TABLE II

Typical Data—Miscella Refining Process—Ranchers Cotton Oil Company (*Model 6150 extractor*)

Pressure, p.s.i.g.		Flow rate	Rotor speed	T.f.a. water out	Soap in oil
Oil inlet	Oil outlet				
		g.p.m.	*r.p.m.*	%	
140	90	3	3,000	.009	Trace
140	105	3	3,000	.02	Trace
140	90	3	3,000	.02	6 p.p.m.
125	20	1	2,850	....	1 p.p.m.
122	50	1⅔	2,850	.003	2 p.p.m.
125	56	6	2,850	.007	2 p.p.m.
125	73	7½	2,850	.002	2 p.p.m.
140	123	4⅓	2,850	.02	1 p.p.m.

The purpose of this installation was to demonstrate the advantages to be obtained by countercurrent water washing of miscella, using the countercurrent multistage contactor. Advantages proved during this installation were these: Entire extractor installation is explosion-proof. Waste water did not contain hexane; water could be discharged direct to the sewer system. Refined oil color was improved from ½ to 1 Lovibond red. Extractor has wide latitude of capacity for this operation.

Summary

This paper has discussed the early methods of the refining of vegetable oil and present-day continuous refining equipment. The purpose was to report on the advantages of the centrifugal contactor for water washing of vegetable oil. There are important advantages to be obtained by the use of Podbielniak Rotating Contactor for water washing of alkali-refined oils. One-to-ten tank car capacity with one centrifugal contactor results in space and installation savings. Stainless steel construction permits use of acid treats. Pressure operation prevents oxidation of hot oil and emulsions formed by mixing with air. Installation can be made fully automatic. Periodic cleaning is not required. Countercurrent flow produces higher quality refined oil with 50% lower neutral oil loss in wash water.

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Tallow Alcohol Sulfates. Properties in Relation to Chemical Modification[1]

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THE PRINCIPAL COMPONENTS of saturated tallow alcohol sulfates, sodium hexadecyl sulfate, and sodium octadecyl sulfate are excellent detergents at higher washing temperatures (e.g., 60°) but are less generally useful as surface-active agents at lower temperatures because of limited solubility in water.

Reports from this laboratory in the past few years have shown that the solubility of tallow alcohol sulfates is increased by blending with other detergents (14), also by methods which alter properties as a result of changes in chemical composition.

Thus tallow alcohols retaining the original unsaturation, sulfated with special sulfating agents which do not affect the double bond, result in the presence of the readily soluble sodium oleyl sulfate as a major component (17). Low-temperature additive chlorination at the double bond and sulfation under more usual conditions has a similar effect, producing the readily soluble sodium 9,10-dichlorooctadecyl sulfate as a major component (18). Reaction of ethylene oxide with tallow alcohols and subsequent sulfation also results in improved solubility (1). Another method included in the present report is the formation of the more soluble triethanolammonium salt instead of the sodium salt.

Properties other than solubility are affected by these changes in chemical composition. The present report concerns the detergent and surface-active characteristics of the individual compounds involved, measured under the same conditions, with particular reference to the effect of chemical structure on fundamental solution properties, such as the critical micelle concentration (c.m.c.) and the Krafft point.

Tallow Alcohol Sulfates and Related Compounds

Sodium alkyl, alkenyl, and dichloroalkyl sulfates were prepared as described in previous publications (15, 17, 18): sodium oleyl and elaidyl sulfates by sulfation with pyridine-sulfur trioxide (17), and sodium 9,10-dichlorooctadecyl sulfate from oleyl alcohol by chlorination and subsequent sulfation (18).

Individual ether alcohols of the hexadecyl and octadecyl series, prepared from the alkyl bromide, sodium, and the appropriate glycol (20), were sulfated (16) to give eight compounds of the general formula $R(OC_2H_4)_iOSO_3Na$ where $R = C_{16}H_{33}$ or $C_{18}H_{37}$ and $i = 1, 2, 3, 4$. These compounds are comparable to sulfated ethenoxylated tallow alcohols (1), $R(OC_2H_4)_n$-OSO_3Na, where n is the average number of moles of ethylene oxide condensed. Since they are chemical individuals rather than a mixture of homologs, they more clearly illustrate the relation between chemical composition and properties. The sodium salts of the ether alcohol sulfates did not have very definite melt-

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TABLE I

Solution and Surface-Active Properties of Alcohol Sulfates

Alcohol sulfate *compound*	Abbreviation	Krafft point[a]	Critical micelle conc.[b]	Surface and interfacial tension, 0.1% solution, 25°, dynes/cm.		Wetting time (13) 0.1% solution, 60°
				s.t.	i.t.	
			millimoles/l.			*seconds*
$C_{12}H_{25}OSO_3Na$	12	16°	6.8	49.0	20.3	19.1
$C_{16}H_{33}OSO_3Na$	16	45°	0.42	35.0[c]	7.5[c]	11.6
$C_{16}H_{33}OSO_3NH(C_2H_4OH)_3$	16–T	clear at 0°	0.34	41.0	10.0	14.9
$C_{16}H_{33}OC_2H_4OSO_3Na$	16–1	36°	0.24	36.2	7.2	12.1
$C_{16}H_{33}(OC_2H_4)_2OSO_3Na$	16–2	24°	0.14	39.4	8.7	16.6
$C_{16}H_{33}(OC_2H_4)_3OSO_3Na$	16–3	19°	0.12	41.6	10.2	21.1
$C_{16}H_{33}(OC_2H_4)_4OSO_3Na$	16–4	1°	0.12	43.5	11.7	22.9
$C_8H_{17}CH{=}CH(CH_2)_8OSO_3Na$	18–cis	clear at 0°	0.29	35.8	7.4	10.8
$C_8H_{17}CH{=}CH(CH_2)_8OSO_3Na$	18–trans	29°	0.18	36.1	6.5	10.3
$C_8H_{17}CHClCHCl(CH_2)_8OSO_3Na$	18–Cl_2	clear at 0°	0.26	35.8	5.8	15.2
$C_{18}H_{37}OSO_3Na$	18	56°	0.11	40.6[c]	14.2[c]	18.4
$C_{18}H_{37}OSO_3NH(C_2H_4OH)_3$	18–T	26°	0.07	40.9	9.0	19.6
$C_{18}H_{37}OC_2H_4OSO_3Na$	18–1	46°	0.09	39.0[c]	11.0[c]	21.8
$C_{18}H_{37}(OC_2H_4)_2OSO_3Na$	18–2	40°	0.07	39.5	8.5	24.1
$C_{18}H_{37}(OC_2H_4)_3OSO_3Na$	18–3	32°	0.07	41.1	8.9	30.5
$C_{18}H_{37}(OC_2H_4)_4OSO_3Na$	18–4	18°	0.07	43.1	10.3	32.8

[a] Temperature at which a 1% dispersion became a clear solution on gradual heating.
[b] Pinacyanole chloride method 50°.
[c] Turbid dispersion at 25°.

ing points but passed through an intermediate glassy state before finally melting with some decomposition as follows, (i = 1, 2, 3, 4): hexadecyl series, 184°, 177°, 161°, 93°; octadecyl series, 193°, 187°, 191°, 96°. The compounds with four ethenoxy groups were more readily soluble in water, also in organic solvents as well, readily forming 1% solutions in benzene, butanol, or carbon tetrachloride, at room temperature.

Triethanolammonium salts of the sulfated alcohols were prepared by neutralization of the sulfation reaction mixture with triethanolamine. The salts were purified by crystallization from carbon tetrachloride or from a carbon tetrachloride-ethanol mixture; analyses for neutralization equivalent, carbon, hydrogen, nitrogen, and sulfur agreed with the theoretical values. The melting points of the triethanolammonium salts of the 12, 14, 16, and 18 carbon alkylsulfuric acids are 121–122.5°, 106–7°, 82.4–83.0°, and 86.0–86.8°, respectively.

The solution and surface-active properties of 16 compounds are shown in Table I and detergent and related properties in Table II.

Solution and Surface-Active Properties

Krafft Point. The Krafft point, originating in the study of soap solutions (9), is also significant with respect to synthetic detergents. It is the temperature, nearly independent of concentration, at which there is a marked increase in solubility with concomitant changes in the nature of the solution. The Krafft points of Table I were determined by the procedure recommended for soaps (5); a hot clear 1% solution was cooled to turbidity, then gradually heated until there was a sharp change to a clear solution.

The Krafft points are a convenient indication of comparative solubility, showing the greater solubility of the unsaturated compounds, the dichloro compound, the ether alcohol sulfates, and the triethanolammonium salts. The Krafft point increased with the number of carbon atoms in the paraffinic chain but decreased with the increase in the number of ethenoxy groups. In some cases, because of super-cooling, it is possible to make measurements on clear solutions at 5° to 25° below the Krafft point.

Critical Micelle Concentration. The c.m.c. was measured at 50° to ensure clear solutions in every case and thus include all of the compounds of Table I. Pinacyanole chloride was used in the dye titration method (4). A solution 10^{-5} molar with respect to the dye, containing about twice the critical concentration of the surface-active agent, was titrated with 10^{-5} molar dye solution. The end-point was determined by visual observation of the complete color change from blue (micelles) to purple (simple ions). Sodium hexadecyl sulfate, sodium oleyl sulfate, and sodium 9,10-dichloro-octadecyl sulfate, purified by ether extraction until free from surface tension minima, gave c.m.c. values by the surface tension method which confirmed those of Table I. The values found were 0.41 (30°), 0.30 (25°), and 0.31 (25°), respectively.

Table I shows the expected decrease in c.m.c. with increase in the length of the alkyl chain. Many properties tend toward the optimum with increase in concentration up to the c.m.c. Sodium dodecyl sulfate has the highest c.m.c. (6.8 millimoles/l. = 0.20%), and since most of the properties of Tables I and II were measured at lesser concentrations, the data do not show this compound to be a very effective surface-active agent and detergent.

Table I also illustrates some interesting structural effects. The presence of the double bond causes an increase in c.m.c., which seems to be in agreement with the work of Klevens (8), relating c.m.c. to the total effective length of the long chain ion. The *cis* double bond, in particular, would be expected to result in some contraction and therefore an increase in c.m.c. Additive chlorination has the same result.

Comparing the sodium alkyl sulfates and the ether alcohol sulfates, the introduction of ethenoxy groups lowers the c.m.c. until a limiting value is reached. The decrease is not proportional to an increase in chain length by the three atoms of each ethenoxy group. Apparently an increase in hydrophilic properties tends to reduce effects because of an increase in chain length (16).

The lower values for the triethanolammonium salts compared to the sodium salts may be caused by the inclusion of neutral salt within the micelle with the result of an increase in effective chain length.

Surface and Interfacial Tension. The du Noüy tensiometer was used to measure the surface tension of 0.1% solutions and the interfacial tension against light

TABLE II

Detergency and Related Properties

Alcohol Sulfate[a]	Foam height (12) 0.25% built[b] solutions, 300 p.p.m. 60°	Detergency,[c] 0.25% built[b] solutions, 300 p.p.m., 60°	Dishwashing test,[d] 0.2%, 100 p.p.m. 50°	Emulsion stability (3), 0.1% 25°	Calcium stability (19), 0.5%, 25°, p.p.m. CaCO$_3$	Lime soap dispersing power (2), 0.25%, 25°
	mm.	ΔR	ΔR	*sec.*		%
12	185	6.6	13.8	130	650	30
16	240	31.3	20.4	......[e]	......[e]	....[e]
16–T	240	27.8	14.7	470	420	65
16–1	210	20.7	16.2	240	1060	3
16–2	200	11.4	12.7	290	1600	3
16–3	170	8.3	10.6	260	>1800	4
16–4	170	7.6	9.3	240	>1800	4
18–cis	230	33.5	14.8	200	920	10
18–trans	220	32.9	......	......	870	10
18–Cl$_2$	210	31.3	19.6	300	920	7
18	190	30.4	16.6	......[e]	......[e]	....[e]
18–T	190	28.9	15.1	280	320	....[e]
18–1	140	18.9	10.2	......[e]	......[e]	14
18–2	120	12.4	10.1	440	>1800	16
18–3	105	8.1	......	390	>1800	10
18–4	100	7.2	5.2	340	>1800	10

[a] Abbreviations of Table I.

[b] Built solutions: 0.05% with respect to alcohol sulfate, 0.20% with respect to a mixture of $Na_5P_3O_{10}$, Na_2SO_4, $Na_4P_2O_7$, Na_2SiO_3, CMC (14).

[c] Launder-Ometer, 1 swatch of standard soiled cotton/100 ml./jar, 30 steel balls, 5 replicates; ΔR = increase in reflectance after washing.

[d] Terg-O-Tometer, method of Leenerts (11), glass slides soiled with greasy soil, 6 replicates; ΔR = increase in reflectance.

[e] Compounds not adequately soluble at 25°.

petrolatum at 25 ± 1°. Sodium dodecyl sulfate has the highest surface tension because the concentration is less than the c.m.c. Most of the compounds have values in the range 35–41 dynes per centimeter. There is a slight but orderly increase in surface tension with the increase in the number of ethenoxy groups.

Wetting Time. Wetting properties were measured, using a 9-in. length of 1¼-in. binding tape, a 1-g. hook, and a 40-g. anchor (13). At 60° there was not much difference in wetting efficiency, but, in general, compounds with higher c.m.c. were the better wetting agents.

Detergency and Related Properties

Foam Height. The foaming properties of built solutions in hard water are shown in Table II. The foam was stable for at least 5 min. The ether alcohol sulfates have less foam, and the height decreases with the increase in the number of ethenoxy groups.

Detergency. Detergency was measured as the increase in reflectance after washing G.D.C. No. 26 standard soiled cotton (6) in built solutions of the detergents in hard water in the Launder-Ometer at 60°. Analysis of variance (10) showed that differences of 2.5–3.0 were significant, with 95% probability. The best seven compounds were the unsaturated compounds, the dichloro compound, sodium hexadecyl and octadecyl sulfates, and the triethanolammonium salts. Detergency of the ether alcohol sulfates decreased with the increase in the number of ethenoxy groups.

Other detergency measurements carried out in the Terg-O-Tometer in hard or soft water, with or without builder, with the same or another type of standard soiled cotton, gave generally the same results. An exception was that sodium oleyl sulfate and sodium 9,10-dichlorooctadecyl sulfate did not wash as well in hard water in the absence of builders.

Dishwashing Test. Glass slides soiled with greasy soil were washed in the Terg-O-Tometer by the method of Leenerts (11) in water of 100 p.p.m. at 50°. The detergents proved effective in about the same order as for cotton detergency. The results with a protein-carbohydrate soil instead of a greasy soil were similar, but differences between detergents were less marked.

Emulsion Stability. Emulsions were prepared from 40 ml. of light petrolatum and 40 ml. of a 0.1% solution of the detergent, by a method of intermittent, violent shaking (3). The time in seconds for 10 ml. of the aqueous phase to separate is a measure of emulsifying properties. There is not much difference in emulsion stability. The individual ether alcohol sulfates are less effective than the sulfated ethenoxylated tallow alcohols $R(OC_2H_4)_nOSO_3Na$ previously reported (1).

Calcium Stability. Calcium stability values (19) are recorded in Table II. The ether alcohol sulfates are outstanding in their stability to the calcium ions of very hard water.

Metallic Ion Stability. All of the compounds, with the exception of sodium hexadecyl sulfate and sodium octadecyl sulfate which were not adequately soluble at 25°, were quite stable to Mg^{++}, Fe^{++}, Ni^{++}, Cu^{++}, and Zn^{++} in the metallic ion stability test (7). Most of the compounds formed precipitates at certain concentrations of Al^{+++}, Ca^{++}, Ba^{++}, and Pb^{++}. The stability of ether alcohol sulfates increased with the number of ethenoxy groups; $C_{18}H_{37}(OC_2H_4)_4OSO_3Na$ was stable to all metal ions, and other ether alcohol sulfates with two or more ethenoxy groups were sensitive to Al^{+++} or Ba^{++}.

Lime Soap Dispersing Power. Sodium oleyl and elaidyl sulfates, sodium 9,10-dichlorooctadecyl sulfate, and the ether alcohol sulfates were found to have good or excellent lime soap dispersing power (2). This suggests the possibility of favorable combinations with soap for use in hard water.

Summary

Retention of unsaturation, additive chlorination at the double bond, the introduction of ethenoxy groups, and the formation of triethanolammonium salts have been compared as methods for increasing the solubility of tallow alcohol sulfates.

These methods represented in a study of 16 compounds, increased the solubility, as shown by the Krafft point. Other properties were altered as well: the critical micelle concentration, surface and interfacial tension, wetting, foaming, detergent and emulsifying properties, calcium stability, metallic ion stability, and lime soap dispersing power.

Sodium oleyl sulfate and sodium 9,10-dichlorooctadecyl sulfate, in contrast to sodium octadecyl sulfate, are very easily soluble. The Krafft point is less than 0°, and the c.m.c. lies between values for sodium hexa-

decyl and octadecyl sulfates. The unsaturated compounds and the dichloro compound are good wetting agents and lime soap dispersing agents, also excellent detergents in built solutions in hard water.

The ether alcohol sulfates whose properties were measured are chemical individuals $[R(OC_2H_4)_iOSO_3Na, i = 1, 2, 3, 4]$ rather than a mixture of homologs $[R(OC_2H_4)_nOSO_3Na]$. The Krafft point, c.m.c., foam height, and detergency decreased with the number of ethenoxy groups; surface tension and wetting time increased. They are good emulsifying agents with excellent calcium stability, metallic ion stability, and lime soap dispersing power.

The triethanolammonium salts have much lower Krafft points than the sodium salts and a slightly lower c.m.c. They are much more soluble than the sodium salts but may form precipitates in the presence of large amounts of Na^+ or Ca^{++} ions. Their properties suggest a possible use as a component in shampoos or liquid detergents.

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Thermal Oxidation of Methyl Esters of Fatty Acids

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A REVIEW OF THE LITERATURE has shown that relatively little work has been done in a systematic and quantitative manner on the thermal oxidation of saturated fatty acid esters (1–12). In the present study, methyl esters of lauric, stearic, and oleic acids were oxidized in the presence of oxygen for various intervals of time. The decomposition products and the residual materials were subjected to chemical analysis in order to gain an insight into the mechanism of oxidation.

Experimental Procedures and Data

The methyl esters of lauric and stearic acids were prepared in this laboratory from technical high grade fatty acids.[2] The acids were twice crystallized from acetone (1 g./10 ml.), and the methyl esters were prepared from them by refluxing in absolute methanol, which had been saturated with hydrogen chloride gas (1 g./5 ml. methanol). The ester was fractionally distilled twice *in vacuo* in an all-glass apparatus, at 1 mm. of Hg. pressure. U.S.P. grade of oleic acid was crystallized twice from acetone (1 g./10 ml.) at −45°C. It was then kept at −15°C. over-night to remove traces of saturated fatty acids. Methyl oleate was prepared from oleic acid as described for the methyl esters of the saturated fatty acids. The analytical values of the pure methyl esters and the theoretical values are given in Table I.

To handle small quantities of the sample and to have maximum contact with bubbling oxygen, a fritted glass disk was fused into the side of a 125-ml. round-bottomed, glass-stoppered flask so that the disk nearly touched the bottom of the flask. In order to follow the oxidation of the esters and to insure trapping of condensible and noncondensible volatile products, the system shown in Figure 1 was devised. The reaction flask A was placed in the constant temperature bath F maintained at 200° ± 1°C. Tank oxygen was freed of moisture, carbon dioxide, and carbon monoxide by means of purification Train I. This train consisted of absorption tubes containing magnesium perchlorate and ascarite to remove moisture and carbon dioxide, a Vycor tube packed with copper oxide heated to red heat in order to convert carbon

TABLE I

Analysis of Methyl Esters of Fatty Acids, and Comparison with Theoretical Values

	Iodine value		Sap. value	
	Theory	Obtained	Theory	Obtained
Methyl laurate	0.00	0.03 0.00	261.8	262.2 261.4
Methyl stearate	0.00	0.18 0.15	188.0	187.8 187.3
Methyl oleate	85.65	85.16 84.74	189.2	189.3 189.8

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