

# Solubilization of Fatty Soils by a Radiotracer Technique

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A technique for measurement of solubilized radiotagged triolein and tristearin fatty soils is described. By using surfactant solutions under standardized conditions of temperature and agitation, the solubilized soils are removed from emulsified materials by filtration through 0.1 and 0.01 micron-pore size of filters. The radiotagged fat is recovered by solvent extraction from the clear filtrate by salting-out under centrifugal force and is measured by conventional counting technique.

The nonionic alkanol- and alkylphenol-ethylene oxide (EO) adducts solubilized up to 0.058% triolein (weight percentage at 75°C.) while anionic surfactant and sodium tripolyphosphate solubilization was negligible. These findings suggest for these nonionics that solubilization is one of the main, if not the controlling factor in the mechanism of soil removal. Non-ionic solubilization was at a maximum for 10 molar EO adducts and at near cloud-point temperatures.

For the same surfactant more triolein than tristearin was solubilized, possibly on account of spatial considerations. For tridecanol-10 EO at 0.25% the heat of solubilization of triolein,  $\Delta H_s$ , was 15 kcal/mole while the heat of micellization of the adduct was 1.3 kcal/mole of adduct. Differences in the colloidal ion lengths of the micelles and their aggregation numbers may explain the differences in solubilization between the anionic and nonionic surfactants tested.

FATTY AND OILY MATTER are important components of natural soil. Wagg reported 80% of articles laundered were soiled mainly by excretions from sebaceous skin glands (14). Sebum contains fats and waxes, fatty acids, hydrocarbons, and cholesterol. On extracting domestically-soiled fabrics, Brown (5) found from 0.25% to 1.2% oil present by weight of fabric, with the greatest amounts on shirt collars. The isolated oil consisted mainly of fatty matter, primarily oleic, palmitic, and stearic in nature. Powe and Marple (11) extracted cotton articles which had been repeatedly laundered to remove all but problem soil and found that it consisted of 2-8% organic matter by weight. The organic matter contained mostly fatty esters with lesser amounts of lime soaps and free fatty acids. Other important ingredients are present in natural soils, such as clays, carbonaceous matter, etc. These particulate soils are often attached to the substrate through adherence with greasy matter, hence removal of greasy matter can be instrumental in removing particulate soils.

The usual conception of fatty soil removal is that preferential displacement of soil takes place (2), followed possibly by emulsification. However solubilization of fatty soil as a possible mechanism of removal has not been investigated. McBain and Hutchinson (8), in a thorough review of the field, showed only an occasional isolated reference to fatty soil solubilization, but nothing directed specifically at the detergency mechanism. They properly pointed out that solubilization is only one of many factors involved in detergency and is particularly applicable to oily or greasy soils. They disagreed sharply with Moilliet (10), who claimed that solubilization was too specific a phenomenon to be important to detergency. They also disagreed with Preston (12), who relegated solubilization to a minor role in washing. Harris (6), in reviewing the role of solubilization in

detergency, indicated that it might be a controlling factor under certain conditions.

In previous work (2,3) it was demonstrated that radiotagged tristearin and triolein were removed from a glass substrate by a mechanism of preferential displacement of adsorbed soil. However the fate of cohesively-bonded soil, also removed, might either be emulsification by a "rolling up" mechanism described by Adam (1) or, since the wash solutions were perfectly clear, by a solubilization mechanism. The objective of this paper is to present data to verify this possible mechanism of soil removal.

## Experimental Procedures

*Apparatus.* Microanalytical balance, sensitivity 1  $\mu\text{g}$ . Micrometer syringe, "Alga" (Burrhoughs Wellcome and Company), graduated to 0.0002 ml. accuracy for 0.01 ml. of  $\pm 0.00005$  ml.

Sampling flasks, Florence, 100 ml., modified with side arms for sampling and venting, 24/40 glass-bearing joint (Figure 1).

Stirrers, stainless steel, ground to fit through Pyrex 24/40 glass-bearing.

Agitator apparatus, multispindle wash bath, temperature control  $\pm 0.5^\circ\text{C}$ . from 25-75°C., rate agitation 76 c.p.m. through an arc of 370°.

Filters, 4-5.5  $\mu$  fritted glass; 0.1 and 0.01 micron porosity filters, Millipore Filter Corporation, Bedford,

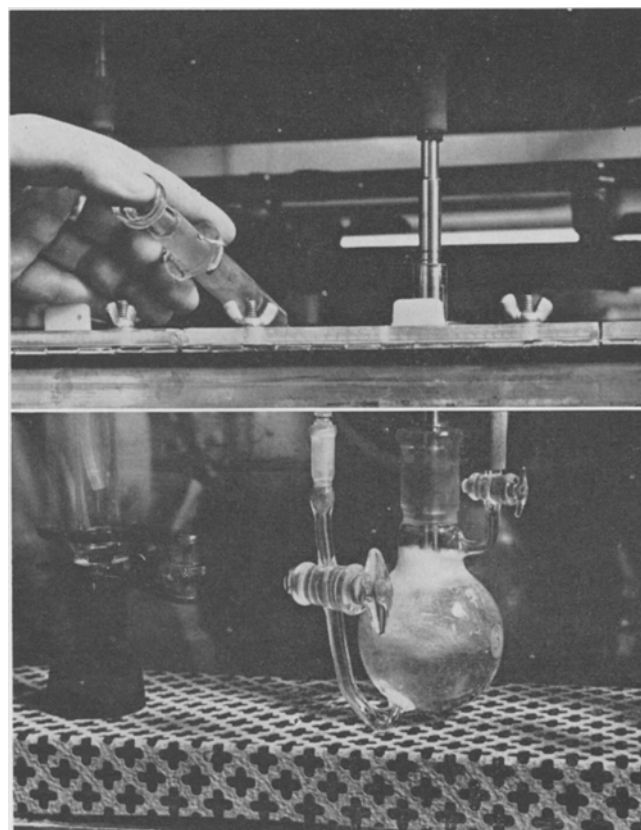


FIG. 1. Dynamic sampling flask.

TABLE I  
Calculation of Solubilization from Radiotracer Data  
System: 0.25% conc. tridecanol-10 EO  
60°C.  
0.1% triolein level  
Duplicate runs

Solubilization data, 45-min. stirring period			
Counting times, min. for 6,400 counts		Calcd. c.p.m. <sup>a</sup>	
1	2	1	2
1.68	1.67	3810	3830
1.63	1.68	3930	3810
1.67	1.73	3830	3700
Corrected triolein solubilized (% conc.) <sup>b</sup>			
1	2	Aver.	
0.0328	0.0329	0.0328 (95% confidence limits) ± 0.0008	
0.0338	0.0328		
0.0329	0.0318		

<sup>a</sup> Counts measured/counting times.

<sup>b</sup> Filtrate counts × initial fat concentration (%)  
Control counts

(Control counts = 11,630 c.p.m. at 0.1% triolein level from calibration curve.)

Mass. (Nos. VCWP 02500 and RAWP 02500) and hydrosol microanalysis filter holder No. XX 1002500.

Air oven, ±2°C. from 30–75°C.

Centrifuge, International Clinical, and tubes.

Planchets, Nuclear Chicago Corporation.

Scaling unit, micromil window flow-counter, automatic sample changer, and printing timer, Nuclear Chicago Corporation.

*Solubilizates.* Radiotagged triolein, glyceryl 1,3-C<sup>14</sup> trioleate, 0.12 millicuries/millimole, obtained in 50-microcurie lots from New England Nuclear Corporation, Boston, Mass.

Unlabelled triolein, technical, T-6912 from Matheson, Coleman, and Bell, kept refrigerated between uses.

Radiotagged tristearin, C-14, stearyl-tagged, 1.73 millicuries/millimole, from Nuclear Chicago Corporation in 50-microcurie lots.

Unlabelled tristearin, No. 1380, from Eastman Organic Chemicals.

#### Solubilizers.

Sodium tripolyphosphate, STP, commercial.

Sodium dodecyl (tetrapropylene) benzene sulfonate, NaDDBS.

Sodium pentadecylbenzene sulfonate, NaPDBS.

Sodium lauryl sulfate, Fisher Scientific Company

Sodium oleate, Fisher Scientific Company.

(oxo) Decanol-10(.14)<sup>1</sup> EO (ethylene oxide).

n-Dodecanol-10 EO.

(oxo)Tridecanol (TDA)

- 5(.15)<sup>1</sup> EO (ethylene oxide) adduct.

-10(.14) EO

-15(.15) EO

Dodecylphenol-10 EO.

Nonylphenol-10(9.8) EO.

The surfactants used were salt-free. The nonionic products are ethylene oxide (EO) adducts on a molar-addition basis, shown to the nearest unit; the figures in parentheses are the actual molar weight of the adduct.

#### Experimental

Briefly the solubilization procedure consists of adding radiotagged fat to a surfactant solution, stirring for a period of time, removing samples during stirring, filtering through Millipore filters to remove emulsified from solubilized fat, recovery of solubilized fat by salting out into a solvent by centrifugation, and measuring fat content by aliquotting and counting, using standards curves.

<sup>1</sup> These were the actual molar weight ratios, subsequently shortened to the nearest unit.

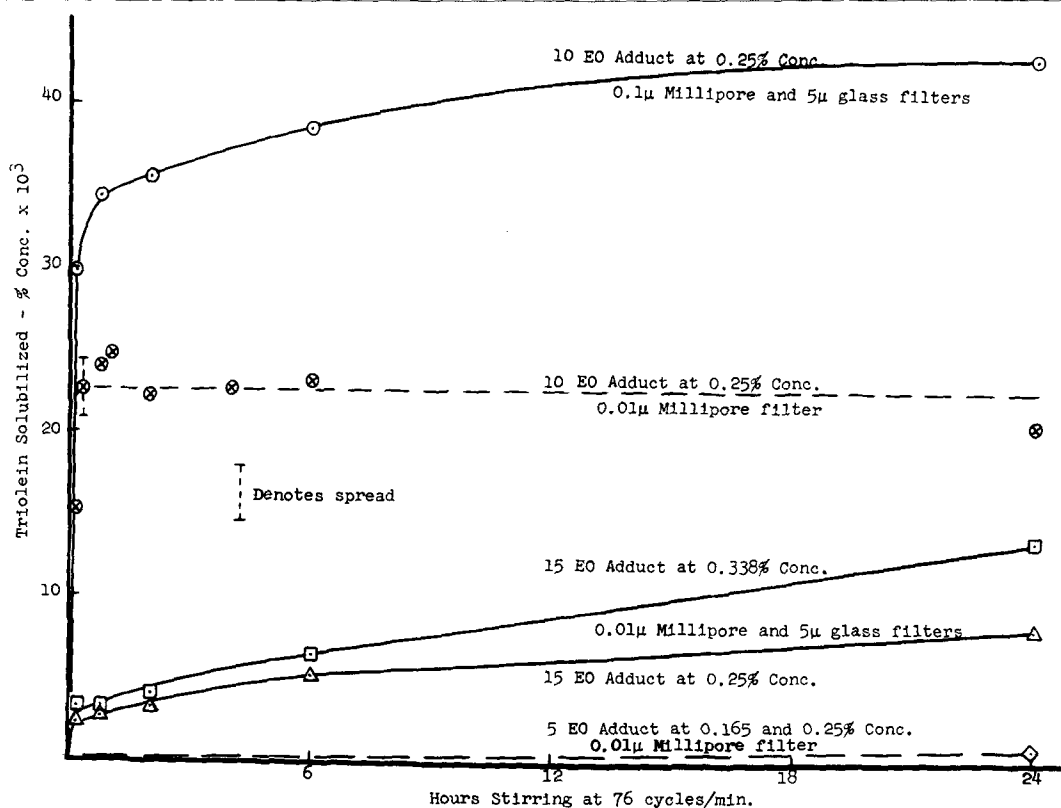


Fig. 2. Effect of ethylene oxide mole ratio on solubilization by tridecanol + EO adducts at 60°C. (0.1% triolein level).

**Calibration Curves.** Tagged triolein was weighed on a microanalytical balance, dissolved in benzene, diluted to given concentrations, and 500- $\lambda$  aliquots transferred by spotting randomly onto planchets at 120°F. on a hot plate, stored 2–10 min. at 60°C., then counted. Curves were prepared from these data.

Blends of tagged with untagged solubilize were made to maintain the count level below 15,000, and counts for 1% recovery (or solubilization) were at least twice background.

**Recovery Technique.** Data were obtained after salting-out and centrifuging benzene solutions from surfactant solutions, and reference curves from counting data were linear for recovery; solubilization counts were directly and linearly proportional to triolein recovery. Counting error lies in the  $\pm 5\%$  range and was generally greater than the recovery error. At a 95% confidence level, variation in the amount of fatty soil solubilized was of the order of  $\pm 3\%$ , e.g., 0.0360  $\pm$  0.0011%.

**Detailed Procedure.** Transfer 125 ml. of surfactant solution to the sampling flasks and heat to temperature. Transfer a known quantity (by weight) of triolein by microsyringe to the surface of the surfactant solution (tristearin was transferred as a solid, weighed by difference). The stirrer and bearing were fitted, and agitation was begun in the agitator apparatus at 76 cycles/minute in an arc of ca. 370°. A 10-min. elapse between fat transfer and initiation of stirring was usual.

Ten-ml. portions of the dispersion were withdrawn through the sampling arm of the flask, using a pre-heated pipet. The samples were transferred to test tubes maintained in the bath, and the fluid in the flask sampling arm was returned to the flask (the venting tube was open only during this operation). Alternatively the samples were transferred directly

by displacement with air to the filtering apparatus as shown in Figure 1.

The dispersion samples were filtered through various porosity filters; the filtering apparatus was housed in an air bath or in the agitator bath at the test temperature. Recoveries of tagged triolein from filtered, completely-solubilized systems was quantitative, proving that adsorption by the filters was not a factor in the separation procedure.

Four-ml. aliquots of the clear filtrates were transferred to the centrifuge tubes. Unfiltered samples of identical size were used throughout for total dispersion values. Then 1.2 g. of sodium chloride c.p. and 2.00 ml. of benzene (reagent grade) were added; the tubes were stoppered and shaken until dissolution of the salt occurred. The stoppered tubes were then centrifuged at about 3,000 r.p.m. ( $\sim 1300$  g.) to separate phases. Then 500- $\lambda$  aliquots of the benzene layer were withdrawn and spotted on planchets as described under Calibration. (Fat recovery was complete in a single extraction as further extraction failed to recover additional fat.)

For each surfactant concentration duplicate runs were usually made, and for each run not fewer than duplicate 500- $\lambda$  aliquots were tested.

Table I shows the data for a single point on a curve.

**Calculation.** Solubilization-fat % concentration =

$$\frac{\text{filtrate counts}}{\text{control counts}} \times \text{initial fat concentration} \\ (\% \text{ by weight})$$

### Data and Discussion

**Particle Size.** Solubilization data were obtained from optically-clear filtrates. Surfactant solutions in the absence of fat, filtered in identical procedures, gave full recovery of surfactant even though concentrations greatly in excess of critical micelle concen-

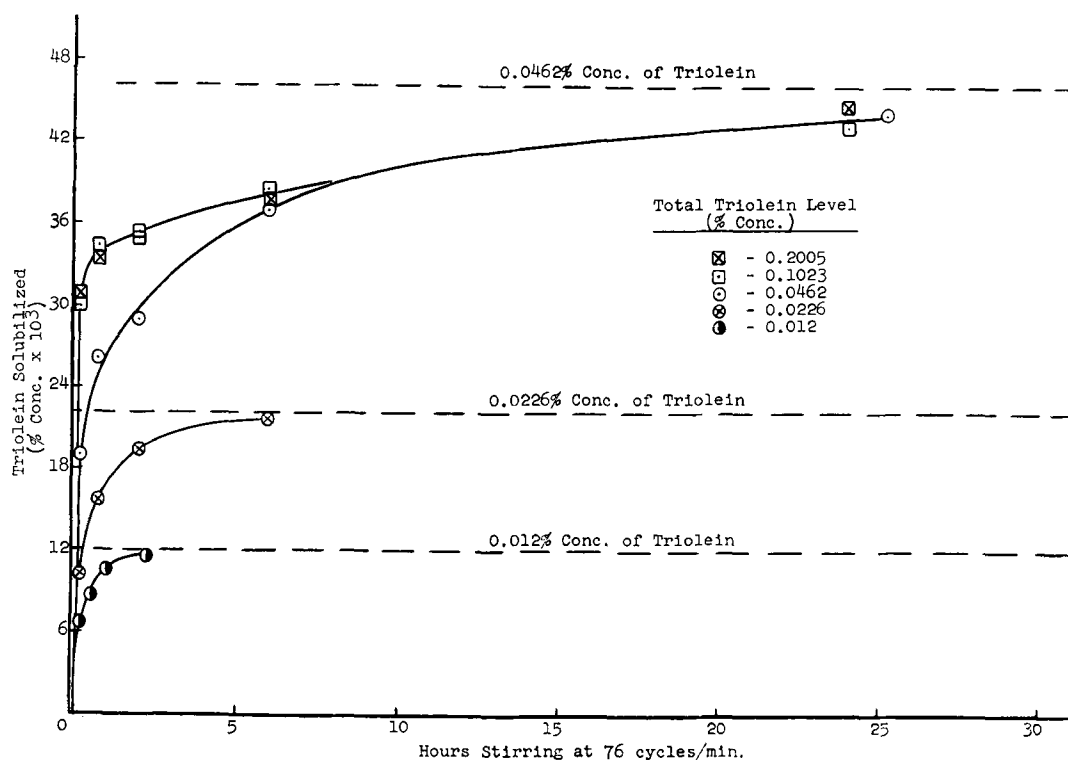


Fig. 3. Approach to equilibrium solubilization of various triolein quantities in 0.25% tridecanol + 10 EO solution at 60°C.

tration (cmc) were used. Clear filtrates were usually obtained, using the 4–5.5  $\mu$  porosity fritted-glass filter, which seemed to filter out some larger suspended particles. A 0.01  $\mu$  Millipore filter was required for obtaining clear filtrates for triolein dispersed in TDA-5 EO solutions (Figure 2). The TDA-15 EO sample yielded similar solubilization, using both 0.01  $\mu$  and 4–5.5  $\mu$  filters.

Triolein solubilized by TDA-10 EO at 60°C. was reduced about 50% in employing the 0.01  $\mu$  filter. At the smaller porosity, dissolved triolein amounted to 0.021–0.025% compared to 0.044% for 4–5.5  $\mu$  porosity (Figure 2). The filterability data suggest two particle-size ranges for triolein-TDA-10 EO mixed micelles: a) a colloidal dispersion or swollen micelle range (particles apparently 0.01–0.1  $\mu$  diameter), and b) a micro-colloid range (<0.01  $\mu$ ) (4). Filtrates throughout the colloidal dispersion and micro-colloid ranges were transparent: 0.044% triolein concentration represents total solubility. Undissolved triolein remains in fairly coarse suspension, as expected for the low shear-rate agitation. Reduction to micro-colloid state occurs very rapidly; equilibrium is reached within 20 min. Micelles in the micro-colloid range contain 14 surfactant molecules for every triolein molecule.

*Time Effects.* Figure 2 shows data for tridecanol-5, -10, and -15 EO adducts at indicated surfactant concentration levels, and at 0.1% triolein level. The strong time dependency of solubilization is apparent, as might be expected from the mild agitation employed (approximating that of washing machines). The most rapid solubilization rate occurred within the first 15 min. of agitation, with 40–60% of maximum solubilization occurring in 10 min., approximating a normal washing-time. True equilibrium occurred only after protracted mixing to about 24 hrs. or more.

Increase in triolein concentration level, Figure 3, demonstrates the rapid attainment of equilibrium, consistent with higher soil excesses. Figure 4 shows equilibrium values for the several time-intervals studied, further clarifying effect of soil concentration.

*Temperature Dependence.* TDA-10 EO at 60°C. increases triolein solubilization more than 20-fold for that at 35°C.

Cloud point has been shown to have a major effect upon soil removal (7), hence it might be expected that some similar effect upon solubilization might be anticipated. Figure 5 for tridecanol-10 EO demonstrates this time-temperature dependency, showing the sharp increase in solubilization as the cloud point (65°C.) is approached. Temperatures in excess of the cloud point conversely are detrimental. Verification of these findings with other nonionic agents would be informative.

Figure 6 shows that the level of solubilization exerted by NaDDBS is so low that temperature has only comparatively slight effect. However the sharp reduction in solubilization with temperature lowering of TDA-10 EO is quite marked.

In Figure 5 solubilization maximum occurred in the cloud-point range (at 65°C.), where micelle concentration is highest. The maxima are most pronounced at shorter time intervals of stirring, *i.e.*, at 10 and 20 min. Up to the maxima, solubilization fits the equation (Figure 7):

$$\log C = m(1/T) + k$$

where C = triolein solubilized in concentration units  
T = temperature  
m = slope  
k is a constant

This is a form of the Clausius-Clapeyron equation

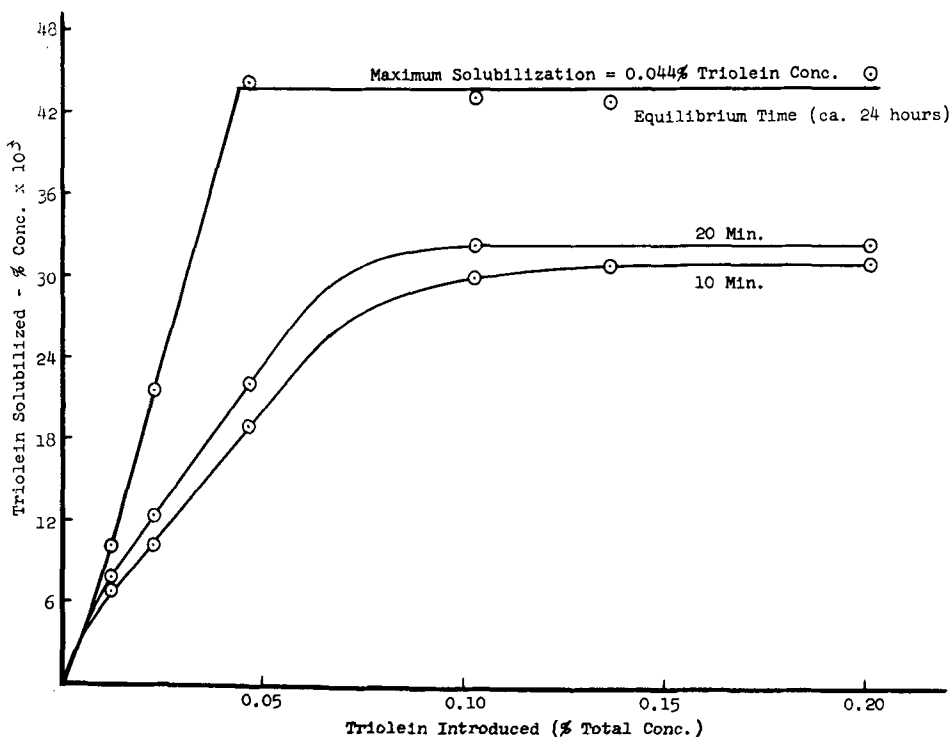


Fig. 4. Relation of triolein solubilized to quantity introduced at equilibrium and nonequilibrium states. (System: 0.25% tridecanol + 10 EO solution at 60°C.)

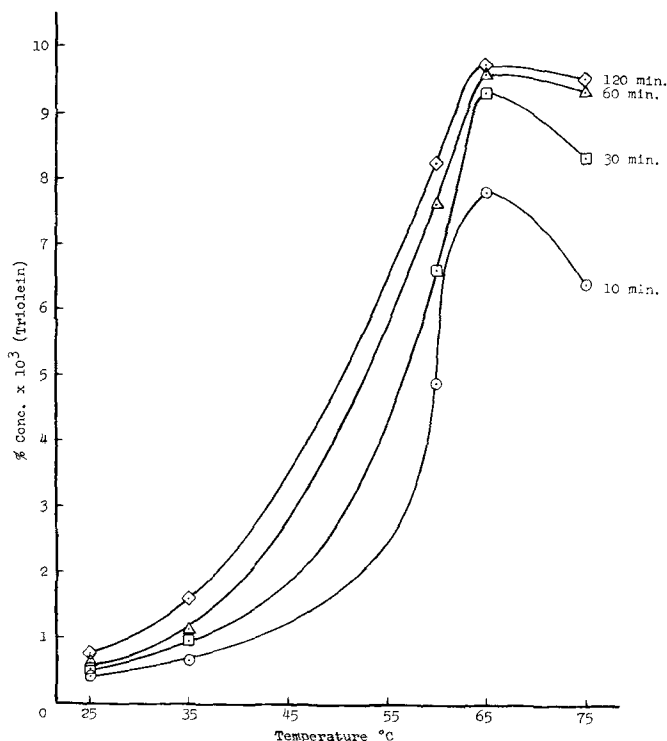


FIG. 5. Influence of cloud point (temperature) on triolein solubilization by tridecanol + 10 EO at 0.25% concentration. (Radiotagged triolein introduced at 0.012% level—solutions stirred for indicated times.)

(8,13) from which  $\Delta H_s$ , the enthalpy of solubilization may be estimated:

$$m = \frac{-\Delta H}{2.303 R} \quad \text{and} \quad \Delta H = \frac{2.303 R \log (C_2/C_1)}{(1/T_1 - 1/T_2)}$$

where R = gas constant in cal./mole/degree.

$\Delta H_s$  was calculated at 15 kcal/mole of triolein for the 0.25% concentration of TDA-10 EO. This solubilization heat is approximately 12 times greater than the heat of micellization,  $\Delta H_m$ , which was estimated at 1.3 kcal/mole of TDA-10 EO from the Clausius-Clapeyron treatment of cmc data. The positive enthalpy indicates that heat must be supplied to effect solubilization.

**Surfactant Structure and Type.** Figure 2 shows that the TDA-10 EO ratio is the most effective; the 15 molar ratio is only moderately more effective than the 5 EO product, which, in turn, is little more effective than water.

Table II shows further that other hydrophobe 10 EO adducts vary in their degree of effectiveness. The alkanol products, in general, were more effective than the alkylphenol materials, but, as the decanol adduct shows, optimum hydrophobe effective carbon chain-lengths exist.

It is important that triolein, perhaps because of spatial configuration, is solubilized to a greater extent than is tristearin.

Compared with the nonionic surfactants tested, the anionics show negligible solubilization for fatty soil. Sodium oleate was most effective of the anionics, followed by sodium lauryl sulfate. Of the alkylbenzene sulfonates, the pentadecyl compound was slightly superior to the dodecylbenzene product, but it is only slightly superior to water.

Important is the character of the surfactant micelle, which determines whether a soil molecule can be incorporated. Anionic molecules constituting micelles have estimated colloidal ion lengths of 20–25 Å compared to 26 Å for triolein, the soil molecule. Lengths of 10 EO adduct-nonionics were estimated at 49–56 Å. High detergency may depend on micellar surfactant molecules being at least as long as and preferably much longer than the soil molecule. From light scattering measurements, Mankowich (9) and others have demonstrated the large size of nonionic surfactant micelles compared to anionic types. For example, the iso-octylphenol nonaethylene glycol ether micelle had a molecular weight of 66,700 (aggregation number of 111) and NaDDBS only 1,000 (aggregation number of 3–5). It is logical that the larger micelle size for nonionics accounts for their superiority over anionics. Anionic micelle size is substantially increased by adding builder, and this may partly explain the builder effect in solubilization.

**Builder Effect.** Solubilization by sodium tripolyphosphate, which proved so effective a fatty soil remover (3), was only slightly more effective than water. Interestingly its combination with NaDDBS increased solubilization to four-fold that of NaDDBS alone (Figure 6 and Table II), and speeded the rate of equilibrium attainment, but acted essentially as a proportional diluent for the decanol-10 EO adduct. Possible explanation for this was given above.

These data demonstrate that solubilization is a potential mechanism for fatty soil removal by the nonionic surfactant type tested. Conversely soil removal by solubilization is either entirely absent or a negligible factor with tripolyphosphate or the anionic surfactants.

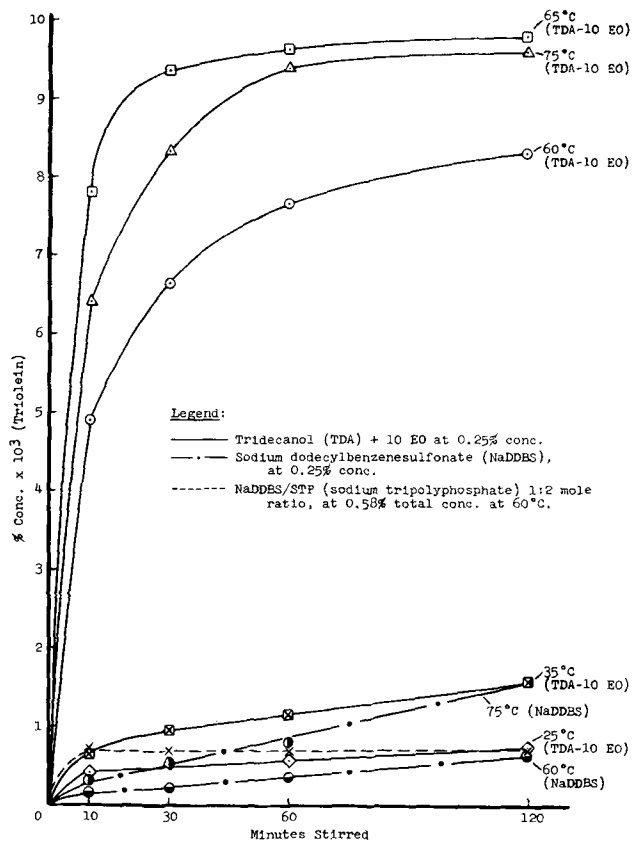


FIG. 6. Triolein solubilization rate curves at various temperatures. (Radiotagged triolein introduced at 0.012% level.)

TABLE II  
Solubilization Data for Detergent Actives at 75°C.

Surfactant	Fatty Soil <sup>a</sup> Solubilized as % Concentration $\times 10^3$							
	Triolein Surfactant concentration				Tristearin Surfactant concentration			
	0.25% Filter $\mu^b$		0.05% Filter $\mu$		0.25% Filter $\mu$		0.05% Filter $\mu$	
	0.10	0.01	0.10	0.01	0.10	0.01	0.10	0.01
Water.....	.....	.....	.....	.....	0.067	0.024	.....	.....
STP (sodium tripolyphosphate).....	.....	.....	.....	.....	0.12	0.09	.....	.....
TDA + 10 EO.....	58.0	15.7	6.4	0.78	29.6	17.76	2.16	0.31
Decanol + 10 EO.....	21.1	9.1	1.5	0.14	14.6	2.1	0.62	0.08
Decanol/STP at 1:2 m.r. <sup>c</sup> (0.112%) (0.138%).....	.....	.....	.....	.....	0.34	0.074	.....	.....
Decanol/STP at 1:4 m.r. (0.07%) (0.18%).....	.....	.....	.....	.....	0.14	0.062	.....	.....
Decanol-10 EO @ 0.25% + STP @ 0.25%.....	.....	.....	.....	.....	7.07	2.79	.....	.....
n-Dodecanol + 10 EO.....	41.5	23.6	2.16	0.31	26.9	16.3	2.47	0.13
Nonylphenol + 10 EO.....	52.1	33.1	18.1	8.1	11.53	10.1	1.8	0.42
Dodecylphenol + 10 EO.....	48.5	15.5	9.77	2.50	6.06	5.19	2.44	0.27
Sodium oleate.....	.....	.....	.....	.....	0.48	0.06	.....	.....
Sodium lauryl sulfate.....	.....	.....	.....	.....	0.35	0.23	.....	.....
Sodium DDB sulfonate.....	.....	.....	.....	.....	0.16	0.13	.....	.....
NaDDBS/STP 1:2 m.r. (0.08%) (0.17%).....	.....	.....	.....	.....	0.30	0.22	.....	.....
NaDDBS @ 0.25% + STP @ 0.25%.....	.....	.....	.....	.....	0.40	0.34	.....	.....
Sodium PDB-sulfonate.....	.....	.....	.....	.....	0.21	0.15	.....	.....

<sup>a</sup> Fats introduced at 0.1% concentration level, sampling of dispersions after 20 min. of stirring.

<sup>b</sup> Millipore filter-pore diameters.

<sup>c</sup> Molar ratio.

### Conclusions

Solubilization of fatty soils may be one of the main, if not the controlling factor, in the mechanism of soil removal by alkanol and alkylphenol-ethylene oxide adducts.

Anionic surfactants and sodium tripolyphosphate fail to exhibit effective fatty soil solubilization, hence their mechanism of soil removal appears to differ markedly from that of the ethylene oxide adducts tested.

As with fatty soil removal, the 10-molar ethylene oxide adducts appear at an optimum for solubilization though their degree of effectiveness also is dependent upon the hydrophobe.

Nonionic surfactants are most effective for solu-

bilization at near their cloud-points. No such maximum was found for the anionics.

Surfactant concentration increase causes greater fat solubilization but to a lesser degree than the effect of increase in temperature.

Sodium tripolyphosphate (which showed no solubilization), in combination with NaDDBS, increased solubilization of the mixture almost four-fold, attributable to a considerable increase in micelle aggregation size through builder addition.

Triolein was solubilized to a greater extent than was tristearin, attributable possibly to spatial configuration. Mixed micelles of tridecanol-10 EO and triolein less than 0.01 micron in diameter (60°C.) contained 14 surfactant moles for every triolein molecule.

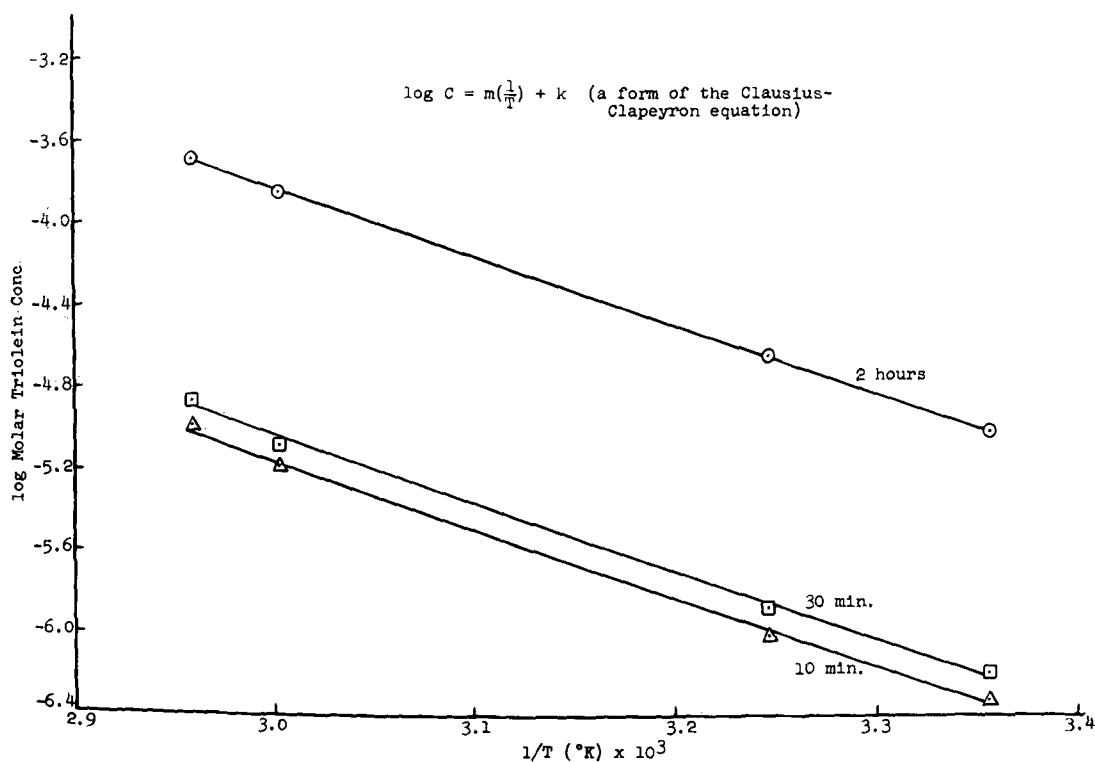


Fig. 7. Plot of  $\log_{10}$  triolein solubilization vs.  $1/T$  for tridecanol-10 EO at 0.25% concentration at various stirring times. (Data from Figure 6.)

Colloidal ion lengths of the anionic (20–25 Å) and nonionic (49–56 Å) surfactants may help to explain the ability of the latter to accommodate the length of triolein (26 Å), in addition to the nonionic aggregate size.

The heat of solubilization,  $\Delta H_s$ , for triolein in 0.25% solution of tridecanol-10 EO adduct, calculated by the Clausius-Clapeyron equation, was 15 kcal/mole. This was approximately 12 times greater than the adduct's heat of micellization,  $\Delta H_m$ , estimated at 1.3 kcal/mole from cmc data.

Solubilization of triolein by 0.25% tridecanol-10 EO increased linearly with triolein level up to the saturation point (0.044%) for equilibrium data at 60°C.

No attempt was made at correlation between solubilization, soil removal, and critical micelle concentration, reserving this for another presentation.

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## Analysis of Fat Acid Oxidation Products by Countercurrent Distribution Methods. V. Low-Temperature Decomposition of Methyl Linoleate Hydroperoxide

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Methyl *cis,trans* diene conjugated linoleate hydroperoxide isolated by countercurrent distribution from 4°C. autoxidation of methyl linoleate was stored in atmospheres of oxygen and of nitrogen at 4°C. in darkness. Besides manometric changes, infrared and ultraviolet characteristics, peroxide value, diene conjugation, and molecular weights were followed on samples removed at various periods of storage up to 53 days. These same analyses were obtained on fractions obtained by countercurrent distribution.

Evidence for the reaction that occurs on storage in oxygen may be summarized thus: 1 mole oxygen absorbed by linoleate hydroperoxides destroys 1 mole *cis,trans* diene conjugation, ½ mole peroxide group, and 1 mole linoleate hydroperoxide; dimers of varying polarities, scission acids, and isolated *trans* bonds are formed.

Since no volume changes were observed in the nitrogen storage of methyl linoleate hydroperoxide, changes in chemical and physical characteristics can only be related to time of storage. Storage in nitrogen at 4°C. destroys diene conjugation, peroxides, and linoleate hydroperoxide and produces dimers of varying polarities, scission acids, and isolated *trans* bonds. Destruction of diene conjugation was one-fourth as rapid in a nitrogen atmosphere as in oxygen. While differences in reactions and products were observed between oxygen and nitrogen storage, particularly in rates and in countercurrent distribution patterns, the similarity of products from oxygen and nitrogen storage is remarkable. Once methyl linoleate hydroperoxide is formed regardless of storage atmosphere, dimerization and attendant destruction of double bonds and peroxides proceed.

SEVERAL REVIEWS and original papers have been published on the autoxidation of methyl linoleate within the past 10 years (2,4–6,8,9). General agreement exists that methyl linoleate oxidizes to yield methyl *cis,trans* diene-conjugated linoleate hydroperoxide (MLHP) as the primary oxidation product.

Previous work at this laboratory concerned the autoxidation of methyl linoleate at low temperature (0°C.) to give mixtures of methyl linoleate, MLHP, and their reaction products. To interpret these results fully, it was necessary to study the decomposition of MLHP by itself and under comparable and controlled conditions. This paper therefore reports low-temperature decomposition of MLHP in atmospheres of oxygen and nitrogen.

### Experimental Procedures

MLHP formed by the 4°C. light-catalyzed autoxidation of 233 g. of methyl linoleate was separated from the parent methyl linoleate by large-scale countercurrent extraction (12). The isolated material (82 g.) was further purified by a 100-tube countercurrent distribution in the system 80% aqueous ethanol and pentane-hexane; the recovered MLHP had the chemical and physical constants given in Table I.

The reaction of MLHP with oxygen was studied at 4°C. Two simultaneous runs designated as A and B were made in manometric equipment, which consisted of a flask, approximately 25 ml. in size, sealed to a 50-ml. mercury-filled gas burette and equipped with magnetic stirrers. The side arm of flask A was closed with a rubber serum cap in order that samples could be periodically withdrawn by use of syr-

TABLE I  
Analysis of Methyl Linoleate Hydroperoxide

Absorptivity at 233 m $\mu$ .....	75.1
Absorptivity molar at 233 m $\mu$ .....	24,500
Molecular weight (cryoscopic-theory 326.47).....	321.6
Partition coefficient (80% EtOH-pet. ether).....	0.57
Elementary analysis (theory calculated for C <sub>19</sub> H <sub>34</sub> O <sub>4</sub> : C, 69.90; H, 10.50).....	{ C-69.09 H-10.30
Peroxide value (theory 6125 meq./kg.).....	5,253
Iodine value [after reduction of OOH group (Benham and Klee) theory 166.2].....	148.9

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<sup>2</sup> This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.