that stability differences might be accounted for by the larger amount of moisture in the expressed oil and/or the presence of more free sulfhydryl groups in the extracted oil (11), these factors were found to be without effect.

The oils of garden cress and wild mustard seeds, when added to linseed oil, were effective in delaying its oxidation. The optimum stabilizing concentration for both additives was found to be 10%. In each case above 25% no further increase in the stability was achieved. The addition of 10% garden cress or wild mustard oil to linseed oil showed a protective value of 2 for the expressed linseed oil and 4 for the extracted one. However the induction periods for both extracted and expressed linseed oils were the same. This could be explained on the basis that garden cress and wild mustard oils contain approximately the same concentration of α-tocopherol per gram of oil, which is higher than its maximum effective concentration (183 γ/g. for wild mustard oil and 190 γ/g. for garden cress oil). The smaller protective value could be explained on the basis that the extracted linseed oil contains more tocopherol than the expressed oil (150 γ/g. for expressed and 190 γ/g. for extracted linseed oil). No synergistic effect was observed when the two oils (garden cress and wild mustard) were added together since α-tocopherol was the only antioxidant that could be detected in the three oils.

Fraction J of the unsaponifiable matter of both wild mustard and garden cress oils was identified as α-tocopheryl allophonate. The melting point of the two fractions, 159°C., corresponded to the reported one for α-tocopheryl allophonate, which was between 158–160°C. (3). The spectrophotometric examination of these two fractions and that of α-tocopheryl acetate showed the same selective absorption in the ultraviolet region of the spectrum with a maxima at 290 mμ and a minima at 225.5 mμ approximately.

Several experimental results indicated that α-tocopherol was the only active antioxidant present in both wild mustard and garden cress oils. All the fractions M, I, and N, with the exception of fraction J, showed no antioxidation effect. Furthermore, upon the separation of α-tocopheryl allophonate from the acetone solution, the residue was inactive. The antioxidation effect obtained from the addition of different concentration of the α-tocopherol present in garden cress and wild mustard oils were the same as those obtained from the addition of chemically pure α-tocopheryl acetate.

REFERENCES

1. Kirschenbauer, H. G., "Fats and Oils, an Outline of Their Chemistry and Technology," Reinhold Publishing Corporation, pp. 122 (1944).
2. Budowski, P., J. Am. Oil Chemists' Soc., *27*, 264–7 (1950).
3. Herbert, M. E., Oliver, H. E., and Gladys, A. E., J. Biol. Chem., *113*, 319–32 (1936).
4. Herbert, M. E., Oliver, H. E., Gladys, A. E., and Mohamed, A., J. Biol. Chem., *122*, 99–107 (1937).
5. Mourea, C., and Dufraisse, C., Chem. Rev., *3*, 113 (1926).
6. Mourea, C., and Dufraisse, C., Chemistry and Industry, *47*, 819 (1928).
7. Chipault, J. R., Mizuno, G. R., Hawkins, J. M., and Lundberg, W. O., Food Research, *17*, 46–55 (1952).
8. Lundberg, W. O., Halverson, H. O., and Burr, G. O., Oil and Soap, *21*, 33–35 (1944).
9. Winton, A. L., and Winton, K. B., "The Analysis of Foods," John Wiley and Sons Inc., pp. 386–7 (1945).
10. Association of Official Agricultural Chemists, "Official Methods of Analysis," pp. 430, 441, and 442 (1950).
11. El-Rafey, M. S., Richardson, G. A., and Henderson, J. L., J. Dairy Sci., *27*, 807–20 (1944).
12. Lange, W., Oil and Soap, *27*, 418–21 (1950).
13. Lundberg, W. O., "A Survey of Present Knowledge of Researches and Practices in the United States Concerning the Stabilization of Fats," University of Minnesota, Minneapolis, Minn., No. 20, 1–39 (1947).
14. Jacobs, M. B., "The Chemistry and Technology of Food and Food Product," Interscience Publishers Inc., vol. 2, ch. 13, pp. 410–1 (1944).

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Synthetic Detergents from Animal Fats. IX. Triethanolammonium, Lithium, Alkaline Earth, and Other Salts of α-Sulfonated Fatty Acids[1]

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α-Sulfopalmitic acid and α-sulfostearic acid have aqueous solubility in excess of 10% at room temperature. In contrast, the sodium salts, $RCH(SO_3Na)\text{-}CO_2H$ and $RCH(SO_3Na)CO_2Na$, which have detergent properties (9) and show promise as components in detergent mixtures (7), have limited solubility except at higher temperatures. Difference in solubility may be related to the fact that aqueous solutions of the "diacids" $[RCH(SO_3H)CO_2H]$ contain micelles, while the sodium salts do not form micelles, at room temperature (11).

Properties of a variety of salts of α-sulfonated acids have been reported only in the case of the lower fatty acids, for example, salts of α-sulfobutyric and α-sulfovaleric acids (1, 2). Triethanolammonium α-sulfopalmitic acid has been shown to be exceedingly soluble (8); and the detergent and foaming properties of the sodium salts of α-sulfopalmitic and stearic acids can be favorably affected by the presence of the Ca^{++} and Mg^{++} ions of hard water. These considerations suggest there may be considerable differences in the solubility and surface-active properties of different salts of α-sulfonated higher fatty acids. Accordingly ammonium, triethanolammonium, lithium, sodium, potassium, silver, magnesium, calcium, barium, zinc, copper, aluminum, and iron salts of α-sulfopalmitic acid and α-sulfostearic acid were prepared. Most of the salts were made from aqueous solutions of the isolated diacids (10). Where solubility and purity of the salts permitted, detergent and other surface-active properties were measured.

Preparation of Salts

Ammonium, Lithium, Sodium, Potassium, and Silver. Acid ammonium, sodium, and potassium salts $[RCH(SO_3M)CO_2H]$ were prepared from the diacid

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by neutralization and re-acidification (9, 10). Potassium α-sulfopalmitic acid and the acid sodium salts were purified by recrystallization from water and extraction with hot acetone to remove small amounts of unsulfonated fatty acids. Recrystallization from alcohol was necessary to purify the acid ammonium salt. Diammonium, disodium, and dipotassium salts [$RCH(SO_3M)CO_2M$] were made by neutralizing the purified acid salts. Analyses for N, Na, K, and S differed from the theoretical values by 0.02–0.40% for the acid and neutral salts.

Lithium salts were prepared in a similar manner with proper allowance for different solubility behavior. Since acid lithium salts were too soluble to be crystallized from water, the partial neutralization of the diacid and purification of the salt was carried out in alcoholic solution. The neutralization equivalent and analysis for Li indicated a purity of 95–96% for $RCH(SO_3Li)CO_2H$.

Dilithium α-sulfostearate could not be dissolved in boiling water, even at 3 g. per 100 ml. It was necessary to add 15% by volume of alcohol to obtain a clear solution for crystallization. Analyses for Li on the neutral lithium salts [$RCH(SO_3Li)CO_2Li$] were within 0.3% of the theoretical value.

Reaction of silver nitrate and α-sulfostearic acid in aqueous solution promptly precipitated an acid silver salt [$RCH(SO_3Ag)CO_2H$]. Insolubility in water or alcohol made further purification difficult.

Triethanolammonium. Triethanolamine was added in 10% excess to a solution of the diacid in 10 volumes of methanol. Crystallization at —25° gave an 85% yield of the crude acid triethanolammonium salt. Purification by crystallization from methanol, decolorization with carbon, and two crystallizations from chloroform gave 50–60% yields of triethanolammonium α-sulfopalmitic acid m.p. 204° N.E.[3] 243.5 (calculated for $C_{22}H_{47}NO_8S$, 242.8), and triethanolammonium α-sulfostearic acid, m.p. 156°, N.E. 257.7 (calculated for $C_{24}H_{51}NO_8S$, 256.9).

Neutral triethanolammonium salts [$RCH(SO_3M)$-CO_2M] were not isolated but were prepared in aqueous solution by neutralization of the acid salt with an equimolar amount of triethanolamine.

Magnesium, Calcium, Barium, Zinc, Copper, Aluminum, and Iron. Salts of divalent metals were formed by adding slightly more than the equivalent amount of the metal chloride, dissolved in water, to an aqueous solution of the diacid. The acid salts of magnesium, calcium, and zinc [*e.g.*, $RCH(SO_3Mg/2)$-CO_2H], which precipitated from aqueous solution, were purified by treatment with carbon and crystallization from methanol. The copper salt which precipitated in the same way was not further purified because of the gelatinous nature of the alcoholic solution. Neutral magnesium and calcium salts [*e.g.*, $RCH(SO_3Mg/2)CO_2Mg/2$] were formed by adding the stoichiometric amount of magnesium carbonate or calcium hydroxide to a hot aqueous solution of the acid metal salt. All measurements of surface-active properties of neutral magnesium salts were made on the aqueous solution at this point. The high solubility of magnesium α-sulfopalmitate made it necessary to evaporate the solution to recover the salt. Neutral calcium salts and magnesium α-sulfostearate could be crystallized from the aqueous solution. The analysis for magnesium or for calcium was within 0.1% and 1.0% of the theoretical value, for the acid and the neutral salts, respectively.

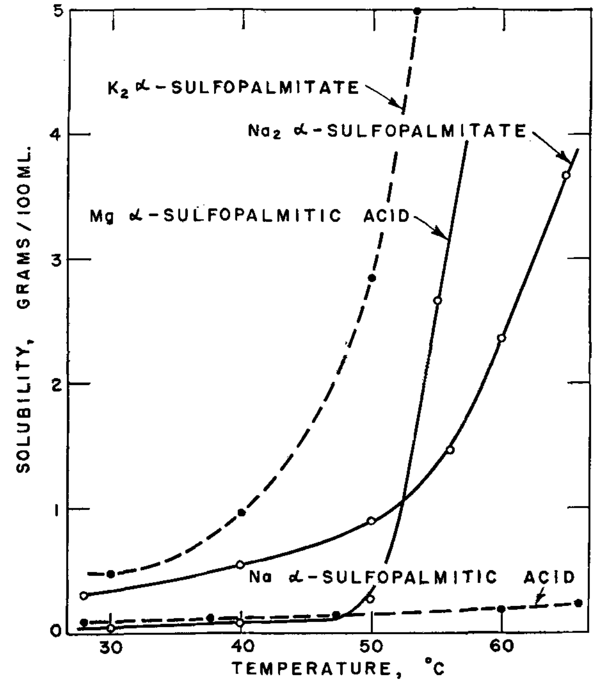

FIG. 1. Solubility of salts of α-sulfopalmitic acid.

The mixing of aqueous solutions of barium chloride and α-sulfostearic acid gave an immediate precipitate of barium α-sulfostearate, too insoluble to be easily purified.

Acid aluminum and ferric salts, which precipitated when aqueous solutions of aluminum sulfate or ferric chloride were mixed with α-sulfostearic acid, were not further purified because of their insolubility in water and their gelatinous nature in alcoholic solution.

pH Values. The pH values of 0.1% solutions were about 3.5–4.5 for the acid salts, about 5 for diammonium, and about 8 for disodium salts.

Solubility

Aqueous Solubility. Solubility was conveniently measured using the Launder-Ometer[4] as a constant

TABLE I

Aqueous Solubility of Acid and Neutral Salts of α-Sulfopalmitic and α-Sulfostearic Acids, g./100 ml., at 30 to 60°.

	30°	40°	50°	60°
α-Sulfopalmitic acid salts				
Ammonium	0.2	0.5	5	10
Triethanolammonium	>20	....	....	....
Lithium	> 5	....	....	....
Sodium	0.07	0.10	0.12	0.19
Potassium	0.04	0.05	0.08	0.10
Magnesium[a]	0.06	0.06	0.25	>3
Calcium	0.28	0.42	0.87	4.6
α-Sulfostearic acid salts				
Triethanolammonium	>20	....	....	....
Sodium	0.05	0.05	0.05	0.06
Lithium	> 5	....	....	....
Magnesium	< 0.01	0.01	0.01	0.06
Calcium	0.03	0.04	0.74	5 (gel)
Neutral α-sulfopalmitates				
Diammonium	0.70	1	....	10
Dilithium	0.30	....	....	....
Disodium	0.34	0.54	0.92	2.4
Dipotassium	0.49	0.94	2.9	19
Magnesium[b]	> 5	....	....	....

[a] $C_{14}H_{29}CH(SO_3Mg/2)CO_2H$. The acid calcium salt has a similar formula.

[b] $C_{14}H_{29}CH(SO_3Mg/2)CO_2Mg/2$.

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[3] Neutralization equivalent.

[4] Reference to a commercial product does not imply recommendation by the U. S. Dept. of Agriculture over similar products not mentioned.

temperature bath (9). Table I lists the aqueous solubility of ammonium, triethanolammonium, lithium, sodium, potassium, magnesium, and calcium salts of α-sulfopalmitic and α-sulfostearic acids at 30 to 60°. Solubility was not accurately measured for the very soluble acid triethanolammonium and lithium salts, which formed somewhat gelatinous solutions, or for the very soluble magnesium α-sulfopalmitate.

Table I shows that the acid lithium salts are considerably more soluble than acid or neutral sodium salts while the neutral lithium and sodium α-sulfopalmitates are about equally soluble at room temperature. Although magnesium α-sulfopalmitate is highly soluble ($>5\%$ at 30°), the dry salt obtained by evaporation of the aqueous solution gave a small amount of an insoluble residue on re-solution. This instability, the high solubility of acid calcium salts, and the behavior in the pinacyanole test described below points to the complex nature of aqueous solutions of salts of the divalent metals.

Figure 1 illustrates some effects of changing the cation of acid and neutral salts of α-sulfopalmitic acid. Although the acid sodium and magnesium salts have about the same solubility below 50°, above 50° there is a sharp rise for the acid magnesium salt. Acid ammonium and calcium salts (see Table I) show similar sharp increases at about 40 to 55° while the acid sodium salt does not show a rapid increase in solubility until at about 95°.

The neutral potassium salt shows a marked increase in solubility at a lower temperature than does the disodium salt. Dilithium α-sulfostearate has limited solubility even in boiling water.

Pinacyanole Test. A test for the presence of micelles in 0.1% solutions was carried out by mixing 10 ml. of a 0.0039% (1×10^{-4} molar) solution of pinacyanole chloride with a solution of 0.1 g. of the salt in 90 ml. of water. Acid triethanolammonium and lithium salts immediately gave clear blue solutions, indicating that micelles were present. Ammonium α-sulfopalmitic acid gave a cloudy solution with a color between blue and purple, indicating that both micelles and larger particles were present. Acid sodium, potassium, magnesium, and calcium salts of α-sulfopalmitic acid were not in complete solution at room temperature, and the purple color of the dye showed that none of the dissolved material was present as micelles. On heating, these four acid salts gave clear blue solutions, showing that micelles were present. On cooling again to room temperature, the solution of the acid calcium salt retained some of its blue color.

Neutralization of these acid salt solutions with the appropriate alkali led to observations concerning the neutral salts. The color of the ammonium, triethanolammonium, lithium, sodium, and potassium salt solutions became clear purple, indicating that a concentration of 0.1% was below the critical micelle concentration (c.m.c.) for these neutral salts. This agrees with previously reported data on the c.m.c. and the solubility of the disodium salts (11). The blue color of the neutral magnesium salt, showing micelles, is further evidence for the complex nature of solutions of salts of the divalent metals. Rapid precipitation of the neutral calcium salt during neutralization of the acid calcium salt obscured observations.

Nonaqueous Solubility. Acid triethanolammonium and magnesium salts were soluble to the extent of about 1 to 5% in benzene, butanol, or chloroform at room temperature. Acid aluminum salts were more readily soluble.

Surface-Active Properties

Surface and Interfacial Tension. Surface and interfacial tensions of 0.1% solutions were measured with the Du Nouy tensiometer. At 30° the surface tension values were as follows, in dynes/cm.:

Ammonium α-sulfopalmitic acid	40
Triethanolammonium α-sulfopalmitic acid	43
Magnesium α-sulfopalmitic acid	39
Triethanolammonium α-sulfostearic acid	43
Magnesium α-sulfostearic acid	47

The acid magnesium salts did not form clear solutions. The interfacial tension values against petrolatum were about 10 dynes/cm. These values are not very different from those of the sodium salts.

Detergency. The detergency of several acid and neutral salts of α-sulfopalmitic and α-sulfostearic acid was measured, using the Terg-O-Tometer, washing 10 swatches of G.D.C. No. 26[5] (3) standard soiled cotton in one liter of a 0.1% solution in distilled water, at 110 cycles per minute, for 20 min. at 60°. Detergency was measured as ΔR, the increase in reflectance after washing. The results are recorded in Table II.

TABLE II

Detergency, ΔR,[a] of Acid and Neutral Salts of α-Sulfopalmitic Acid and α-Sulfostearic Acid; 0.1% Solutions in Distilled Water at 60°. (Terg-O-Tometer, 20 min., 110 cycles/min., 10 swatches G.D.C. No. 26/l.)

Cation	α-Sulfopalmitic		α-Sulfostearic	
	Acid	Neutral	Acid	Neutral
Ammonium	30.8	29.8	....	....
Triethanolammonium	31.7	18.0[b]	34.1	28.5
Lithium	35.2	....	36.6	....
Sodium	31.4	22.2[c]	26.5	26.7
Potassium	27.1	17.7	....	....
Magnesium	32.3	30.1	33.6	34.4
Calcium	30.3	....	33.3	....

[a] ΔR = Increase in reflectance after washing. For comparison the values for 0.1% solutions of sodium palmitate and sodium dodecyl sulfate were 43.4 and 17.8, respectively.
[b] ΔR = 27.8 at 0.25% concentration.
[c] ΔR = 31.7 at 0.25% concentration.

An analysis of variance (4) showed that differences in ΔR of 0.5 to 0.7 were significant with 95% probability. From Table II the acid lithium and magnesium salts were better detergents than the corresponding sodium α-sulfopalmitic acid; magnesium and diammonium salts were better than disodium α-sulfopalmitate; acid lithium, triethanolammonium, magnesium, and calcium salts were better than the corresponding sodium α-sulfostearic acid; and magnesium and ditriethanolammonium salts were better than disodium α-sulfostearate. The acid ammonium, triethanolammonium, sodium, potassium, and magnesium salts of α-sulfopalmitic acid were better detergents than corresponding neutral α-sulfopalmitates. For the stearic acid derivatives the acid triethanolammonium salt was better than the neutral salt, but the acid and neutral sodium salts were equal in detergency, and the neutral magnesium salt was better than the acid salt. In general, acid lithium, triethanolammonium, and magnesium salts, calcium α-sulfo-

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[5] Reference to a commercial product does not imply recommendation by the U. S. Dept. of Agriculture over other commercial products not mentioned.

stearic acid and magnesium α-sulfostearate, were the best detergents.

A concentration of 0.1% is considerably below the c.m.c. for neutral monovalent metal α-sulfopalmitates [$C_{14}H_{29}CH(SO_3M)CO_2M$]. At 0.25%, nearer the c.m.c., the ΔR value for ditriethanolammonium and disodium α-sulfopalmitate increased to 27.8 and 31.7, respectively.

Wetting Properties. Wetting properties were measured as the time in seconds required to sink a standard binding tape (6) suspended by means of a 1-g. hook and a 40-g. anchor in 500 ml. of a 0.1% solution. The wetting time values were as follows:

Triethanolammonium α-sulfopalmitic acid	50
Magnesium α-sulfopalmitic acid	32
Ditriethanolammonium α-sulfopalmitate	56
Magnesium α-sulfopalmitate	25
Triethanolammonium α-sulfostearic acid	66
Ditriethanolammonium α-sulfostearate	51

The value for disodium α-sulfopalmitate lies in this range.

Foaming Properties. Foaming properties, measured by the Ross-Miles pour-test (5) on 0.1% solutions in distilled water at 60°, are recorded in Table III.

TABLE III

Immediate Foam Height (5), mm., of Acid and Neutral Salts of α-Sulfopalmitic Acid and α-Sulfostearic Acid; 0.1% Solutions in Distilled Water at 60°.

Cation	α-Sulfopalmitic		α-Sulfostearic	
	Acid	Neutral	Acid	Neutral
Ammonium	175	190	....	....
Triethanolammonium	160	100	160	190
Lithium	190	....	205	....
Sodium	175	25[a]	75	15
Potassium	200	125	....	....
Magnesium	220	215	160	220
Calcium	220	....	125	....

[a] Foam height = 175 mm. at 0.25% concentration.

Most of these salts had better foaming properties than the sodium salt. The acid and neutral magnesium salts of α-sulfopalmitic acid, magnesium α-sulfostearate, and calcium α-sulfopalmitic acid had the highest and most stable foams. This may explain the better foaming properties of the sodium salt in hard water. Here again a concentration of 0.1% is below the c.m.c. for salts such as disodium α-sulfopalmitate, and an increase to 0.25% concentration improved the foam height.

Summary and Discussion

Of the several salts of α-sulfopalmitic and α-sulfostearic acid prepared, salts of adequate purity with measurable or considerable solubility in water are naturally those of greatest interest. These are, in general, the ammonium, triethanolammonium, lithium, sodium, potassium, magnesium, and calcium salts. A study of the wide variation in their aqueous solubility leads to an explanation of corresponding differences in surface-active properties. Outstanding differences were observed in the comparison of the slightly soluble acid sodium and potassium salts with the highly soluble acid triethanolammonium and lithium salts. At room temperature sodium and potassium salts appear to have the properties of a simple electrolyte and crystallize from solution as their ionic solubility is exceeded while at this concentration acid triethanolammonium and lithium salts exist in micellar solutions.

Each salt seems to have a critical temperature, somewhat similar to the Kraft point of soaps, above which crystalline properties give way to colloidal properties. This critical temperature appears on a solubility curve as a sharp increase in solubility. Dilithium α-sulfostearate is the only salt in this group which does not show marked increase in solubility below 100°. Acid magnesium and acid calcium salts, and dipotassium α-sulfopalmitate show marked solubility increases at temperatures lower than for corresponding sodium salts. Neutral magnesium salts exist in colloidal solution at concentrations lower than the solubility of corresponding neutral ammonium, sodium, or potassium salts. Salts of the divalent metals appear to form complex solutions which may not contain exclusively the same anionic species as corresponding salts of the monovalent metals. In general, salts forming micellar solutions at lower temperatures have better detergent and foaming properties.

REFERENCES

1. Backer, H. J., and de Boer, J. H., Rec. trav. chim., *43*, 420–433 (1924).
2. Backer, H. J., and Toxopéus, M., Rec. trav. chim., *45*, 890–907 (1926).
3. Draves, C. Z., and Sherburne, O. L., Am. Dyestuff Reptr., *39*, P 771–2 (1950).
4. Duncan, D. B., "Multiple Range and Multiple F Tests," Virginia Agricultural Experiment Station, Technical Report No. 6 (1953).
5. Ross, J., and Miles, G. D., Oil and Soap, *18*, 99–102 (1941).
6. Shapiro, L., Am. Dyestuff Reptr., *39*, P 38–45, P 62 (1950).
7. Stirton, A. J., Maurer, E. W., and Weil, J. K., J. Am. Oil Chemists' Soc., *33*, 290–291 (1956).
8. Stirton, A. J., Weil, J. K., and Bistline, R. G. Jr., J. Am. Oil Chemists' Soc., *31*, 13–16 (1954).
9. Stirton, A. J., Weil, J. K., Stawitzke, Anna A., and James, S., J. Am. Oil Chemists' Soc., *29*, 198–201 (1952).
10. Weil, J. K., Bistline, R. G. Jr., and Stirton, A. J., J. Am. Oil Chemists' Soc., *32*, 370–372 (1955).
11. Weil, J. K., and Stirton, A. J., J. Phys. Chem., *60*, 899–901 (1956).

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Continuous Soap Washing and Finishing, Using Multistage, Countercurrent, Centrifugal Contactors

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THIS PAPER PRESENTS a significant advance in soap technology, consisting of a process for continuous washing and finishing of soap employing multistage, countercurrent, centrifugal contactors.

Introduction

Soap boiling, although known for many hundreds of years, has been generally considered an art rather than a science until approximately the last 30 years. The work of Martin Fischer in 1921 was the first serious attempt to explain the physical chemistry of the various soap phases encountered in soap-boiling operations (1). This was followed by the important work of J. W. McBain and others (2, 3). But even with this present well-developed knowledge soap boiling is still largely an art in many of the soap plants.