Film Drainage: A Study of the Flow Properties of Films of Solutions of Detergents and the Effect of Added Materials

G. D. MILES, JOHN ROSS, and L. SHEDLOVSKY, Colgate-Palmolive-Peet Company,
Jersey City, New Jersey

It has been shown previously that the drainage rates of foam appear to be a function of both bulk and surface viscosity (1). For some detergents the addition of several per cent (on a solids basis) of materials such as long chain alcohols or fatty acids produces a marked decrease in the drainage rate of foams made from the solutions. These effects seem to be due to an increase in surface viscosity. The influence of temperature on flow rates through foams has been shown (1) to vary considerably for different solutions. For example in the range from 20° to 30°C. there is a sharp increase in the flow rate for a solution of sodium salts of sulfated coconut oil monoglycerides where the surface viscosity is relatively high when compared to solutions of pure sodium lauryl sulfate. Both solutions contain sodium sulfate. Differences in flow characteristics through foam as a function of temperature for certain systems suggest that there is a very large change in surface viscosity in certain narrow temperature ranges.

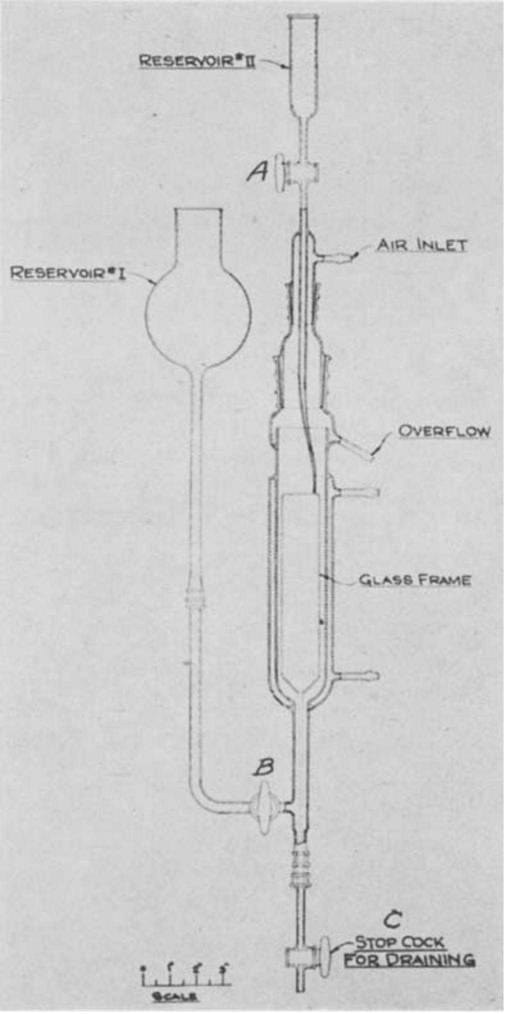

FIG. 1. Film drainage apparatus.

Film drainage measurements offer a means of observing films whose shape and dimensions are constant, regardless of the materials from which they are formed. Of course this is not true of foams where both the shape and size of the bubbles may vary considerably and alter the drainage characteristics for this reason. For example, for foams where the bubble size was uniform in each case (1), for two bubble sizes whose volume ratios were 6.5 to 1, the rates of flow of solution through the foam differed by as much as a ratio of 2.5 to 1.

Since film drainage rates appear to be a function of the surface viscosity, they could be used to give some information regarding the physical state of the surface. This is usually obtained from surface pressure vs. film area diagrams. The fluid, fast draining films correspond to a two dimensional "gas," and the slow draining films, to various "condensed" film types.

Experimental

Two forms of apparatus were used in this work. The first is shown in Figure 1. The procedure was as follows: Reservoirs I and II were filled with solution. Stopcock B was opened, and the film section filled until it overflowed and the surface was swept clean. B was closed and C opened so that the solution was drained until the top of the glass frame was reached. B was then adjusted so that a very slow flow through the film was maintained. C was opened again until the film was about 10 cm. long. The solution from Reservoir II was allowed to flow through the film in order to reach a steady state between the surfaces of the film and the bulk liquid. A was now closed, and the entire reservoir assembly turned so that the end of the capillary was removed from the frame. Observations on the film drainage were then started. These were made visually with the aid of a cathetometer, or photographically. For this purpose a red filter was attached to a camera loaded with panchromatic film. As soon as the first order colors appeared at the top of the film, the flow rate measurements were started. Flash pictures of the film were taken at suitable intervals with an S. M. flash bulb placed behind a light shield, not shown in Figure 1. Usually three or four pictures of each film were sufficient to obtain the necessary drainage data. If another determination on the same film was required, the only necessary operation was to wet the film again from Reservoir II.

The second apparatus to study film drainage consisted of a rectangular glass frame sealed in a test tube (Figure 2). The film was formed by taking slightly more than half a tube of solution and gently tilting the tube to a horizontal position and back to vertical several times, taking care to avoid forming large bubbles and foam. The film was illuminated by a fluorescent bulb and the colored bands observed

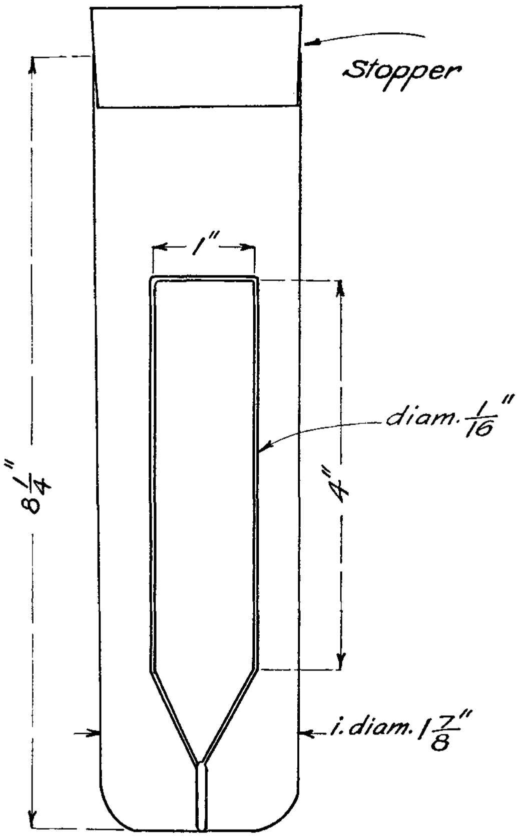

FIG. 2. Film drainage frame.

with a magnifying glass to follow the drainage characteristics. Dimensions of the apparatus have been made to fit in with the following conditions. When the tube is slightly more than half filled, the surface area of the liquid is the same whether the tube is in the vertical or horizontal position. In the horizontal position the surface area is only that of the bulk liquid since the frame is immersed. However in the vertical position the surface area is twice the area of the film held by the frame plus the area of the bulk liquid. This permits the formation of a film without much contraction or expansion of the surface area. However it should be noted that when the film changes from the horizontal to the vertical position, its surface undergoes some contraction and expansion.

When the surface viscosity of the film is low, horizontal interference bands of color appear at the top and descend rapidly over the film. In this case drainage is rapid and the whole fluid film is soon covered with a series of broad spectral bands and on subsequent drainage a "black film" is formed in the upper portion. Just below this the film appears silvery white. When the film is sufficiently stable, the "black film" eventually covers most of the frame. The thickness of this film has been estimated to be of the order of 50 to 100 Å and the second order violet 2160 Å thick. Each order of colored bands corresponds to an increase in thickness of about 2000 Å (2).

In addition to the observations with respect to the rate at which interference bands shift with time, there are other visible effects associated with the film drainage, especially when this is rapid. At the sides of the frame there appear to be regions of considerable turbulence. Here, instead of the orderly progression of horizontal colored bands which are characteristic of the central part of the film, colored portions stream and swirl upward and toward the center of the film in patterns resembling curled fern fronds. At first these colored areas shift very rapidly, but as the drainage proceeds, this movement diminishes both in speed as well as in the area which it covers until it is confined to a very small region adjacent to the edge of the glass frame. In this work our concern has been chiefly with the orderly progression of horizontal interference bands.

When the surface viscosity of the film is high, the rate of film drainage is so slow that very little motion in the film is noted. Changes in drainage at various temperatures were observed by submerging the tube up to the stopper in a heated water bath.

The solutions were prepared by warming a 3 to 5% solution of the detergent to about 80°C. The organic material was added and heating continued for several minutes, after which sufficient water was added to dilute to the concentration of detergent used (0.25%). The solution was then adjusted to the temperature of the test.

Results and Discussion

Several typical results of drainage rates are given in Table I. There is no apparent change in rate over a range of concentration of 0.05 to 0.5% for fast draining films. These data show that in general the drainage rate falls into two main categories: a) fast drainage rate which is the same for solutions of sodium salt of oleyl derivative of methyl taurine, containing sodium sulfate (Igepon T type product) I, sodium salts of sulfated coconut oil monoglycerides, containing sodium sulfate, II, (solids ether extracted), and sodium salts of mixed alcohol sulfates containing sodium sulfate (Gardinol type product), III, (solids ether extracted). The rates for sodium laurate and sodium oleate solutions are somewhat lower, and b) very slow drainage rates—1/70 to 1/350 of rate for a)—which are shown by solutions of II and III, (not ether extracted). Both of the samples in category b) show slow drainage due to the presence of an ether-soluble material which is selectively adsorbed and has

TABLE I

Rates of Film Drainage Obtained From Photographs

Material	Conc'n gms. per 100 cc.	°C.	Centimeters per minute for	
			1st order extinction band	2nd order extinction band
I. (Igepon T type)	0.05	26.5	3.6	6.7
	0.10	26.5	3.6	6.6
	0.25	26.5	3.6	6.3
	0.50	26.5	3.4	6.6
II. (Ether extracted)	0.20	27.0	3.3	6.8
II. (Not extracted)	0.20	27.0	0.01[a]	0.02
III. (Ether extracted)	0.25	27.0	3.3	6.5
III. (Not extracted)	0.20	28.0	0.015[a]	0.02
Sodium laurate	0.25	27.5	2.8	5.3
Sodium oleate	0.05	27.0	2.9	5.3
	0.20	27.0	2.8	5.4

[a] Values obtained visually.

I. Sodium salt of oleyl derivative of methyl taurine containing sodium sulfate.

II. Sodium salts of sulfated coconut oil monoglycerides, containing sodium sulfate.

III. Sodium salts of mixed alcohol sulfates containing sodium sulfate (Gardinol type product).

film properties characterized by high surface viscosity. For II this material consists mostly of small amounts of fatty acids and for III it is the presence of relatively small amounts of fatty alcohol.

The characteristic bands obtained for fast draining fluid films are shown in Figure 3, and the relatively slow draining type is shown in Figure 4. The positions of the bands at various time intervals are apparent.

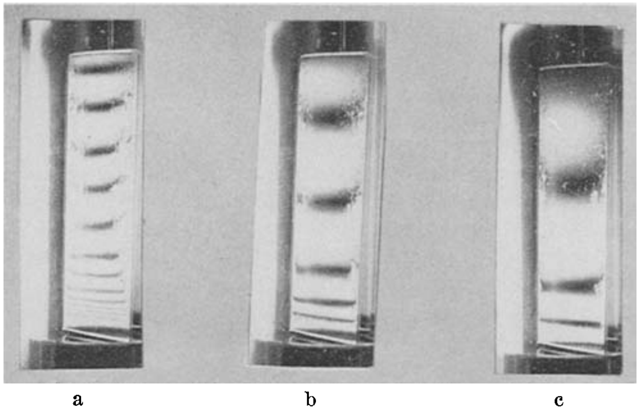

FIG. 3. Film drainage photograph, 0.25% coconut monoglyceride sulfate, containing sodium sulfate (II) (ether extracted).

(a) After 12 seconds
(b) After 41 seconds
(c) After 79 seconds

Table I characterizes the relative and typical drainage rates obtained quantitatively. Since it is not necessary to make quantitative rate measurements to show the large differences indicated by categories a) and b), qualitative observations have been made for various detergents in the presence and absence of added materials. These data are presented in Tables II, III, IV, and V.

Saponin solution (0.025%) gives a very slow draining film at 25°C., and this is typical of materials whose films have a high surface viscosity. For solutions of II, not extracted, (Tables I and III) very slow draining films are obtained at 25° and 30°C. This is due to the presence of fatty acids which increase the surface viscosity of the film.

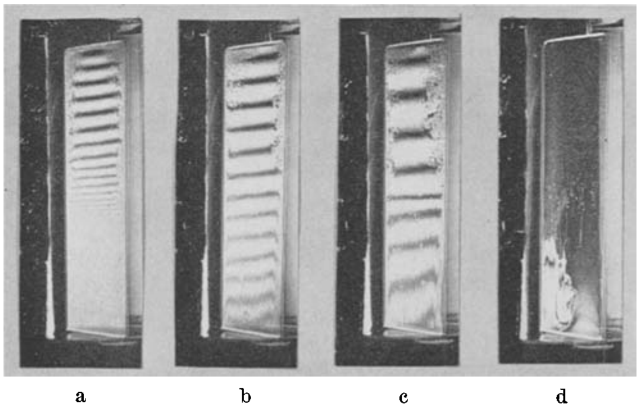

FIG. 4. Film drainage photograph, 0.25% solution of (II) (not extracted).

(a) After 30 seconds
(b) After 925 seconds
(c) After 2,250 seconds
(d) After 16 hours

The flow characteristics of films made from soap solutions would be expected to be determined by the hydrolysis products so that in general the concern is with a mixture of soap and fatty acid. Since the fatty acids with longer chains than lauric acid do not give two-dimensional "gaseous" types of films, the hydrolysis products of soap solutions would be expected to give very slow draining films. Among the fatty acids, for example, myristic acid at 25°C. has been shown to give an "intermediate liquid phase," and palmitic acid at 19°C., a "liquid condensed film" (3). Typical drainage data for tallow soap are given in Table III. A 0.2% solution (pH 10.1) gives stable and very slow draining films at 25° and 45°C., but when NaOH is added to pH 11 to repress hydrolysis, the films are much less stable and are still fluid even when cooled to 20°C. This difference in behavior between the two solutions can be attributed to the high surface viscosity due to the presence of higher saturated fatty acids in the film for the hydrolyzed solution (pH 10.1).

TABLE II
Film Drainage for Solutions of Pure Sodium Alcohol Sulfates With Lorol or Cetyl Alcohol Added

Solution	°C.	Drainage
0.25% sodium tridecane-2-sulfate (13-2)	25	F
0.25% sodium tridecane-2-sulfate (13-2)	35	F
	25	F
0.25% (13-2) + 2 drops/100 cc. lorol	20	V S D
0.125% sodium pentadecane-2-sulfate (15-2)	20	F[a]
0.125% (15-2) + 2 drops/100 cc. lorol	30	V S D
0.175% sodium pentadecane-2-sulfate (15-2) + 0.25% Na_2SO_4 + cetyl alcohol (10% solids basis)	25	F
0.04% sodium nonadecane-2-sulfate (19-2)	27	F
0.04% (19-2) + 2 drops/100 cc. lorol	25	V S D
Sodium nonadecane-10-sulfate (19-10)	25	F
(19-10) + 2 drops/100 cc. lorol	25	F
0.25% sodium tridecane-7-sulfate (13-7) +2 drops/100 cc. lorol	25	F
0.25% sodium pentadecane-4-sulfate (15-4) +2 drops/100 cc. lorol	22	F
0.25% sodium pentadecane-8-sulfate (15-8)	20	F
0.25% (15-8) + pentadecanol-8 (10% solids basis)	25	F[b]
0.25% sodium pentadecane-8-sulfate (15-8) +2 drops/100 cc. lorol	22	F

[a] Solution turbid.
[b] Very unstable film.
F. Fluid.
V S D. Very slow draining.

Solutions of sodium alcohol sulfates (Table II); sodium dodecane-1-sulfate (12-1); sodium tridecane-3-sulfate (13-2); and sodium nonadecane-2-sulfate (19-2) and III, ether extracted (a mixture of sodium primary alcohol sulfates) give fluid films which are changed to slow draining films by the addition of 10% (solids basis) of lorol. Lorol is a mixture of essentially lauryl, myristyl, and cetyl alcohols.

For the sodium alcohol sulfates such as sodium pentadecane-4-sulfate (15-4); sodium pentadecane-8-sulfate (15-8); and sodium nonadecane-10-sulfate (19-10) addition of lorol still gave fluid films. It appears that with the sulfate group further from the end of the chain than the beta position, addition of lorol does not make the film of the slow-draining type.

In the considering of the properties of materials necessary to give very slow-draining films, it has been noted previously that this is due largely to high surface viscosity since in most cases the bulk viscosities are very low.

First, the properties of the detergent used will determine the ultimate flow characteristics of the films when organic substances are added. For example, 2% cetyl alcohol added to 0.25% sodium lauryl sulfate will give a very slow-draining film whereas when it is added to 0.25% sodium alkyl aryl sulfonate, the film is fluid down to 20°C. Of the large number of various organic additives which had been tried, none were found effective for decreasing the rate of film drainage for solutions of sodium alkyl aryl sulfonate.

The addition of either lorol or cetyl alcohol to solutions of sodium-lauroyl-N-methyl taurine as well as to solutions of the sodium salt of coconut fatty acid isethionic ester (Table III) gives slow-draining films. However when cetyl alcohol is added to solutions of I, the films are fast draining at 23°C. The difference between the flow behavior of the first two mixtures and the mixtures with product I, may be attributed chiefly to the presence of the unsaturated oleyl group, which tends to prevent the formation of slow-draining films.

TABLE III

Film Drainage for Anionic Detergents + Organic Additives

Solutions	°C.	Drainage
0.25% (II). (See Table I)	25, 30	V S D
0.25% ether extracted (II). (See Table I)	30	F
0.25% (II) + 5% lauryl alcohol. (Solids basis)	30, 40	V S D
0.25% (II) + ethylene glycol monostearate	45	V S D
0.25% sodium salt of oleyl derivative of methyl taurine containing sodium sulfate (Igepon T type) (I)	23	F
0.25% (I) + 2% cetyl alcohol. (Solids basis)	23	F
0.2 gms. sodium-lauroyl-N-methyl taurine +0.05 gms. Na_2SO_4 per 100 cc.	27	F
0.2 gms. sodium-lauroyl-N-methyl taurine +0.05 gms. Na_2SO_4 per 100 cc. + 2 drops lorol/100 cc.	25	S D
0.2% tallow soap	45	V S D
(pH 10.1 very stable films)	25	V S D
0.2% tallow soap + 1 milliequivalent NaOH/100 cc. pH = 11 (very unstable films)	40, 35 20	F V S D

F. Fluid.
S D. Slow draining.
V S D. Very slow draining.

Ether-extracted III, which is a mixture of sodium primary alcohol sulfates in 0.25% solution, was used to study the effect of adding numerous organic materials on film drainage (Table IV.)

Saturated (octadecane) and unsaturated hydrocarbons (hexadecene and octadecene) do not form slow-draining films. Lorol, lauryl alcohol, hexadecanol, and octadecanol give very slow-draining films at 25° C., but lower primary alcohols such as octanol do not. Secondary alcohols, such as heptadecanol-2 and nonadecanol-2, and mixtures of secondary alcohols do not decrease the film drainage rates. Cyclic alcohols such as hydroabietic and lanolin alcohols are not effective in slowing down film drainage. Of the unsaturated straight chain alcohols, oleyl alcohol is ineffective, but elaidyl alcohol tends to slow down the film drainage rate.

Dihydric alcohols such as 1,2-dihydroxy-n-tetradecane and 1,2-dihydroxy-n-hexadecane give slow-draining films comparable to those obtained when cetyl alcohol is added.

TABLE IV

Film Drainage for 0.25% Solutions of Mixed Sodium Alcohol Sulfates Containing Sodium Sulfate (III) (Gardinol Type Product) (Ether Extracted) With Added Materials

% (Solids basis)	Material added	°C.	Drainage
10	Hydrocarbons		
	Saturated		
	Octadecane	15	F
	Unsaturated		
15	Hexadecene	22	F
15	Octadecene	20	F
	Alcohols, Monohydric		
	Primary, saturated		
10	Octanol	20	F
2	Cetyl alcohol	30	S D
	Secondary, saturated		
10	Heptadecanol-2	24	F
10	Nonadecanol-2	23	F
	Cyclic		
10	Cholesterol	20 15	F V S D
10	Hydroabietic alcohol	23	F
10	Lanolin alcohols	19	F
	Unsaturated		
2	Oleyl	35	F
10	Oleyl	30	F
10	Elaidyl	25	S D
	Alcohols, Dihydric		
10	1.2-dihydroxy tetradecane	17	S D
10	1.2-dihydroxy hexadecane	20	S D
10	Mixture alkyl, 1.2-diol	21	S D
	Esters of -N- primary alcohols		
30	Lorol acetate	21	F
30	Hexadecanol acetate	21	F
	Esters of hydroxy acids		
10	Methyl 12-hydroxy stearate	20	F
10	Methyl 9:10-dihydroxy stearate	20	F
10	Mixed methyl 9,10,12-trihydroxy stearate	20	F
	Esters of Glycol		
10	Ethylene glycol monostearate	50	F
10	Ethylene glycol monostearate	40	S D
10	Diethylene glycol monostearate	20	F
10	Trimethylene glycol monostearate	20	F
	Esters of Glycerol		
10	Glyceryl monomyristate (pure)	20 22	S D F
4	Glyceryl monopalmitate	18	S D
10	Glyceryl monostearate (pure)	23	F

F. Fluid.
S D. Slow draining.
V S D. Very slow draining.

Among the glycol monoesters, ethylene glycol monostearate was the most effective in slowing down the film drainage. When this was added, a slow-draining film was obtained at 40°C. The addition of glyceryl monomyristate and glyceryl monopalmitate decreases film drainage, but not very slow-draining films were obtained when the solutions were cooled to 20°C. or below.

TABLE V

Film Drainage for Solutions of Cationic Detergents

	°C.	Drainage
0.5%lauryl amine hydrochloride + 0.5% sodium chloride, pH 3.9	20	F
Above solution + 5% sodium myristate (at 0.10, 0.15, and 0.25%)	20	F
0.131% cetyl amine hydrochloride + 0.131%	20	V S D
NaCl + .013% sodium myristate	25	V S D
above	26	F

F. Fluid.
S D. Slow draining.
V S D. Very slow draining.

For cationic detergents the data in Table V shows that addition of sodium myristate, which is present in the hydrolyzed forms, to cetyl amine hydrochloride solution shows very slow-draining-films up to 25°C.

This effect is not obtained for lauryl amine hydrochloride plus sodium myristate. It was found that addition of sodium chloride stabilizes the films formed from these solutions.

Films of solutions of 0.25% sodium dodecyl sulfate are fluid even when the temperature is decreased to 20°C. The effect of adding long chain alcohols to this solution is to obtain slow-draining films. Differences among a series of added alcohols can be demonstrated by the transition temperatures. Typical values for these transitions are given in Table VI. It will be noted that these temperatures increase in going from dodecanol to hexadecanol, but the value for octadecanol is much lower than that for tetradecanol. Both the concentration of detergent and of the alcohol added have a significant effect on the transition temperature.

TABLE VI
Transition Temperatures From Slow-Draining to Fluid Films for Solutions of Sodium Dodecyl Sulfate

0.01% material added to 0.25% solution	Transition temperature °C.
Dodecanol	32
Tetradecanol	44
Hexadecanol	51
Octadecanol	40*
0.02% hexadecanol + 0.25% sodium dodecyl sulfate	52
0.02% hexadecanol + 0.50% sodium dodecyl sulfate	42

* Very unstable film.

These temperatures appear to be a function of surface adsorption and solubilization of the alcohol. For example, for 0.25% sodium dodecyl sulfate solution plus 0.02% hexadecanol, the transition temperature is 52°C. whereas for 0.50% solution of sodium dodecyl sulfate plus 0.02% hexadecanol the transition takes place at 42°C. The first solution (0.25%) corresponds to the critical concentration for micelle formation for sodium dodecyl sulfate, where solubilization begins. For 0.5% solution the solubilization of the alcohol would be greater and the surface adsorption would be less.

It has been shown before (1) that there is a very large change in surface viscosity in certain narrow temperature ranges. It was demonstrated that only very small differences in flow rates were shown at 40°C. for two detergent solutions. At 20°C., on the other hand, the flow rate for one of these solutions was about 2.4 times that of the other. In terms of transition temperatures this suggests that at 40°C. the films of the second solution had become fluid, but at 20°C. the films were very slow-draining.

We have seen that both the detergent and the added material determine the flow characteristics of the films formed so that film drainage is not necessarily retarded by adding a material which can form condensed films in the absence of detergent. For example, sodium alkyl aryl sulfonates plus cetyl alcohol do not give very slow-draining films. Several possible factors may be involved in film drainage. In general, the film characteristics are influenced by the composition of the film which in turn is determined by the relative adsorption of the constituents present in the solution. The relative composition of the film is usually different from that of the solutio [illegible] has been demonstrated previously in foam ad[illegible]on experiments that for mixtures of sodium [illegible]ol sulfates and added alcohols the alcohol can b[illegible]ctively adsorbed to a very high degree. This [illegible]s that the composition of such a film has a very much higher concentration of alcohol than the bulk solution, and this leads to slow drainage of the film if the alcohol is dodecanol or a higher member of this series, but there is no change from fluid flow if it is octanol (Table IV). Furthermore the adsorbed film shows flow characteristics determined not entirely by the properties of the added constituent (fatty alcohol, acid, etc.) nor by the detergent (the principal constituent) but by the mixture of the two.

The relative adsorption of the constituents in the film can also be considered to be a function of the solubilization of the organic compound which is added. Thus in several papers (4, 5) by G. D. Miles, L. Shedlovsky, J. Ross, and C. W. Jakob were reported the surface tension-concentration curves which indicate adsorption at air-liquid interfaces for solutions of sodium alkyl sulfates and sulfonates plus fatty alcohols for concentrations of detergent beyond the critical concentration for micelle formation. It was suggested that these data can be explained by considering the increased solubilization of the fatty alcohol and a corresponding decrease in adsorption of the alcohol. This indicates the possibility that the detergent should have some degree of solubilizing power on the organic compound added, but at the same time it should be available for adsorption at the air-liquid interface (film or foam). It is apparent that adsorption of the material added is essential before a surface effect on film drainage occurs. For the surface adsorption, the surface tension concentration and foam fractionation data are useful, but such data do not indicate the physical properties and flow characteristics of the films formed. For this purpose film or foam drainage data are required. Some of the differences between the last two types of experiments have been noted previously.

Conclusions

The effect of added materials on the flow properties of films of solutions of detergents is to show a decrease in their drainage rates and the formation of very slow burning films. This slow drainage is attributed to high surface viscosity, which is a function of both the detergent as well as the added material. When a slow-draining film is formed, a sufficient increase in temperature causes a change to a fluid type. Such transition temperatures are useful in characterizing the flow properties of various mixtures. These properties have been related to foam drainage. However an additional factor which affects the properties of foams is a variation in bubble size.

Methods are described for observing the flow characteristics of films made on rectangular glass frames. Drainage rates were followed from the movement of light interference bands, photographically or visually. Qualitative observations were made and the transition temperatures from slow draining to fluid films were estimated by slowly raising the temperature of the apparatus containing the film and solution. These temperatures are a function of the concentration of all the constituents in the solution.

In the following some preliminary indications of the structural characteristics for the detergents and additives [illegible]h tend to give fluid or very slow-draining films [illegible]ggested from the available data.

a) In [illegible]al it appears that aqueous solutions of pure deterge[illegible]e fluid films which show relatively fast-drainage rate.

b) Some detergents to which certain types of organic polar compounds are added give very slow-draining films. Such detergents generally contain a normal saturated hydrocarbon chain of at least 12 carbon atoms with a hydrophilic group in the terminal or in the beta position. Examples are soaps (sodium salts of long straight chain fatty acids), sodium normal primary alcohol sulfates as well as the sodium paraffin 2-ol sulfates.

c) The organic polar additives which tend to give slow-draining films have essentially similar hydrophobic structural characteristics to the detergents described in b) above. However they are relatively insoluble in water and in the presence of detergent may form non-gaseous (condensed) types of surface films which have high surface viscosity. Most of these additives however are probably solubilized by the detergent solution. It is postulated that the extent of solubilization should not be so great as to interfere with adsorption at the air-liquid interface (film or foam). Typical examples are fatty acids and long straight chain primary alcohols as well as 1,2-diols.

d) On the other hand, there are some types of detergents which apparently give fluid films when the above organic additives are present. In these cases the hydrophobic part of the detergent may have a highly branched chain, a cyclic structure, or unsaturated groups (cis form). Examples are sodium secondary alcohol sulfates where the sulfate group is further from the end of the chain than the beta position, sodium alkyl aryl sulfonates, and sodium salt of oleyl derivative of methyl taurine.

e) A variety of organic additives do not give slow-draining films when added to solutions of detergents described under b), and these additives have similar structural characteristics to the detergents described under d). When no polar group is present in the additive, the film remains fluid. Saturated and unsaturated hydrocarbons are typical examples. Cyclic alcohols (hydroabietic and lanolin alcohols) do not form slow draining films and among the unsaturated primary alcohols, oleyl alcohol has no effect, but elaidyl alcohol does tend to slow down film drainage. This again shows that unsaturated compounds (of the cis form) do not give slow-draining films.

REFERENCES

1. Miles, G. D., Shedlovsky, L., and Ross, J., J. Phys. Chem. *49*, 93-107 (1945).
2. Lawrence, A. S. C., Soap Films, G. Bell and Sons, London (1929), pp. 62-78, 137.
3. Harkins, W. D., in Alexander, J., Colloid Chemistry, Reinhold Publishing Corp., N. Y., 1944, Vol. 5, Chapter 2.
4. Miles, G. D., and Shedlovsky, L., J. Phys. Chem. *48*, 57 (1944); *49*, 71 (1945).
5. Shedlovsky, L., Ross, J., and Jakob, C. W., J. Colloid Science *4*, 25 (1949).

[Received December 20, 1949]

Isopropanol as a Solvent for Extraction of Cottonseed Oil* III. The Use of Recycling to Effect Solvent Economy[1]

W. D. HARRIS and J. W. HAYWARD, Department of Chemical Engineering,
A and M College of Texas, College Station, Texas

EXTRACTION of oil and other substances from cottonseed meats with isopropanol has been shown to produce a meal of superior nutritive value for swine as compared with the average meal obtained by hydraulic methods. When isopropanol was used to extract the oil, free gossypol in the meal was reduced to a safe level for consumption by single-stomached animals (1). Subsequent tests show that the meal may be safely fed to laying hens without lowering productivity or causing the stored eggs to become off-color.

Since isopropanol extracts gossypol and other compounds as well as oil from the meal, the extracted matter may contain as high as 10 to 15% non-oil material. This material includes significant quantities of carbohydrates, gossypol, and resinous substances related to gossypol in addition to the fatty acids, phosphatides, and sterols normally occurring in crude oil. In previous work a study of the phase relationships of oil and other substances in aqueous isopropanol has shown that the oil may be separated from the miscella substantially free of impurities (2). Liquid-liquid extraction principles may be used to improve the efficiency of this separation and prevent loss of oil with the impurities.

Although isopropanol has many advantages as a solvent for extraction of vegetable oils, it has several serious disadvantages. The latent heat of vaporization is nearly double that of hexane. In addition, it forms a constant boiling mixture with water at 91% by volume. To obtain higher concentrations, a special process, such as azeotropic distillation is required; therefore it is desirable to use 91% isopropanol for extractions. On the other hand, 91% isopropanol has a low solvent capacity for oil, and the miscella is limited to about 10% extractables. This requires a high solvent-to-meats ratio which, when combined with the high latent heat, causes steam requirements for the process to be high.

To reduce heat requirements, acetone was considered as a substitute for isopropanol and was tested in parallel extraction runs. Acetone has a low latent heat and can readily be concentrated by simple rectification. Its disadvantages are a considerably greater fire hazard, though not greater than hexane, and somewhat higher cost.

The primary objective of this work was to determine the advantages which might be obtained by cooling the miscella to separate a solvent phase from the oil and recycling this phase back through the rich end of the extractor. This principle has previously been tried with ethanol and mixtures of ethanol and isopropanol (3, 4). However it was desired to determine the effect of recycling on fresh solvent requirements and extraction efficiency as well as on the products, oil and meal.

Procedure

Examination of the solubility curves for isopropanol-water-cottonseed oil at 30°C. and 70°C. (Figure 1) shows a high increase in oil solubility with a concurrent temperature rise for 91% isopropanol.

---

* The research projects on "Isopropanol as a Solvent for Extraction of Cottonseed Oil" at A. & M. College of Texas are sponsored by the Texas Engineering Experiment Station and The Cotton Research Committee of Texas, College Station, Texas.

[1] Presented at the fall meeting, American Oil Chemists' Society, Oct. 31-Nov. 2, 1949, Chicago, Ill.