> dissolved in 250 ml. of liquid SO<sub>2</sub> were added to 85 g. of crotonic acid mixed with 300 ml. of liquid SO<sub>2</sub>. The SO<sub>2</sub> was evaporated, and the anhydrous acid was brought to a temperature of 45-50°C., at which point a vigorous reaction occurred, causing a temperature rise to 100°C. After the reaction subsided and the acid had cooled to 60°C., 375 ml. of water and 49.5 g. NaOH were added to neutralize the strong acid present. This slightly acidic, aqueous solution was then extracted with two 150-ml. portions of diethyl ether which, upon evaporation, left 10.0 g. of unsulfonated material. The extracted aqueous solution was then further neutralized to pH 9.5 with 41.5 g. of additional NaOH dissolved in 125 ml. of water. This solution was dried to constant weight (224 g.) and ground to a fine light tan powder.

A 5-g. sample of this solid was de-salted by warming with 100 ml. of glacial acetic acid and 5 ml. of H<sub>2</sub>O to extract the organic material. After filtration and drying, the residue weighed 0.650 g. and lost only 30 mg. upon ashing in the muffle at 900°C. The total Na<sub>2</sub>SO<sub>4</sub> in the run was calculated to be 27.8 g. The de-salted material was analyzed for S by the Parr bomb method and was found to contain 35.6% SO<sub>3</sub>. The theoretical value is 38.1% SO<sub>3</sub> for the di-sodium salt of monosulfonated crotonic acid. From these data the following calculations may be made:

SO <sub>3</sub> Used	Crotonic Acid Used	After Extraction NaOH to pH 9	Na <sub>2</sub> SO <sub>4</sub> Formed	Unsulfonated
98.8 g.	85.0 g.	91.0 g.	27.8 g.	10.0 g.
1.235 mole	0.988 mole	2.27 mole	0.195 mole	0.116 mole

Total crotonic acid used.....0.988 mole  
 Total crotonic acid extracted.....0.116 mole  
 Difference (sulfonated).....0.872 mole  
 Total SO<sub>3</sub> used.....1.235 mole  
 Min. SO<sub>3</sub> to Na<sub>2</sub>SO<sub>4</sub>.....0.195 mole  
 Difference (organically combined SO<sub>3</sub>).....1.040 mole  
 $\frac{1.040}{0.872} = 1.19$  maximum mole ratio of SO<sub>3</sub> to sulfonated crotonic acid

This mole ratio of SO<sub>3</sub> to crotonic acid is considered to be actually high since small amounts of SO<sub>3</sub> escape during the sulfonation. This loss is reflected here as combined SO<sub>3</sub>.

## Results and Discussion

Reacting 1 mole of high grade commercial oleic acid with 1 to 1.25 mole of sulfur trioxide in liquid sulfur dioxide at atmospheric pressure leads to a high conversion, up to 85-90%, of a monosulfonated, largely unsaturated derivative. Under similar conditions 1 mole of n-propyl oleate gives only approximately 0.5 mole of sulfonated-sulfated derivative, leaving approximately 50% of unsulfonated ester. Similar results are obtained with the ethyl and n-butyl esters. It therefore appears that the presence of a free carboxylic group leads to an entirely different course of sulfonation. Comparative conversion data are presented in Table I.

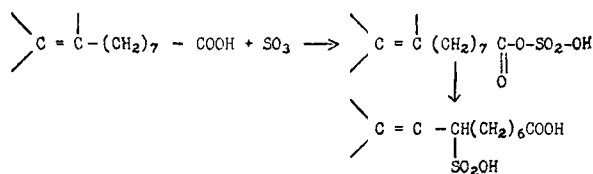
TABLE I  
 Conversion of Oleic Acid and n-Propyl Oleate to Sulfonated Derivatives with Varying Mole Ratios of SO<sub>3</sub>

	Mole Ratio SO <sub>3</sub> to Fat	Conversion to Sulfonated Product Based on Fat Charge
Oleic Acid	1.00	77%
	1.15	84%
	1.25	85%
n-Propyl Oleate	1.00	42%
	1.34	63%
	1.47	67%
	2.62	87% <sup>a</sup>
	3.00	88%

<sup>a</sup> As the mole ratio of sulfur trioxide to ester exceeds 2.25, dark products with unpleasant odors result.

Based on the sulfur trioxide requirements for converting one mole of the olefinic acid or ester to a sulfonated derivative, it appears that the ester undergoes the well-known carbyl sulfate reaction at the carbon-carbon double bond whereas the free oleic acid, in all probability, first forms an acyl sulfate, followed by sulfonation of the chain through a rearrangement involving the elements of SO<sub>3</sub> and hence bears a resemblance to the effects found with acetic acid in the sulfonation of benzene, toluene, or xylene (1, 2). Upon hydrolysis or neutralization with sodium hydroxide the sulfonated oleic acid produces chiefly a monosulfonate while the sulfonated n-propyl oleate results chiefly in a mixture of hydroxysulfonate and sulfonate-sulfate. These different reactions can be written according to the following schemes:

### Scheme A. Oleic Acid--Acyl Sulfate Route



### Scheme B. Oleic Acid Ester--Carbyl Sulfate Route

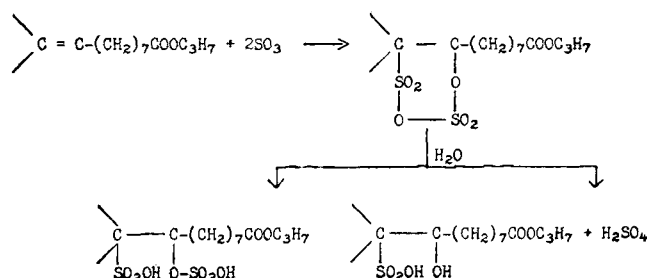


TABLE II  
Composition of Product Obtained from One Mole Oleic Acid and 1.25 Mole of Sulfur Trioxide

Compound	Mole Wt., Calculated	Theoretical Element Composition			Estimated Wt. % in Total Product
		Sulfur	Weight % Carbon	Hydrogen	
$\text{CH}_3(\text{CH}_2)_7\text{CH} = \underset{\text{SO}_2\text{Na}}{\text{CH}}\text{CH}(\text{CH}_2)_6\text{COONa}$	406.7	7.88	53.20	7.93	54.3
$\text{CH}_3(\text{CH}_2)_7\underset{\text{OH}}{\text{CH}} - \underset{\text{SO}_2\text{Na}}{\text{CH}}(\text{CH}_2)_7\text{COONa}$	424.7	7.55	50.95	8.07	28.3 <sup>a</sup>
$\text{CH}_3(\text{CH}_2)_7\underset{\text{OSO}_2\text{Na}}{\text{CH}} - \underset{\text{SO}_2\text{Na}}{\text{CH}}(\text{CH}_2)_7\text{COONa}$	526.7	12.17	41.08	6.31	17.4
		9.11	Found: 50.45	7.97	

<sup>a</sup> By hydroxyl determination.

Although the reaction of sulfur trioxide with oleic acid, in liquid sulfur dioxide at  $-10^\circ\text{C}$ ., yields chiefly an unsaturated monosulfonate, as written in Scheme A above, lesser amounts of products resulting from carbonyl sulfate formation or similar mechanism occur also. This is indicated by the sodium hydroxide requirement for the sulfonated product after hydrolysis and expulsion of sulfur dioxide. Thus, for two separate runs, employing zero and 14 mole % excess sulfur trioxide, the analysis of the product indicates that the mole ratio of combined sulfur trioxide to oleic acid sulfonated is 1.06 and 1.09, respectively. Consequently the product so formed contains from 6 to 9 mole % more combined sulfur trioxide than is expected from the simple monosulfonation Scheme A. As the mole ratio of sulfur trioxide to oleic acid is increased, the combined sulfur trioxide ratio exceeds these values, being as high as 1.14 where 25 mole percentage of excess sulfur trioxide is used in the sulfonation.

Elemental analysis of a dry, de-oiled, de-salted sample of the di-sodium salt of a Scheme A reaction product confirmed the results obtained from sodium hydroxide consumption calculations of combined sulfur trioxide. Table II gave the theoretical and found values for sulfur, carbon, and hydrogen contents of the three suspected product components. Determination of hydroxyl groups showed the presence of 27 to 30 weight percentage of a hydroxy sulfonate in this sulfonation product made with 25 mole % excess sulfur trioxide.

From the percentages of hydroxy-sulfonate and total sulfur, carbon, and hydrogen the approximate composition of the product is calculated and reported in Table II.

A purified sample from a run which used only one mole of  $\text{SO}_3$  per mole oleic acid was found to contain only 20% of the hydroxy sulfonate, approximately 8% sulfonate-sulfate, and approximately 72% monosulfonate.

Although neither the hydrogenation nor the bromination procedures gave absolutely quantitative results as to the degree of residual unsaturation in the product, the latter was sufficiently good to conclude that the chief component of the sulfur trioxide reaction product with oleic acid is a monosulfonated, unsaturated material, as was suspected from the sulfur trioxide consumption and materials balance in the sulfonation.

So far as structure is concerned, it can only be assumed at this point that the sulfonation occurs on

one of the two carbon atoms in the allyl position to the double bond in the oleic acid molecule. This assumption, at least, would agree with Suter's findings that, in the dioxane-sulfur trioxide sulfonation of certain olefins (6), allyl sulfonation predominates. Experiments designed to saturate the residual double bond in the product with either hydrogen or halogen resulted in only partial reaction. Presumably such unsaturates where a sulfo group is located in the allyl position exhibit lower reactivity than the unsulfonated product. The true sulfonate character is further established by the resistance to hydrolysis under both acidic and basic conditions. The removal of combined  $\text{SO}_3$  is confined to the sulfate group in the sulfonate-sulfate component of the mixture. Further work is being considered to resolve the question of structure.

Undecylenic acid (10-undecene-1-oic acid) and crotonic acid were reacted with sulfur trioxide in liquid sulfur dioxide at  $-10^\circ\text{C}$ . in the foregoing manner yielding similar results, with the relative amounts of monosulfonate greater and the amount of sulfonate-sulfate and hydroxy sulfonate less than those found with oleic acid. As before, it was found difficult to saturate the double bond in the sulfonated product with halogen, the iodine absorption, according to the standard Wijs method, giving only 30-40% reaction. Basic potassium permanganate oxidation of the sulfonated undecylenic acid resulted, after acidification, in an evolution of oxides of carbon, indicating that no extensive double bond shift occurred during the sulfonation.

Crotonic acid treated with sulfur trioxide in liquid sulfur dioxide at  $-10^\circ\text{C}$ . was found not to react until the liquid sulfur dioxide had been expelled and the reaction mass heated to  $45-50^\circ\text{C}$ . Apparently either resonance stabilization of the double bond or reduced allyl hydrogen reactivity, or both, lower the over-all reactivity of crotonic acid with sulfur trioxide as compared with oleic and undecylenic acids. There was obtained however a 90% yield of a monosulfonate, which was isolated as the di-sodium salt containing 35.6% combined sulfur trioxide.

The sulfonated oleic acids produced by this method were suspected to possess unique properties as surface-active agents aside from their inherent stability as true sulfonates. When their surface tensions are measured at different pH values from 2 to 12, the observed surface tension goes through a minimum at pH 8 and a maximum at pH 10, as shown in Figure 1 for three different concentrations of the material in

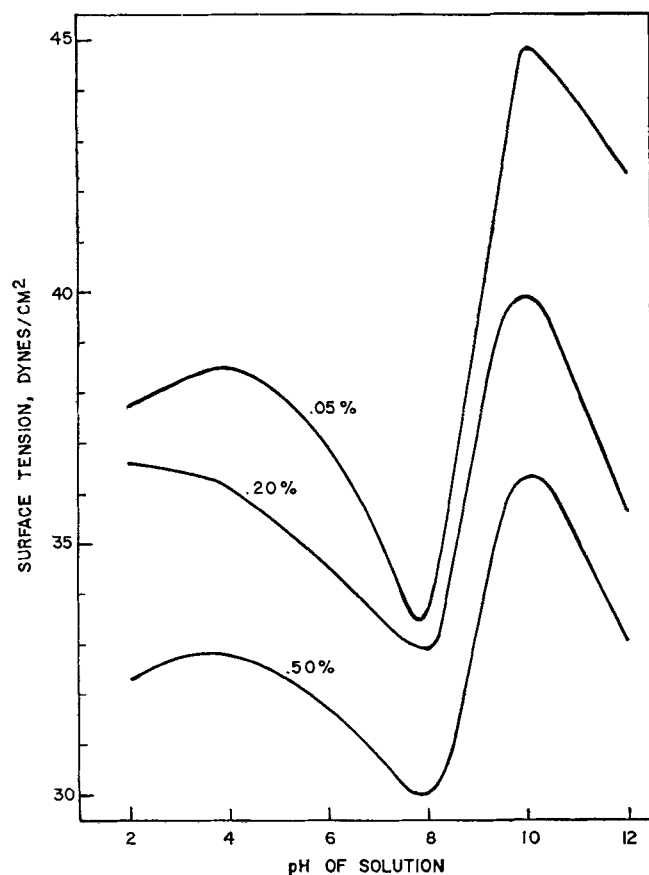


FIG. 1. Effect of pH on surface tensions of aqueous sulfonated oleic acid solutions at 25° C.

water. The maximum at pH 10 corresponds to the completely neutralized salt, both in the carboxyl and sulfonic groups. Increasing the pH beyond 10 probably may result in a "salting-out" effect of the product to the surface, as indicated by a lowering of surface tension. The minimum surface tension observed at pH 8 corresponds to partial neutralization of the carboxyl groups in addition to all of the sulfonate groups and undoubtedly represents some form of complex colloidal configuration for which the surface tension should be a minimum. It is noteworthy that, at acid pH values, the solutions exhibit low surface tensions. Most likely, the hydrogen ions in solution depress the ionization or hydrophilicity of the carboxyl-containing end of the sulfonated molecule and free this end to act as a surface-active agent. Conversely on the basic side the carboxylic group-containing end of the molecule will be totally ionized in the water as carboxylate ion, thus causing about one-half of the sulfonated molecule to lie flat on the water surface and hence contribute little to surface activity.

The Clarkson-Draves (7) wetting test offers a convenient method of determining surface activity by measuring the time required for a standard piece of unmercerized cotton yarn to sink in an aqueous solution. In Figure 2 the wetting times of various strengths of monosodium sulfonated oleic acid in water and 3% and 10% sulfuric acid are shown. The rate of wetting was found to increase markedly as the acidity of the solution was increased. At pH 11 the wetting time is 56 seconds for a 0.05% solution and 29 seconds for a 0.5% solution; again this indi-

cates the decreased surface-activity of sulfonated oleic acid in basic aqueous media.

### Summary

The direct action of one mole of sulfur trioxide in liquid sulfur dioxide at atmospheric pressure at  $-10$  to  $-9^{\circ}\text{C}$ . on one mole of unsaturated fatty acids such as oleic acid, undecylenic acid, and crotonic acid yielded 85–90% of sulfonated products in which a monosulfonated derivative, rich in residual carbon to carbon unsaturation, predominates. Hydroxy sulfonates and sulfonated-sulfated products, postulated to form from carbyl sulfate intermediates, are present in lesser amounts.

Esters of unsaturated fatty acids, such as *n*-propyl oleate, require at least two moles of sulfur trioxide for 80–90% yields of sulfonated product. These sulfonated products are postulated to form almost exclusively through the carbyl sulfate intermediate.

The free carboxyl group apparently determines the course of sulfonation. Its action is believed to be that of first forming an acyl sulfate or mixed anhydride with sulfur trioxide, followed by hydrogen replacement in a methylene group, probably in an allyl position to the double bond, with a sulfonic acid group. The mechanism and nature of products resemble those previously observed by Suter in the dioxane-sulfur trioxide sulfonation of methallyl chloride (6).

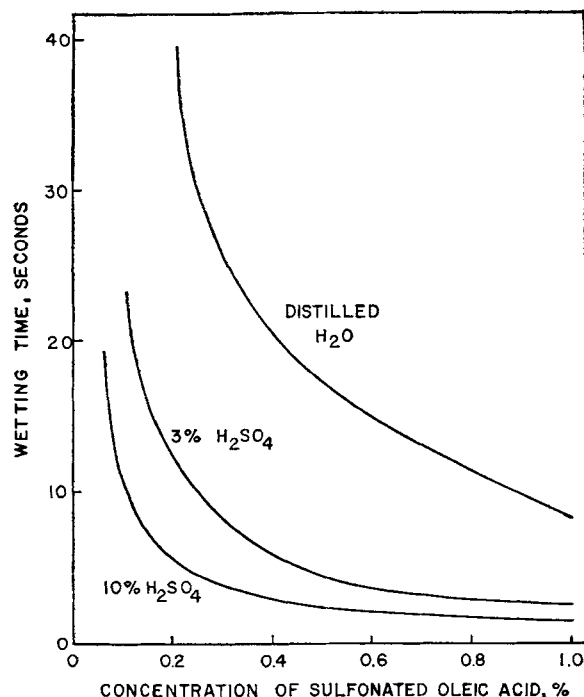


FIG. 2. Clarkson-Draves tests at 25° C.

The sulfonated unsaturated reaction products from oleic and undecylenic acids exhibit lower double bond reactivity toward hydrogen and halogen addition than the unsulfonated starting materials.

The monosulfonated oleic acid, because of its stability toward hydrolysis, holds promise as an important surface-active agent, particularly under acidic conditions.

### Acknowledgment

The authors are indebted to W. J. Barrett of Southern Research Institute, Birmingham, Ala., for his valuable help in the determination of unsaturation and to J. E. Singley of the Tennessee Corporation Research Laboratories for his aid in the determination of surface-active properties of these products.

### REFERENCES

1. Rueggeberg, W. H. C., Sauls, T. W., and Norwood, S. L., *J. Org. Chem.*, **20**, 455-65 (1955).

- Gilbert, Everett, and Giolito, Silvio L., U. S. Patent 2,704,295 (March 15, 1955).
- Weil, J. K., Bistline, R. G., and Stirton, A. J. *J. Am. Oil Chemists' Soc.*, **32**, 370-2 (1955).
- Reactions of SO<sub>3</sub>*, a bulletin of General Chemical Division, Allied Chemical and Dye Corporation, 40 Rector street, New York 6, N. Y. (1948), p. 7-8.
- Lucas, Howard J., and Pressman, David, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140-2 (1938).
- Suter, C. M., and Bordwell, Frederick J., *J. Am. Chem. Soc.*, **65**, 507-17 (1943).
- Clarkson and Draves, *Technical Manual and Yearbook, American Association of Textile Chemists and Colorists*, vol. 29, 1953, p. 156-158.

[Received August 22, 1955]

## Alcoholic Extraction of Vegetable Oils. III. Solubilities of Babassu, Coconut, Olive, Palm, Rapeseed, and Sunflower Seed Oils in Aqueous Ethanol

RAMA KANTH RAO and LIONEL K. ARNOLD, Iowa Engineering Experiment Station, Iowa State College, Ames, Iowa

IN EARLIER communications (1, 2) solubility data for seven vegetable oils in aqueous ethanol were reported. This paper deals with similar data for other common vegetable oils for which no data were found in the literature.

### Experimental

The apparatus and solubility determination method used were the same as described previously (1).

Commercially available unrefined oils were used in each case. Their characteristics were as follows:

Oil	Acid value	Iodine value Wij's	Sap. value
Babassu.....	2.82	12.86	248.62
Coconut.....	2.76	8.82	257.20
Olive.....	1.12	84.62	190.40
Palm.....	3.42	53.86	199.64
Rapeseed.....	2.66	105.62	171.65
Sunflower seed.....	1.72	123.84	190.76

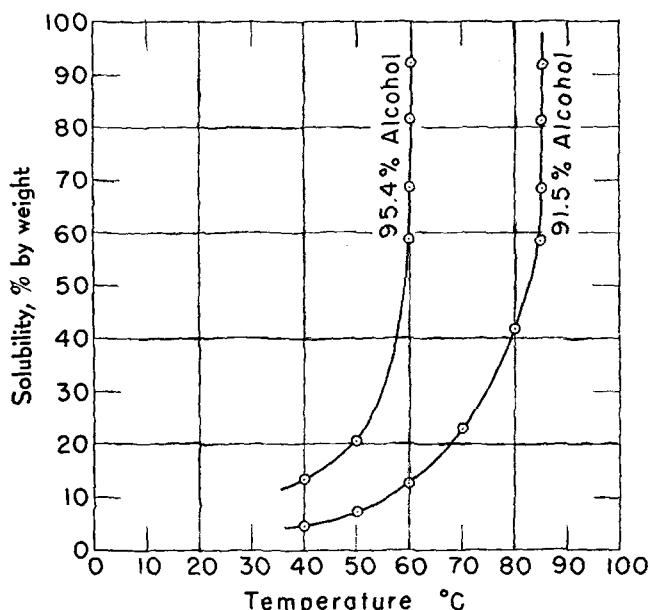


Fig. 1. Solubility curves for babassu oil.

The various aqueous solutions of ethanol were obtained by diluting absolute alcohol. The concentrations of the alcoholic solutions were determined by determining the densities by the pycnometer method. All the values are reported as weight percentages.

### Results

*Solubility Data.* As might be expected from the similarity in chemical composition, the solubility characteristics of babassu and coconut oils in ethanol are similar. Babassu oil (Figure 1) was miscible in 99.9% ethanol at 30°C., and coconut oil (Figure 2)

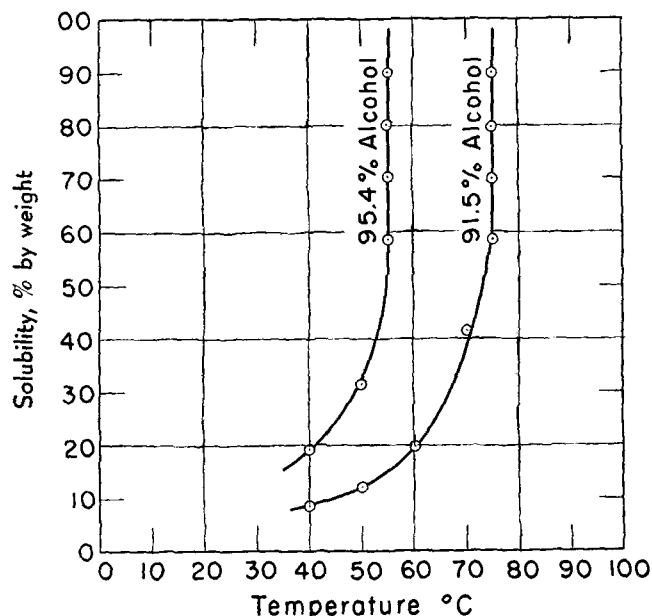


Fig. 2. Solubility curves for coconut oil.

was miscible at 23°C. In 98.0% ethanol miscibility was attained at 45°C. for babassu oil and at 35°C. for coconut oil. In 95.4% and 91.5% ethanol miscibility temperatures were 60° and 85°C. for babassu oil and 55° C. and 75°C. for coconut oil, respectively.