# Structure and Surfactance—Evaluation of Ricinoleyl Alcohol

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m T}_{
m HE}$  POSITION of the hydrophilic group such as sulfate in a long aliphatic chain governs its surfactant properties. If the sulfate group is terminal, detergency is exhibited; if central, wetting properties are manifested. It seemed of interest to study the surfactant properties of a series of model compounds with sulfate salt groups and an unsaturated center at various positions, such as are exemplified by Turkey red oil, oleyl sulfate, ricinoleyl sulfate, methyl 12-sulfato-oleate, methyl 9- or 10-sulfatostearate, stearyl sulfate, and lauryl sulfate. These are pictured in Figure 1. Lauryl sulfate, though of shorter chain length than the others, was included as a compound of known surfactant properties useful as a standard. Apart from the comparative study, the purpose of the present work was also to evaluate ricinoleyl alcohol, the fatty alcohol corresponding to ricinoleic acid or to castor oil, as a surfactant base. Here the presence of two hydrophilic groups in the sulfated salt, separated by 12 carbon atoms, was expected to lead to unpredictable and interesting surfactant properties.

## EXPERIMENTAL

**Base Materials.** Refined castor oil of undoubted purity obtained locally was used for the preparation of the Turkey red oil and methyl ricinoleate.

Methyl oleate used for direct sulfation and for reduction to the alcohol was derived from commercial U.S.P. oleic acid from which saturated acids had been removed by a single adduction with urea in methanol. The chief impurity left was up to 2% of linoleic acid.

Oleyl, ricinoleyl, stearyl, and lauryl alcohols were obtained by sodium reduction of the corresponding methyl esters, all of over 90% purity, by the method of Hansley (7). The raw materials used for further sulfation had the characteristics shown in Table I.

Sulfation of Base Materials. Castor oil was sulfated in 25% stoichiometric excess with concentrated sulfuric acid, oleum containing 20% sulfur trioxide, and chlorosulfonic acid. Oleyl alcohol was sulfated with a 5% excess of the same three sulfating agents. Since sulfations at  $10^{\circ}$  to  $15^{\circ}$  C. offered no particular advantage in certain trials, all subsequent sulfations were done at room temperature of  $30^{\circ}$  to  $35^{\circ}$  C., with the vessel standing in running tap water. The addition was carried out dropwise with mechanical stirring over 1 hour, with subsequent stirring for 5 hours. The sulfated product was analyzed for iodine value, acid value, and per cent sulfur trioxide (1) with the results shown in Table II.

In both castor oil and oleyl alcohol, sulfuric acid resulted in a low degree of sulfation, oleum tended to attack the

	Iodine	Value	Acety	l Value		
	Exptl.	Calcd.	Exptl.	Calcd.	$n_{\rm D}^{25}$	
Castor oil	84.6		145.5		1.4775	
Oleyl alcohol	93.1	94.7	177.5	181.0	1.4617	
Ricinoleyl alcohol	89.0	88.4	273.3	282.6	1.4720	
Methyl oleate	84.4	85.8		Nil	1.4501	
Methyl ricinoleate	80.8	81.3	146.3	158.4	1.4592	
Stearyl alcohol	0.6	Nil	178.0	180.4		
Lauryl alcohol	0.3	Nil	236.7	246.1	1.4437	

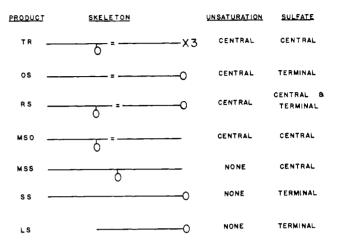


Figure 1. Types of products tested

double bond (this was more pronounced with oleyl alcohol than with castor oil), and chlorosulfonic acid gave high degrees of selective hydroxyl group sulfation. The sulfation of methyl oleate with concentrated sulfuric acid was also not satisfactory. Hence chlorosulfonic acid was used for all subsequent sulfations, and only the excesses varied. Optimum sulfation occurred with about 0.25 molar excess of the reagent, though a little concurrent double-bond attack was unavoidable.

Methyl ricinoleate sulfated somewhat poorly. The resulting product was repeatedly extracted with petroleum ether to remove unsulfated material (34%, iodine value, 70.7,  $n_D^{25}$  1.4676, contaminated or oxidized methyl ricinoleate) and the resulting methyl 12-sulfato-oleate analyzed. The degree of sulfation of methyl oleate with sulfuric acid was rather low, and lauryl alcohol also sulfated to a surprisingly low extent. High-melting stearyl alcohol was sulfated in solution in chloroform, and the sulfated material crystallized from 20 parts of acetone and washed by suspension in petroleum ether.

**Neutralization**. The products were neutralized dropwise with 20° Baumé sodium hydroxide based on the acid value. To obtain purer products, one sample each of neutralized oleyl sulfate (No. 10) and neutralized ricinoleyl sulfate (No. 15) were crystallized from acetone at 10° C. The neutralized product derived from methyl oleate (No. 17) was also purified by several extractions with light petroleum when 18.3% of unreacted methyl oleate was removed. Hence these three products, especially No. 17, will be purer than represented by the analyses recorded in Table II. Aqueous solutions of the products from 1.0 to 0.0625% were prepared for testing.

#### TEST METHODS

**Calcium Tolerance.** This was determined by a modified Hart's method (8, 12) by titrating 50 ml. of 0.05% solution of the sample with 1% calcium acetate solution until the turbidity just obscured a strip of printed matter fastened to one side. The results were expressed as calcium ion tolerance.

Dispersing Power. The rate of settling of 1% manganese dioxide suspended in a 1% solution of the test sample was

		Analyce	is of Sulfated <b>F</b>	Products	Calculated Analytical Characteristics				
	Amount,	Iodine	Acid		Iodine	Acid			
Sulfating Agent	Moles	value	value	% SO <sub>3</sub>	value	value	% SO <sub>3</sub>		
		(	Castor Oil						
Concd. sulfuric acid	1.25	60.1	115.8	16.5					
Oleum	1.25	58.2	146.6	20.9	66.5	123.9	18.6		
Chlorosulfonic acid	1.25	60.1	128.8	18.4					
Concd. sulfuric acid (at 10-15° C.)	1.25	62.7	122.8	17.5					
		•	yl Alcohol						
Concd. sulfuric acid	1.05	58.4	136.9	19.5					
Oleum	1.05	54.0	153.3	21.9					
Chlorosulfonic acid	1.05	57.4	147.1	21.0	71.1	166.6	23.7		
Chlorosulfonic acid	1.25	57.2	170.6	24.3					
Chlorosulfonic acid	1.50	43.8	180.5	25.8					
Chlorosulfonic acid <sup>e</sup> (sample in chloroform)	1.25	68.2	157.4	22.5					
(cumple in one of other			levl Alcohol						
Chlansen lanis said	2.0	46.0	233.6	33.3					
Chlorosulfonic acid Chlorosulfonic acid	$2.0 \\ 2.25$	46.0	253.6 264.5	33.3 37.7					
Chlorosulfonic acid	2.23	43.1	272.1	38.8	56.7	253.7	36.2		
Chlorosulfonic acid	3.0	34.4	291.5	41.6	00.7	200.7	50.2		
Chlorosulfonic acid <sup>®</sup>	0.0	54.4	201.0	41.0					
(sample in chloroform)	2.25	49.9	249.2	35.6					
(F/		Methy	l Ricinoleate						
Chlorosulfonic acid	1.25	52.4	145.0	20.7	65.9	142.4	20.3		
chiolosulloine actu	1.20		hyl Oleate	20.1	00.0	142.1	20.0		
	1.05		•	15.0	<b>N</b> T/1	1 40 0	00.0		
Concd. sulfuric acid <sup>*</sup>	1.25	26.5	104.9	15.0	Nil	142.3	20.3		
		Stear	ryl Alcohol						
Chlorosulfonic acid									
(sample in chloroform)	1.25		154.3	22.0	Nil	160.3	22.9		
		Lau	ryl Alcohol						
Chlorosulfonic acid	1.25		167.5	23.9	Nil	210.8	30.1		

<sup>\*</sup> After analysis, products neutralized and crystallized from acetone at 10° C., hence purer than indicated by analysis.

After analysis, product neutralized and freed of unsulfated methyl oleate, hence considerably purer than indicated by analysis.

determined on a Fisher-Dott apparatus (2, 4) in which the sine of the angle was 0.052.

In another suspension test to measure dispersing power, 0.5 gram of 200-mesh pigment-grade carbon black was dispersed in 250 ml. of a 0.2% solution of the test sample in a 250-ml. graduated cylinder with an outlet at the 130-ml. mark. Dispersion was effected by 10 inversions of the cylinder followed by settling for 30 minutes. A few milliliters of liquid was then drawn through the outlet and rejected; a further small sample was drawn and its absorbance at 650 m $\mu$  determined without undue delay in a 0.5-cm. cell using a Beckman spectrophotometer. Absorbance was directly related to dispersing power.

Wetting Tests. The Draves-Clarkson method as prescribed by Indian Standards (9) was followed. The sinking times of skeins consisting of  $5 \pm 0.1$  grams of gray carded Indian yarn of  $\frac{2}{30}$ 's wound so as to have a 44-cm. circumference were noted using an anchor weight of 27.10 grams and a hook weight of 4.50 grams at two concentrations chosen by trial so as to lie on either side of that concentration which would give a sinking timé of 25 seconds. The latter was then determined from the straight-line graph of log concentration vs. log sinking time. Each test was run in quadruplicate.

**Emolsifying Power**. Ten vigorous shakes were given to 40 ml. of liquid paraffin and 40 ml. of aqueous phase containing 0.5% of the test surfactant in a 500-ml. stoppered conical flask. The mixture was transferred to a measuring cylinder, and the time taken for 10 ml. of the aqueous phase to separate was noted (13).

Surface Tension. This was determined using a DuNuoy tensiometer at room temperature  $(32^{\circ} \text{ C.})$  for several concentrations of each sample. The lowering of surface tension from the value of 71.4 dynes per cm. shown by water is

here recorded only for one concentration of 0.2%, which is sufficiently representative.

Detersive Efficiency. The multi-wash technique was used to minimize the effect of unavoidable mechanical variations. The basic cotton fabric was scoured, bleached, dried, and unmercerized sheeting with a thread count of  $18 \times 22$ . weighing about 5 ounces per square yard. Cut lengths were immersed for 2 minutes in a homogenized solution of 1 gram of refined and bleached peanut oil and 3 grams of Oildag (a commercial graphite-mineral oil suspension) in 1000 ml. of carbon tetrachloride. The pieces were air-dried, allowed to age for a week, and cut into  $3 \times 4$  inch swatches. By this means the cloth with an original reflectance value of 76.5  $\pm$ 0.5 read as a percentage of that of magnesium carbonate in an Eel reflectance spectrophotometer was soiled to one of  $27.2 \pm 0.4$  reflectance value. The efficiency of soil removal was determined by washing 4 swatches in 500 ml. of test solution of 0.2% concentration for 30 minutes at 50° C. with gentle mechanical stirring, followed by similar rinsing with 500 ml. of distilled water for 10 minutes at 50°. The swatches were dried on an aluminum plate at 60° for 2 hours and kept in a desiccator overnight. Two swatches were examined for reflectance at this stage. Two others were given a second detergent wash followed by a water rinse, dried, and examined for reflectance. The reflectance values after each of these washes were averaged, and the extent of detergence was taken as the difference between this average and the original reflectance of the soiled cloth.

Foaming Properties. A standard Ross-Miles pour-foam apparatus (11) was made to the original specifications. Initial foam heights and foam stability were determined both at room temperature and at 60° C.

The absolute values obtained for the various surfactant tests are shown in Table III. For comparative purposes, all

#### Table III. Testing of Products for Surfactance

		<u>.</u>	sing Power	Wetting	E1-:6	0.6					I	Pour Foa	m Tes	t°	
		Fisher- Dott.		Test," Concn. to	Emulsifi- cation,"	Surface Tension	1			A		m Temp			
	<b>.</b>	time to	~ .			of 0.2%							Soln.	At 60° C., 0.25% Soln.	
TR 1	Calcium Toler- ance 191	recede 50 cm., sec. 129	absorbance 600	Sinking Time of 25 Sec., % 0.189	Separation of 10 Ml., Sec. 204	Soln., Dynes per Cm. 60.4	1st wash 0.6	2nd wash 6.8	Av. R 1.8	I.H., mm. 60	S., mm. 50	I.H., mm.	S., mm.	I.H., mm.	S., mm.
TR 2 TR 3 TR 4	$242 \\ 222 \\ 203$	$153 \\ 121 \\ 124$	920 750 500	$\begin{array}{c} 0.085 \\ 0.101 \\ 0.152 \end{array}$	238 210 190	$54.4 \\ 56.1 \\ 54.4$	$1.7 \\ 1.2 \\ 0.4$	$5.8 \\ 4.8 \\ 2.1$	$1.8 \\ 1.5 \\ 0.7$	60	50	Negli- gible	• • •	Negli- gible	
OS 1 OS 2 OS 3 OS 4 OS 5 OS 6	Turbid Turbid Turbid 300 Turbid 477	257 288 255 282 274 287	Turbid Turbid Turbid 1700 Turbid 2270	$\begin{array}{c} 0.239 \\ 0.105 \\ 0.202 \\ 0.121 \\ 0.073 \\ 0.143 \end{array}$	165 176 172 185 184 189	$\begin{array}{c} 45.7 \\ 41.4 \\ 44.9 \\ 44.0 \\ 41.4 \\ 43.1 \end{array}$	$5.6 \\ 9.9 \\ 7.6 \\ 11.8 \\ 13.0 \\ 15.1$	$16.8 \\ 20.9 \\ 18.0 \\ 23.2 \\ 26.3 \\ 19.2$	5.5 7.5 6.2 8.5 9.5 10.7			144	13	185	55
RS 1 RS 2 RS 3 RS 4 RS 5	303 310 295 300 328	265 298 317 323 290	$1300 \\ 1300 \\ 1050 \\ 920 \\ 1825$	$\begin{array}{c} 0.098 \\ 0.090 \\ 0.081 \\ 0.068 \\ 0.079 \end{array}$	159 169 178 166 183	$\begin{array}{r} 44.0 \\ 44.9 \\ 45.7 \\ 47.4 \\ 45.7 \end{array}$	$8.7 \\ 12.6 \\ 14.7 \\ 15.5 \\ 12.4$	$14.3 \\ 25.3 \\ 24.9 \\ 26.3 \\ 25.1$	$5.6 \\ 9.2 \\ 9.6 \\ 10.1 \\ 9.2$			82	77	126	58
MSO	275		1300	0.094	256	54.2	3.3	11.6	3.6	104	53	78	78	135	75
MSS	278		1250	0.080	218	49.2	1.2	9.1	2.5	123	41	98	87	125	45
SS	Turbid		Turbid	Not deter- minable	c	41.1	13.5	29.0	10.3	Negli- gible		Negli- gible	•••	155	35
LS	350		2520	0.121	173	35.4	12.4	27.3	9.6	184	11	155	14	195	40
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<sup>a</sup> Values for distilled water: Wetting test, sinking time 195 seconds. Emulsification time, 27 seconds. Surface tension 71.4 dynes/cm. Detersive efficiency 0.6, 2.3, R 0.7.

<sup>b</sup> I.H. Initial height, S. Subsidence.

<sup>°</sup> Oil and water layers separate simultaneously.

Table IV. Surfactant Properties of Products Compo	ared to Laury! Sulfate Taken as 100
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	Calcium	Calcium Dispersing Power		Wetting	Emulsification	Surface Tension Lowering of	Detersive	Foaming
	Tolerance	Fisher-Dott	Suspendability	Test	Test	0.2% Solution	Efficiency	Power
TR 1	55	31	24	64	118	34	19	
TR 2	69	36	27	142	138	50	19	Not
TR 3	63	29	30	120	124	45	15	comparable
TR 4	58	30	20	71	110	50	7	
OS 1	Turbid	61	• • •	51	95	71	57	31
OS 2	Turbid	69		115	102	84	78	77
OS 3	Turbid	61		60	99	74	65	30
OS 4	86	53	68	100	107	76	89	97
OS 5	Turbid	65		166	106	84	99	79
OS = 6	136	68	90	85	109	79	111	93
RS 1	87	63	52	123	92	76	58	51
RS 2	89	71	52	135	98	74	96	64
RS 3	84	76	42	149	103	71	100	58
RS 4	86	77	37	178	96	68	105	61
RS 5	94	69	72	153	106	71	96	53
MSO	79		52	129	151	49	38	50
MSS	78		50	151	126	63	26	64
SS	Turbid			15		84	107	80
LS	100	100	100	100	100	100	100	100

values were calculated as a percentage of the corresponding value shown by sodium lauryl sulfate taken as 100. These comparative percentage values are shown in Table IV.

# DISCUSSION OF RESULTS

The following code is used in the discussion, figures, and tables.

Sodium Salt of	No. of Samples	Code
Turkey red oil	4	TR
Oleyl sulfate	6	os
Ricinoleyl sulfate	5	$\mathbf{RS}$
Methyl 12-sulfato-oleate	1	MSO
Methyl 9- or 10-sulfatostearate	1	MSS
Stearyl sulfate	1	SS
Lauryl sulfate	1	LS

The very poor solubility of the sodium stearyl sulfate resulted in unsatisfactory test values.

**Calcium Tolerance.** This is an indication of the maximum hardness of water in which surfactants can still function

effectively. In this respect they are superior as a class to soaps which form insoluble precipitates in even slightly hard water. Built-up detergents always contain sequestering agents which enhance the calcium tolerance of the surfactant, and hence the absolute value of the latter is only of limited significance. Moreover the turbidity method of determining such tolerance cannot be used when the solution is already turbid as in the OS samples 1, 2, 3, and 5. The purified samples of the alcohol sulfates, OS 6, RS 5, and LS, are slightly more tolerant to calcium ions than the centrally sulfated products, MSO and MSS. The TR samples, which are structurally identical with MSO but consist of a bulky glyceride molecule (Figure 1), are slightly poorer still. However, no marked or regular effect corresponding to position or extent of sulfation can be detected in regard to this property.

**Dispersing Power.** The ability of the surfactant to disperse a soil in water effectively and to prevent its redeposition represents the dispersing power. In commercial practice carboxymethylcellulose is added to the builders for the purpose. Of the two methods used in the present work, the Fisher-Dott method needs specialized apparatus, but is not affected by turbid solutions as is the absorbance suspendability method. Terminal sulfate groups confer far greater dispersing power than do central sulfate groups. The TR samples showed the least power, only about two thirds that of the comparable MSO and MSS samples, again due perhaps to the bulky glyceride molecule. The best samples are the alcohol sulfates, especially LS of low molecular weight and high solubility. The two sulfate groups in RS do not enhance the dispersing power, which falls between that of OS and MSO, but is closer to the superior values of the alcohol sulfates.

Wetting Power. This important property is mostly dependent on central sulfation, the terminally sulfated alcohols being distinctly poor. This property is striking in those samples in which the double bond has been attacked by the sulfating agent (as revealed in low iodine values) to give impure products containing central sulfate groups. These products show a wetting power superior to their pure counterparts. This is seen in the TR, OS, and RS series. Pure RS and MSS are exceptionally good, with MSO closely following. In RS, the high wetting power conferred by the central functional group appears not only to have dominated over the poor power arising from terminal sulfation, but to have been enhanced.

**Emulsification Power**. This also appears to depend, though not so markedly as the power of dispersion, on the degree of central sulfation, as evidenced by the superiority of TR, MSO, and MSS over OS and LS. The effect of the degree of central sulfation arising from double-bond attack is again apparent in the RS and OS series, though not as strikingly as with dispersing power. MSO and MSS with central sulfate groups are outstanding, and TR, again perhaps because of bulk, is slightly inferior. The advantage of a central sulfate group in RS is nullified by the terminal sulfate, and the three fatty alcohol sulfates, irrespective of the presence or absence of unsaturation or sulfate groups along the chain, have a similar and low emulsification power.

Surface Tension. Reduction of surface tension is conferred in a more marked degree when terminal sulfation is present. Thus the three centrally sulfated materials TR, MSO, and MSS reduce aqueous surface tension poorly and increasing in the order given. Of the alcohol sulfates, OS is inferior to LS. The RS series shows a slightly lesser power than the OS series, central sulfation having contributed a drag effect. Because the lowering of surface tension depends chiefly on terminal sulfation, degrees of central sulfation in any series have little effect. The more saturated products, like MSS compared to MSO, and the oversulfated OS and RS samples, appear to posses an enhanced power to lower surface tension.

Detersive Efficiency. Evaluation was on soiled cotton only. Since alkylaryl sulfonates are established products for this purpose, a commercial product built with sodium sulfate was evaluated by the test method, with the intention of using it as a standard for comparison. This material turned out to be only about 10% more efficient than the lauryl sulfate used in the rest of this work as reference standard, so the latter was used for this test also. Central sulfate groups confer poor detersive power. TR is only a trifle more detergent than water, and even MSO and MSS, with less bulky molecules, are only slightly better. Increase in central sulfation among the OS or RS series apparently results in slight corresponding fluctuations in detersive power. This must, however, be only a coincidence because otherwise the RS as a group must be greatly superior to the OS series, which is not so. Perhaps small differences in terminal sulfation, whose extent cannot be determined from the analytical figures, may have caused these fluctuations. Of

the various alcohol sulfates, oleyl and stearyl appear slightly superior to the rest.

Foaming Characteristics. These were determined at several concentrations for all samples. To avoid a mass of figures however, typical data for each class are given only at 0.1 and 0.25% concentrations at room temperature, and at 0.25% concentration at  $60^{\circ}$  C. As expected, the initial foam height is lower at increasing dilutions, and likewise foam stability. The centrally sulfated materials TR, MSO, and MSS demonstrate poor foam height and stability, the heavy TR molecule again showing the poorest characteristics. Of the terminally sulfated materials, OS is almost the equal of LS. In RS the influence of the central sulfate group dominates that of the terminal completely, and the products are indistinguishable from MSO and MSS.

# CONCLUSIONS

While it would perhaps have been preferable to use hydrocarbons rather than methyl or glyceride esters as model centrally sulfated materials, the present compounds show properties very similar to the corresponding hydrocarbons (5), suggesting a small influence if any of the remote terminal ester group. This is also borne out by the great similarity in the surfactant properties of TR, a glyceride ester, and the methyl esters MSO and MSS, suggesting that the common properties are dependent to a very large extent on the common factor of central sulfation. In this comparative study, the effect of central unsaturation was not as obvious as that of sulfate position. Unsaturation of course greatly enhances the solubility of the sulfated salt. To judge from the centrally sulfated oleate and corresponding stearate studied, surfactant properties are not influenced by central unsaturation in a long fatty chain. The only noticeable effect was a slightly greater power to lower surface tension in the saturated product.

Central sulfation gives rise to superior wetting and emulsifying powers. In compounds carrying both central terminal sulfation, such enhanced wetting power is further augmented but emulsification power cancelled by the terminal group present.

Terminal sulfation is associated with enhanced power to reduce surface tension, increased detersive efficiency and dispersing ability, and a high degree of foaming and foam persistence. When a compound carries both terminal and central sulfate groups, such superior ability to lower surface tension and to disperse is only slightly affected. Detersive efficiency is hardly affected at all. Foaming characteristics are suppressed completely.

The cause underlying these properties exhibited by ricinoleyl sulfate could best be considered by determining the hydrophobe-hydrophile balance. Such balances are, however, extremely difficult to estimate or predict on the basis of structure, except in a general way. The presence of two hydrophiles in ricinoleyl sulfate is a further complication. Hence the surfactant properties of this material will be discussed by analogy with the properties exhibited by compounds of known structure, which are in turn dependent on the hydrophobe-hydrophile balance.

Comparable earlier experimental work on the relationship of structure to surfactance in anionic compounds was done by Padgett and Degering (10), who showed that as the sulfate group in a 12-carbon chain moved towards the middle, both surface tension-lowering and foaming power decreased. Dreger, Keim, Miles, Shedlovsky, and Ross (5) also studied a series of sulfated primary alcohols, and concluded that central sulfation lowers surface tension, wetting, and foam stability, and decreases detergent power. These properties are due to the presence of two short-chain hydrophobes in these centrally sulfated materials, and the resulting hydrophobe-hydrophile balance. In this series also, foaming was much higher for the alcohol sulfates, and suppressed, though not to the level of secondary sulfates, in ricinoleyl sulfate. Foam stability is associated with a high rate of surface tension-lowering; judging by good wetting out performance, this rate of lowering has not been reduced in ricinoleyl sulfate. Hence, the other factors known to contribute to low foaming—a low surface viscosity—and to low foam stability—slow draining of the soap laminae must be involved.

Böhme (2) patented certain derivatives of castor oil as surfactants, among them

$$CH_3(CH_2)_5CHCH_2CH = CH(CH_2)_7COONa$$
  
|  
OSO\_3Na

$$CH_{3}(CH_{2})_{5}CHCH_{2}CH = CH(CH_{2})_{7}COONa$$
  
|  
OSO<sub>3</sub>R

and

The first product, like ricinoleyl sulfate, has two hydrophilic groups at identical positions. The product was stated to have good wetting power, but poor stability to acids owing to the carboxylate group. This would not apply to ricinoleyl sulfate because all aliphatic sulfates are not hydrolyzed by dilute acids and are of course stable in hard water. Similar advantages of high stability, wetting, and detergency are claimed for the disulfate derived from oleyl alcohol (6)—i.e., the 1,9-or 10-disulfatostearyl alcohol. However, the solubility of this saturated material is likely to be poorer than that of ricinoleyl sulfate.

Several investigations (5, 10) have shown that when the hydrophobic chain is excessively branched, the wetting activity is greatly enhanced. In ricinoleyl sulfate almost all the linkages in the chain are capable of free rotation. When in aqueous solution, the two hydrophilic groups are attracted to water and the 12-carbon chain connecting them curls up to make this possible, the five-carbon chain meantime sticking out at an angle (Figure 2). Thus the opportunity for organized micelle formation is markedly

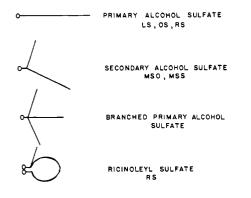


Figure 2. Orientation of surfactant types in dilute aqueous solution

diminished, leading, as in the highly branched examples cited earlier, to enhanced wetting power. Such structural modifications also lead to an increase in solubility, again because the side groupings interfere with the close packing and alignment of the long-chain molecules, and therefore to their tendency to separate from water. Ricinoleyl sulfate may be expected to have a high solubility, to which the presence of a double bond will further contribute.

While usually high wetting is not present together with good detergency, in ricinoleyl sulfate the two go together. The poor detergent power of secondary alcohol sulfates, R-CH-OSO<sub>3</sub>Na, exemplified in the present series by R'

methyl sulfato-oleate and methyl sulfatostearate, has been

Table V. Summary of Surfactant Properties of Products Tested

Calcium tolerance	TR L	OS M	RS M	MSO M	MSS M	<b>S</b> S 	LS M
Dispersing power, both methods Wetting power,	L	М	М	L	L	•••	Н
Draves-Clarkson Emulsification power Foam test, Ross-Miles	M H	M M	H+ M	H H	H+ H	L+ 	M M
Height of foam Sustaining of foam Lowering of surface tension	L L	H H	M L+	M M	M M	M L	H H
by 0.2% solution Detersive power for	L	Μ	Μ	L	L	Н	н
soiled cotton	L+	Н	н	L	L+	н	н

attributed to their inability to form condensed unilayers at  $\mathbf{R}^{\prime\prime}$ 

# interfaces. Tertiary alcohol sulfates, $R-C-CH_2OSO_3Na$ ,

on the other hand, have high detergent power, comparable to the straight-chain primary alcohol sulfates (12). The orientation of the ricinoleyl sulfate molecule in aqueous solution (Figure 2), in which a five-carbon chain and two carbon chains in a continuous curve radiate from two, rather than from one, hydrophilic ions, has a similarity to that obtaining in the branched-chain primary alcohol sulfates. The balance of forces, and likewise the resultant detergent properties, may be comparable.

### SUMMARY

Ricinoleyl alcohol, by virtue of its two spaced hydrophilic groups, has good to excellent dispersing power, wetting power, surface-tension lowering ability, and detersive efficiency. Emulsifying power is medium, and foaming characteristics are low (Table V). These several advantages, and in particular a very high wetting power, confer on ricinoleyl alcohol distinctive properties as a surfactant base.

#### ACKNOWLEDGMENT

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