

Molecular Complex Formation in Aerosol Emulsions and Foams

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Synopsis—Previous studies in nonaerosol systems have shown that certain detergents, such as sodium lauryl sulfate, form molecular complexes with long chain alcohols or acids at air/water or oil/water interfaces. In the present investigation it has been shown that molecular complexes are also formed in aerosol emulsion systems. It was found that, in many cases, the addition of a long-chain alcohol to an aerosol emulsion system prepared with the triethanolamine salt of a fatty acid or sodium lauryl sulfate as the surfactant produced a marked increase in emulsion and foam stability and a decrease in foam drainage. In some cases foam viscosity was increased. These effects of the long-chain alcohols occur in nonaerosol and aerosol systems and are indicative of molecular complex formation.

INTRODUCTION

It has been known for a long time that combinations of certain surfactants produce unexpected effects in emulsion systems. The reason for this remained obscure for many years, and in many cases the causes are still unknown. However, the effect of combinations of surfactants and long-chain polar compounds, such as the fatty alcohols, has been shown to be due to the formation of molecular complexes between the surfactants and the alcohols. The study of these molecular complexes has clarified much of the phenomena observed with these combinations.

The investigation of molecular complexes was initiated in 1937 by Schulman and Rideal (1) with the discovery that sodium cetyl sulfate and cholesterol formed stable complexes at air/water interfaces. These complexes formed because of the attraction between the polar groups of

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the two compounds and the association between the hydrophobic portions of the molecules which resulted from the Van der Waal's forces of attraction. The strength of the complexes was found to be dependent upon the stereochemical configurations of the two interacting molecules (2). Sodium cetyl sulfate and cholesterol, cetyl alcohol, or elaidyl alcohol formed strong complexes. However, sodium cetyl sulfate and oleyl alcohol formed weak complexes because the *cis*-configuration of oleyl alcohol prevented a close association between the two molecules.

The effects of the complexes at oil/water interfaces in emulsion systems were found by Schulman and Cockbain (3) to be similar to those observed previously at air/water interfaces. Sodium cetyl sulfate alone or with oleyl alcohol gave poor emulsions of mineral oil in water, while combinations of sodium cetyl sulfate with cetyl alcohol or cholesterol gave good emulsions.

Studies of molecular complexes have also been carried out in connection with an investigation of the drainage rates of liquids through foams and the drainage properties of films from aqueous solutions. Miles *et al.* (4, 5) observed that the drainage rates of liquids through sodium lauryl sulfate foams were markedly decreased by the presence of lauryl alcohol. It was also noted that aqueous solutions containing combinations of sodium alkyl sulfates and cetyl alcohol gave slow draining films, while those with sodium alkyl sulfates alone or with oleyl alcohol gave fast draining films.

The slow draining property of the foams and films was attributed to a high surface viscosity which resulted from complex formation between the alkyl sulfates and alcohols. When the temperature of the slow draining films was increased, the film ultimately became fast draining at a specific temperature, called the film drainage transition temperature. The transition from slow to fast draining of the foams and films occurred at a temperature at which the molecules in the complex had sufficient thermal energy to overcome the bonding energies (6). Similar experiments were carried out on nonionic ethoxylated lauryl alcohols with lauryl or cetyl alcohol by Becher and Del Vecchio (7). These combinations also were found to give slow draining films.

The compositions of a number of molecular complexes have been determined. Epstein *et al.* (8) reported crystalline intermolecular products in which the sodium alkyl-sulfates and long-chain alcohols were combined in a mol ratio of 2:1. Kung and Goddard (9, 10) have also investigated the composition of complexes. Lithium, potassium, ammonium, and magnesium lauryl sulfates formed complexes in which the

sulfate/alcohol ratio was 1:1, while calcium and tetramethyl ammonium salts did not form complexes. Complexes between stearic acid and sodium stearate with mol ratios of acid to salt of 1:1, 3:2, and 2:1, respectively, were reported by Ryer (11), while other acid/soap complexes with ratios of 1:2 were found by John and McBain (12).

The investigation of molecular complexes in aerosol emulsions and foams appeared to be a promising field of study from both a fundamental and practical aspect. Aerosol systems offered a unique opportunity to study complex formation in both an emulsion system and a foam derived from the same emulsion system. Aerosol emulsions consist of dispersions of liquefied propellants in an aqueous phase. When these products are discharged, the liquefied propellants vaporize and produce a foam. From a practical point of view, the use of emulsion systems for formulating aerosol products is now well established, and the number of aerosol products formulated as emulsion systems is increasing each year. Aerosol foams are particularly useful for cosmetic and pharmaceutical applications. These applications vary widely, and so do the properties desired for the aerosol products. Some basic information on aerosol emulsions and foams is already available (13-22), but the present knowledge is relatively small compared to what remains to be learned about these systems. If molecular complexes formed in aerosol emulsions and foams, this could provide an additional method for varying the properties of the systems. This in turn could lead to new and more effective applications for aerosol products.

EXPERIMENTAL

Complex formation was judged by the effect of the alcohols on the properties of the aerosol emulsions and foams. The properties that were determined were as follows:

1. Emulsion viscosity
2. Emulsion stability
3. Foam stiffness
4. Foam drainage
5. Foam stability
6. Foam density
7. Type of discharge

All of the properties, except foam stability, are summarized in tables. As a result of the difficulty of attempting to assign a numerical value to foam stability, the foam stability properties of the systems are discussed in the body of the report and are not present in the tables.

The reasons for selecting the preceding properties and the methods used to determine them were as follows:

Emulsion Viscosity

An increase in the viscosity of the bulk phase when an alcohol is added to an aqueous surfactant solution is generally considered an indication of complex formation between the surfactant and alcohol (4). In the present study, samples were prepared in glass bottles for visual observation. The approximate viscosity of the emulsions was estimated by inverting the bottles slowly and noting the flow characteristics of the emulsions. The viscosity was rated "low" if it was close to that of water and "high" if the emulsion was very thick. Products with viscosities in between these two extremes were rated medium.

Emulsion Stability

Emulsion stability was judged visually by the time required for phase separation to occur after the samples had been hand shaken. The samples were emulsified by a modification of the Briggs intermittent method of emulsification (23). The samples were shaken 20 times by hand, allowed to stand overnight, and reshaken 20 times immediately before stability determination. Phase separation, or creaming, is a common method for judging emulsion stability, even though it does not necessarily indicate coalescence of the droplets and breaking of the emulsions (24). Becher (25) has pointed out that, although creaming does not represent actual breaking of the emulsion, creaming is favored by large droplet size, and this may be an indication of a process which will lead to demulsification. Schulman considered phase separation to be sufficiently valid for comparison purposes when all the samples were prepared in the same way (3). As mentioned previously, Schulman found that complex formation could cause a considerable increase in emulsion stability.

Foam Stiffness

Foam stiffness was determined with a Cherry-Burrell Curd Tension Meter as described in Reference 16. Foam stiffness values are reported in grams and indicate the relative resistance of a foam to deformation resulting from the downward penetration of a curd knife. Although it is difficult to place an exact physical interpretation upon foam stiffness, it is assumed to be an aspect of foam viscosity. Complex formation has been reported to increase the surface viscosity of foams, and in the present case an increase in foam stiffness resulting from the addition of a unionized polar compound was interpreted as an indication of complex formation

Stiffness values below about 30 indicate that the foams have low viscosity and are quite thin. Typical aerosol shaving lather foams have stiffness values ranging from about 50 to over 100.

Foam Drainage Rates

One of the most common indications of complex formation is the decrease in the rate of foam drainage that occurs with the addition of a polar compound to a surfactant solution. This is considered to be due to an increase in the viscosity of the liquid foam films, or laminae, that occurs with complex formation. Foam drainage rates were determined in the present work by discharging a known quantity of foam into a funnel and determining the amount of liquid that drained from the foam at various time intervals. With most series of foams, there were certain time intervals after discharge when the differences in drainage rates between the various foams were the most distinct. The comparative foam drainages that showed the greatest differences in the foams were selected. The time required for this varied with the different series of foams and is given in the tables.

Drainage from foams results from gravitational forces on the liquid films, which causes thinning of the foam laminae without rupture, or from rupture and collapse of the foam structure itself (26). Thus, the liquid which drains from a foam can have two different origins.

Foam Stability

Foam stability has two aspects, foam drainage and persistence of the foam. Thus, a foam may drain and become quite thin but may retain its structure. Foams also may collapse as a result of rupture of the foam structure. In the present study, comparative foam stabilities were judged visually by discharging a series of foams onto paper towels and noting the appearance of the foams after various time intervals. The rapidity with which the foam wet paper was an indication of the drainage, and the rate at which the foam collapsed was an indication of the stability of the foam structure. It was possible to line up a series of foams in order of their relative stabilities by this procedure, but it was not feasible to place any numerical value upon the stability.

Foam Density

Foam density was determined by weighing a known volume of the foam as soon after discharge as possible. The volume of the vessel used for density determinations was 350 cc.

Type of Discharge

The type of discharge of the products is indicated in the tables. Some of the products had a quiet discharge, while others had a noisy discharge. Some samples also discharged as liquids which subsequently expanded into foams. These products are described as having a liquid discharge. Others discharged a mixture of liquid and foam which also expanded into a foam. These are described as having a semiliquid discharge. The remaining products gave an immediate foam during discharge.

Microscopic Examination

Observations of the foam structures were made using a Bausch and Lomb Sterozoom microscope, Model BVB-73, equipped with a 10× paired widefield eyepiece and a power pod magnification of 3×. Approximate bubble sizes in the foams were determined using a micrometer disc (#31-16-08) which measured intervals of 0.001 in.

The fact must be stressed that the bubble sizes reported are approximate. Some of the cells appeared to be fairly round, while others were very irregular in shape. The dimensions given in the report indicate the largest dimension of a specific bubble. All of the foams had bubbles which varied considerably in size. The sizes of the smallest and the largest bubbles were determined in order to show the range of sizes. No attempt was made to determine the frequency of any particular size.

Microphotographs were obtained with a Spencer triocular single-stage microscope, manufactured by the American Optical Company. It was equipped with a 15× eyepiece and a 3.5 objective lens. The camera was focused through 10× eyepieces with 3.5 objectives. The pictures were taken with a MP-3 Polaroid Multipurpose Industrial View camera with a 4 × 5 film adapter, using surface illumination and a one second exposure.

Preparation of the Aerosol Emulsions

The anionic surfactants, sodium lauryl sulfate and the triethanolamine salts of lauric, myristic, palmitic, and stearic acids were used in the present studies. Although sodium lauryl sulfate is not suitable for packaging in metal aerosol containers as a result of its corrosive effect, it has been widely used in complex formation studies in nonaerosol systems; and much information was already available about combinations of sodium lauryl sulfate and the long-chain alcohols. The triethanolamine salts of the fatty acids are used extensively in aerosol products,

and an investigation of systems with these surfactants was particularly desirable from a practical viewpoint.

Emulsions containing the triethanolamine soaps were prepared as follows: The fatty acid was heated until it melted (about 60–70 °C). An equimolar quantity of triethanolamine was dissolved in the water, and the aqueous solution was heated to about the same temperature as that of the melted fatty acid. The hot aqueous solution was then added slowly with stirring to the fatty acid. After the addition was complete, the mixture was removed from the heat and allowed to cool to room temperature with stirring. When alcohols were included in the formulation, they were melted together with the fatty acid.

Aqueous solutions of sodium lauryl sulfate were prepared by dissolving the surfactant in water. When alcohols were included, they were melted, and the aqueous solution of sodium lauryl sulfate, heated to the same temperature as that of the alcohols, was added with stirring to the alcohols.

Concentrations of the Surfactants

The concentrations of the surfactants in the aqueous phase were chosen so that the stability of the emulsions and foams from the surfactants alone would be low. Thus, any effect of the alcohols upon the system would be noticeable. Sodium lauryl sulfate, triethanolamine laurate, and triethanolamine myristate were normally used at concentrations of 0.10 m in the aqueous phase. On a weight percent basis, this amounted to about a 3.5% solution for these compounds. The addition of sufficient alcohol to produce a 1:1 molar ratio with the surfactant increased the weight percent to about 4.5%, depending upon the molecular weight of the alcohol. When other concentrations are used, this is noted in the tables.

Triethanolamine palmitate and stearate normally were used at concentrations of 0.025 m in the aqueous phase. This gave solutions of slightly over 1% on a weight basis. The addition of sufficient alcohol to give a 1:1 molar ratio with the alcohol increased the weight percent of the surfactant-alcohol complex to slightly over 2%.

Composition of the Aerosol Emulsions

Unless otherwise indicated, all aerosol emulsions were prepared with a composition of 90% aqueous phase and 10% Freon-12/Freon-114* (40/60) propellant. In some cases other propellants were tested, and this is indicated in the tables.

* Freon is a registered trademark of E. I. du Pont de Nemours and Co., Wilmington, Del.

Materials

The materials used in the present study were obtained from the following sources:

Fatty Acids

Lauric acid, myristic acid, palmitic acid and stearic acid were obtained from the E. F. Drew Chemical Corp. These acids are marketed under the trade names of "Wecoline" 1295, "Wecoline" 1495, "Wecoline" 1695, and "Wecoline" 1892, respectively.

Alcohols

Lauryl alcohol ("Lorol" 11), cetyl alcohol ("Lorol" 24), and stearyl alcohol ("Lorol" 28) were obtained from the E. I. du Pont de Nemours and Co. Oleyl alcohol was supplied by Croda, Inc., myristyl alcohol by the Eastman Chemical Corp., and cholesterol by American Cholesterol Products.

Sodium Lauryl Sulfate

Sodium lauryl sulfate (Duponol* C) was obtained from the E. I. du Pont de Nemours and Co.

EXPERIMENTAL RESULTS

Sodium Lauryl Sulfate Systems

Variation in Alcohols

The addition of lauryl, myristyl, or cetyl alcohols to sodium lauryl sulfate systems increased emulsion viscosity and stability and decreased foam drainage. This is shown in Table I. Lauryl and myristyl alco-

* Duponol is a registered trademark of E. I. du Pont de Nemours & Co., Wilmington, Del.

Table I
Variation in Alcohols-Sodium Lauryl Sulfate Systems^a

Alcohol ^b	Emulsion Properties		Foam Properties			Type of Discharge
	Viscosity	Stability	Drainage (60 min)	Stiffness (g)	Density (g/cc)	
None	Low	<1 min	82	11	0.055	Quiet
Lauryl	Medium	>5 hr	0	40	0.064	Slightly noisy
Myristyl	Medium	>5 hr	0	38	0.068	Noisy
Cetyl	Low to medium	>5 hr	2	14	0.062	Quiet
Stearyl	Low	<5 min	71	12	0.071	Quiet
Oleyl	High	30-60 min	84	10	0.067	Quiet
Cholesterol	Low to medium	1-5 min	84	13	0.061	Quiet

^a Sodium lauryl sulfate concentration = 0.10 M.

^b Sodium lauryl sulfate/alcohol ratio (molar) = 1:1.

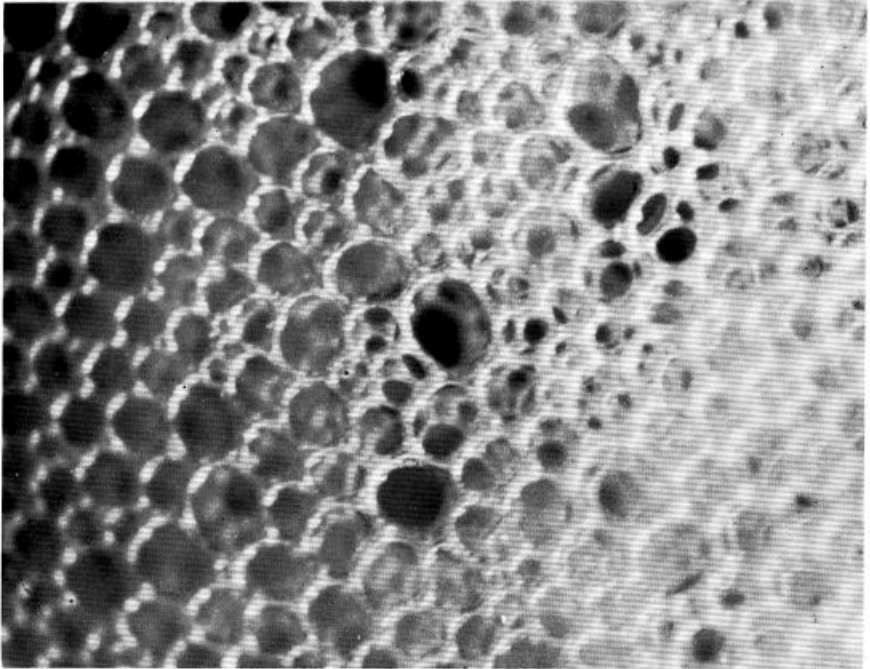


Figure 1. Photomicrograph of a sodium lauryl sulfate foam

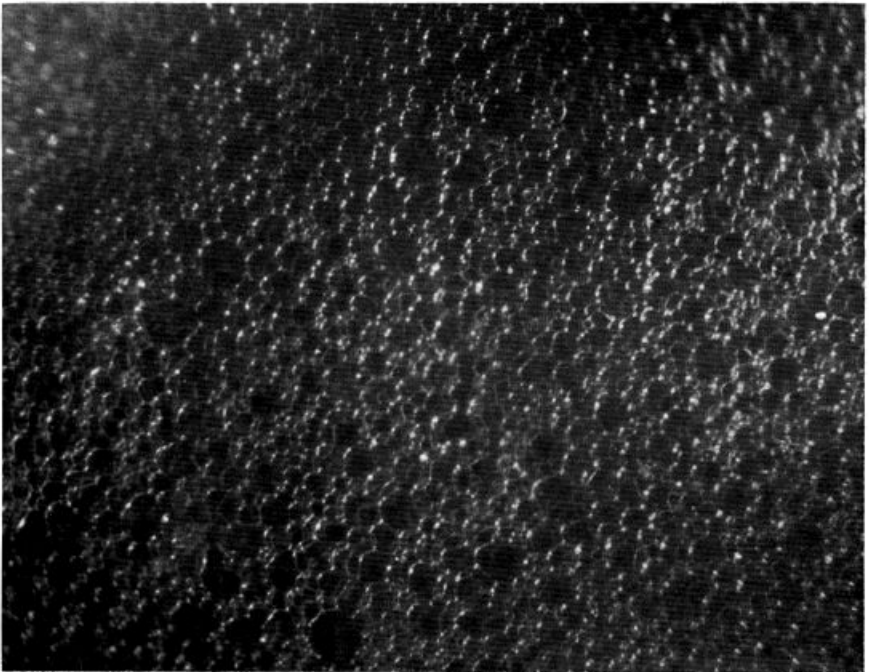


Figure 2. Photomicrograph of a sodium lauryl sulfate/lauryl alcohol foam

hols increased foam stiffness. Judging by these results, sodium lauryl sulfate forms complexes with these alcohols in the aerosol systems. Stearyl alcohol, oleyl alcohol, and cholesterol had little effect.

The effect of the alcohols upon foam stability was quite marked. Wetting results correlated well with drainage tests. Foams from sodium lauryl sulfate alone, or in combination with oleyl alcohol and cholesterol, caused immediate wetting, followed by that with stearyl alcohol. Foams with lauryl, myristyl, or cetyl alcohol did not wet for at least an hour.

The effect upon foam persistence was similar. The foam from sodium lauryl sulfate alone disappeared completely in 15 minutes, followed shortly thereafter by that with oleyl alcohol and cholesterol. The foam with stearyl alcohol was partially collapsed after one hour, while the remaining foams showed slight thinning but very little other change.

The effect of the alcohols upon wettability and foam persistence can be summarized as follows:

Foam wettability (in order of increasing wettability)

Lauryl alcohol	None
Myristyl alcohol < Stearyl alcohol < Oleyl alcohol	
Cetyl alcohol	Cholesterol

Foam persistence (in order of decreasing foam persistence)

Lauryl alcohol	
Myristyl alcohol > Stearyl alcohol > Oleyl alcohol > None	
Cetyl alcohol	Cholesterol

Microscopic observation of the sodium lauryl sulfate foams showed bubble sizes ranging from about 0.001 to 0.01 in., with laminae thicknesses of about 0.001 to 0.003 in. The foams with lauryl alcohol present had a smaller bubble size and thinner laminae. The differences between the two foams are illustrated very effectively by the microphotographs in Figs. 1 and 2. These pictures indicate that complex formation between sodium lauryl sulfate and lauryl alcohol decreases bubble size considerably.

Variation in Concentration of Lauryl Alcohol

Increasing the concentration of lauryl alcohol in sodium lauryl sulfate systems increased emulsion stability and decreased foam drainage, as shown in Table II. The samples that were used to obtain the data in Table II were also photographed four hours after they had been shaken

Table II
Variation in Concentration of Lauryl Alcohol in Sodium Lauryl Sulfate Systems

Sulfate ^a / Alcohol Ratio (molar)	Emulsion Properties		Foam Properties ^b		
	Viscosity	Stability	Drainage (60 min)	Stiffness (g)	Density (g/cc)
1:0	Low	<1 min	93	12	0.056
1:¼	Low	<1 min	33	34	0.059
1:½	Low	15–20 min	24	32	0.062
1:¾	Low	30–60 min	4	38	0.063
1:1	Medium	>16 hr	0	34	0.065

^a Sodium lauryl sulfate concentration = 0.10 *M*.

^b All systems had a quiet discharge.

so that the effect upon emulsion stability could be illustrated visually. This is shown in Fig. 3. The sample on the left in Fig. 3 contained no lauryl alcohol and showed complete phase separation. The remaining samples had increasing concentrations of lauryl alcohol, corresponding to the compositions given in Table II. The sample on the extreme right, which had the highest sulfate/alcohol ratio (1:1), showed no phase separation.



Figure 3. Comparative emulsion stabilities of sodium lauryl sulfate systems with increasing concentrations of lauryl alcohol (from left to right). The picture was taken four hours after the samples were shaken

An increase in foam stiffness occurred with the first addition of lauryl alcohol, but subsequent additions caused little change. There appeared to be a slight tendency towards increasing density with increasing lauryl alcohol concentrations.

Foams with sulfate/alcohol ratios up to 1:½ wet paper immediately, but the other foams with higher concentrations of alcohol did not wet

for an hour. The foam with no lauryl alcohol also collapsed soon after discharge, but the remainder of the foams retained their shapes for at least an hour. However, those that wet paper became quite thin on aging as a result of loss of liquid from drainage. In this series, as in many of the series to be discussed later, it is possible to select foams which wet and collapse, or which wet and retain their structure, or are quite stable.

Variation in Propellants

The effect of different propellants upon the properties of sodium lauryl sulfate/lauryl alcohol systems is shown in Table III. Freon-12 and Freon-12/Freon-114 (40/60) gave foams with the lowest drainage rates, and Propellant 152a and Propellant 142b gave foams with the highest. The former two propellants gave the stiffest foams and the latter two the lowest density foams.

Wettability data generally correlated with the foam drainage results. The foams with Propellant 152a and Propellant 142b wet paper within five minutes after discharge. The foams with the other propellants did not wet during at least one hour after discharge. The foam with Propellant 152a collapsed within 15 minutes and that with Propellant 142b collapsed within one hour. The other foams retained their shape.

Microscopic examination did not reveal any significant differences between foams formulated with Freon-12, Freon-12/Freon-114 (40/60), Freon-114, or Freon-12/Freon-11 (50/50). However, the foams with Propellant 142b or Propellant 152a had much larger laminae that

Table III
Variation in Propellant—Sodium Lauryl Sulfate^a/Lauryl Alcohol Systems^b

Propellant	Emulsion Properties		Foam Properties			Type of Discharge
	Viscosity	Stability	Drainage (2 hr)	Stiffness (g)	Density (g/cc)	
Freon-12	High	>5 hr	20	28	0.061	Slightly noisy
Freon-12/Freon-114 (40/60)	High	>5 hr	0	44	0.062	Quiet
Freon-114	High	>5 hr	0	48	0.073	Quiet
Freon-12/Freon-11 (50/50)	High	>5 hr	2	16	0.059	Noisy
Propellant 142b	High	>5 hr	41	16	0.043	Slightly noisy
Propellant 152a	Medium	>5 hr	84	14	0.039	Slightly noisy

^a Sodium lauryl sulfate concentration = 0.10 *M*.

^b Sulfate/alcohol ratio (molar) = 1:1.



Figure 4. Photomicrograph of a sodium lauryl sulfate/lauryl alcohol foam with Freon-12/Freon-114 (40/60) propellant

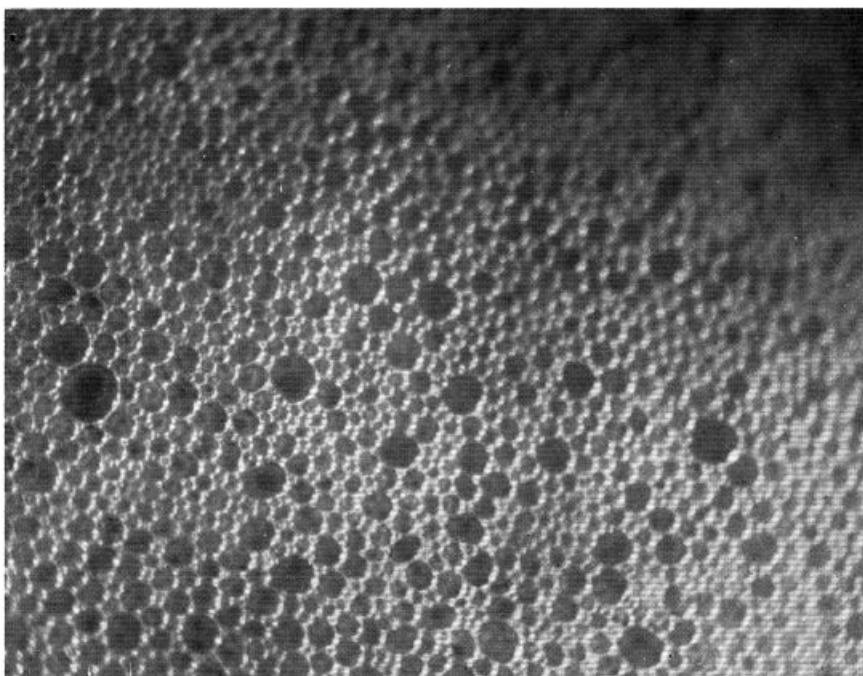


Figure 5. Photomicrograph of a sodium lauryl sulfate/lauryl alcohol foam with fluorocarbon 142b as the propellant

ranged in thickness from about 0.003 to 0.008 in., and the entire system appeared to be very fluid. The foams with the other propellants had a closer packed bubble structure with laminae approximating 0.001 in. in thickness. Microphotographs of the foams prepared with Freon-12/Freon-114 (40/60) and Propellant 142b are illustrated in Figs. 4 and 5. The photographs show the increase in foam bubble size that occurs with Propellant 142b.

The effect of the propellants in systems with sodium lauryl sulfate alone was also investigated. However, in all cases, the foams were very unstable, and no differences due to a variation in propellants were detected.

Triethanolamine-Fatty Acid Systems

Variation in Alcohols

The effect of various alcohols upon the properties of triethanolamine-fatty acid systems is shown in Tables IV, V, VI, and VII. Cholesterol was evaluated separately, and the effect of cholesterol, in comparison with that of the fatty alcohol corresponding to the fatty acid used, is shown in Table VIII. In all of the systems, certain alcohols caused a pronounced increase in emulsion viscosity and stability and a decrease in foam drainage. In these cases, molecular complex formation between the alcohols and the triethanolamine salts was judged to have taken place as a result of the effect of the alcohols upon the properties of the systems.

In each triethanolamine-fatty acid system, certain alcohols were more effective than others as far as complex formation with the triethanolamine salt was concerned. The data indicate that there is a slight tendency for the alcohols having about the same number of carbon atoms as that of the fatty acids involved to be the most effective for that particular system. Thus, lauryl alcohol was fairly effective in forming complexes with triethanolamine laurate but not with triethanolamine stearate. Likewise, stearyl alcohol forms strong complexes with triethanolamine stearate but not with triethanolamine laurate.

The over-all effects of the alcohols upon the various properties of the triethanolamine-fatty acid systems are summarized in Table IX. This summary should aid in the selection of a triethanolamine-fatty acid system with specific emulsion and foam properties. The effects of the various alcohols upon foam stability varied with the particular system involved, and each system will be discussed separately.

Table IV
Variation in Alcohols—Triethanolamine Laurate^a System

Alcohol ^b	Emulsion Properties		Foam Properties ^{c, d}	
	Viscosity	Stability	Drainage (30 min)	Stiffness (g)
None	Low	<1 min	82	8
Lauryl	Low to medium	>5 hr	2	20
Myristyl	Low to medium	>5 hr	0	33
Cetyl	Medium	>5 hr	0	18
Stearyl	Low to medium	>5 hr	67	10
Oleyl	Low	15–30 min	2	12

^a Triethanolamine laurate concentration = 0.10 *M*.

^b Soap/alcohol ratio (molar) = 1:1.

^c All discharges are quiet.

^d Foam densities range from 0.062 to 0.067 g/cc.

Table V
Variation in Alcohols—Triethanolamine Myristate^a Systems

Alcohol ^b	Emulsion Properties		Foam Properties ^c		Type of Discharge
	Viscosity	Stability	Drainage (2 hr)	Stiffness (g)	
None	Low	1–5 min	47	36	Quiet
Lauryl	Medium to high	>5 hr	0	48	Slightly noisy
Myristyl	Medium to high	>5 hr	0	48	Slightly noisy
Cetyl	Medium to high	>5 hr	0	28	Slightly noisy
Stearyl	Medium to high	>5 hr	4	26	Slightly noisy
Oleyl	Medium	>5 hr	3	22	Quiet

^a Triethanolamine myristate concentration = 0.10 *M*.

^b Myristate/alcohol ratio (molar) = 1:1.

^c Foam densities ranged from 0.067 to 0.073 g/cc.

Table VI
Variation in Alcohols—Triethanolamine Palmitate^a Systems

Alcohol ^b	Emulsion Properties		Foam Properties			Type of Discharge
	Viscosity	Stability	Drainage (60 min)	Stiffness (g)	Density (g/cc)	
None	Low	<1 min	33	25	0.09	Slightly noisy—liquid
Lauryl	Low	<1 min	27	20	0.14	Noisy—semiliquid
Myristyl	Medium	>24 hr	1	32	0.15	Noisy—liquid
Cetyl	Medium	>24 hr	5	34	0.18	Noisy—liquid
Stearyl	Medium	>24 hr	2	29	0.15	Noisy—liquid

^a Triethanolamine Palmitate concentration = 0.025 *M*.

^b Palmitate/alcohol ratio (molar) = 1:1.

Table VII
Variation in Alcohols—Triethanolamine Stearate^a Systems

Alcohol ^b	Emulsion Properties		Foam Properties			Type of Discharge
	Viscosity	Stability	Drainage (2 hr)	Stiffness (g)	Density (g/cc)	
None	Low	<1 min	53	14	0.19	Noisy—liquid
Lauryl	Low	5–15 min	52	8	0.21	Noisy—semi-liquid
Myristyl	Low to medium	>24 hr	0.5	32	0.17	Noisy—liquid
Cetyl	Medium	>24 hr	2	21	0.27	Noisy—liquid
Stearyl	Medium	>24 hr	4	15	0.33	Noisy—liquid

^a Triethanolamine Stearate concentration = 0.025 *M*.

^b Stearate/alcohol ratio (molar) = 1:1.

Table VIII
Effect of Cholesterol in Triethanolamine—Fatty Acid Systems

Fatty Acid ^a	Alcohol ^b	Emulsion Properties		Foam Properties			Type of Discharge
		Viscosity	Stability	Drainage (60 min)	Stiffness (g)	Density (g/cc)	
Lauric	None	Low	1–5 min	84	6	0.06	Quiet
Lauric	Lauryl	Low to medium	>24 hr	11	20	0.06	Quiet
Lauric	Cholesterol	Low to medium	>24 hr	36	3	0.08	Noisy
Myristic	None	Low	1–5 min	34	34	0.06	Quiet
Myristic	Myristyl	High	>24 hr	0	50	0.07	Noisy
Myristic	Cholesterol	Medium	>24 hr	5	17	0.10	Noisy
Palmitic	None	Low to medium	5–15 min	0	39	0.06	Quiet
Palmitic	Cetyl	High	>24 hr	0	42	0.09	Slightly noisy
Palmitic	Cholesterol	Medium	>24 hr	2	12	0.10	Slightly noisy
Stearic	None	Low to medium	5–15 min	0	30	0.11	Noisy—semi-liquid
Stearic	Stearyl	High	>24 hr	0	88	0.23	Noisy
Stearic	Cholesterol	Medium to high	>24 hr	2	16	0.12	Slightly noisy

^a Triethanolamine-fatty acid concentration = 0.10 *M*.

^b Soap/alcohol ratio (molar) = 1:1.

Triethanolamine Laurate Systems—Systems which caused the most rapid wetting generally had the highest drainage rates. In the triethanolamine laurate series, the foams from triethanolamine laurate or those with oleyl or stearyl alcohols wetted paper almost immediately after discharge. These foams also had the highest drainage rates. Foams with lauryl, myristyl, or cetyl alcohols did not wet paper for over an hour.

The effect of the alcohols upon foam persistence followed a somewhat similar pattern. The foams from triethanolamine laurate alone, or in combination with oleyl or stearyl alcohols, started to collapse within 30 minutes after discharge. Foams with lauryl, myristyl, or cetyl alcohols retained their structure for over an hour.

Triethanolamine Myristate Systems—All of the alcohols increased the stability of triethanolamine myristate foams. The foam from triethanolamine myristate wetted paper immediately, but none of the foams containing lauryl, myristyl, cetyl, stearyl, or oleyl alcohol wetted paper during one hour after discharge. These results correlate with the foam drainage results.

Although the foam from triethanolamine myristate alone showed rapid drainage, it maintained its structure for over an hour but became progressively thinner. The foams with lauryl and oleyl alcohols showed some thinning after 30 minutes. The most stable foams were obtained with myristyl, cetyl, and stearyl alcohols.

Triethanolamine Palmitate and Stearate Systems—Foams from triethanolamine palmitate or stearate also wetted paper immediately, followed by those that contained lauryl alcohol. It must be remembered that the triethanolamine palmitate and stearate systems have a soap concentration only one-fourth that of the laurate and myristate systems. The foams with myristyl, cetyl, or stearyl alcohols did not wet paper for at least two hours. Those wetting results again correlate well with the foam drainage data.

The foams from triethanolamine palmitate or stearate alone collapsed after about one hour; those with lauryl alcohol became increasingly thinner as a result of drainage but maintained their structures for at least two hours. Foams with myristyl, cetyl, or stearyl alcohols developed slight surface crazing during two hours but otherwise showed little change.

One of the most interesting effects of the alcohols in the triethanolamine palmitate or stearate series was upon the product discharge. All of the systems gave a liquid or semiliquid discharge which sub-

sequently expanded into a foam. However, the rate at which the product expanded into a foam after it had been discharged was a function of the chain length of the alcohol. For example, the discharge from triethanolamine stearate alone expanded almost immediately into a foam, and was followed by that with lauryl alcohol. The discharge

Table IX
Effect of Various Alcohols upon Properties of Triethanolamine-Fatty Acid Systems

Fatty Acid	Alcohol	Emulsion Properties		Foam Properties		
		Viscosity	Stability	Stability	Drainage	Stiffness
Lauric	Lauryl	x	xx	xx	--	x
	Myristyl	x	xx	xx	--	xx
	Cetyl	xx	xx	xx	--	x
	Stearyl	x	xx	o	o	o
	Oleyl	o	o	o	--	o
Myristic	Cholesterol	x	xx	-	-	o
	Lauryl	xx	xx	x	--	o
	Myristyl	xx	xx	xx	--	o
	Cetyl	xx	xx	xx	--	o
	Stearyl	x	xx	x	-	-
Palmitic	Oleyl	x	xx	x	o	-
	Cholesterol	xx	xx	-	-	-
	Lauryl	o	o	x	o	o
	Myristyl	xx	xx	xx	--	o
	Cetyl	xx	xx	xx	--	o
Stearic	Stearyl	xx	xx	xx	--	o
	Cholesterol	x	xx	-	o	-
	Lauryl	o	o	o	o	o
	Myristyl	x	xx	xx	--	?
	Cetyl	xx	xx	xx	--	o
	Stearyl	xx	xx	xx	--	o
	Cholesterol	xx	xx	-	o	-

x = Positive effect.

xx = Pronounced positive effect.

o = Essentially no effect.

- = Negative effect.

-- = Pronounced negative effect.

from the system containing myristyl alcohol required still more time to expand into a foam, and that with stearyl alcohol required almost five minutes for expansion into a foam. The rate at which the liquid discharges expand into a foam may be an indication of the relative strength of the molecular complexes. The strongest complexes might be expected to show the most resistance to expansion during vaporization of the propellant after the product had been discharged.

The foam density also increased in the triethanolamine stearate/

alcohol series as the molecular weight of the alcohol increased. Again, this effect may be related to the strength of the molecular complex.

Microscopic Examination—Microscopic examination of the triethanolamine laurate and triethanolamine laurate/lauryl alcohol foams did not reveal any marked differences, although the presence of lauryl alcohol appeared to cause a slight decrease in bubble size. However, the addition of cetyl alcohol to triethanolamine palmitate systems or the addition of stearyl alcohol to triethanolamine stearate foams caused a very noticeable decrease in bubble size. This effect of the molecular complexes upon the bubble size of the foams is similar to that noted with the sodium lauryl sulfate foams. The effect of stearyl alcohol in decreasing the bubble size of triethanolamine stearate foams is illustrated by the microphotographs in Figs. 6 and 7. These foams had the compositions described in Table VII.

The effect of cholesterol upon the bubble size of foams was opposite to that observed with the long-chain alcohols. Cholesterol caused a noticeable increase in bubble size. This is illustrated by the microphotographs in Figs. 8 and 9 of triethanolamine palmitate systems with and without cholesterol. The data in Table VIII also show that cholesterol decreased foam stiffness, which again is an effect opposite to that found with long-chain alcohols. These two effects, the increase in bubble size and the decrease in foam stiffness, suggest that the triethanolamine-fatty acid/cholesterol complex is very fluid, and during discharge the vaporization of the propellant into a gas expands the film more than when cholesterol is not present. This would explain both the increase in bubble size and the decrease in foam stiffness.

Variation in Alcohol Concentration

The effect of increasing concentrations of alcohol with triethanolamine laurate/lauryl alcohol and triethanolamine myristate/myristyl alcohol systems is shown in Tables X and XI. In the triethanolamine laurate system, increasing concentrations of lauryl alcohol caused an increase in emulsion stability and a decrease in foam drainage. There was a slight tendency toward increasing foam stiffness.

Increasing lauryl alcohol concentration also increased foam stability. The foams with no lauryl alcohol or with a soap/lauryl alcohol ratio of 1:¼ wetted paper immediately after discharge. That with a soap/alcohol ratio of 1:½ wetted paper in about 25 minutes, and the foam with a soap/alcohol ratio of 1:¾ wetted in about an hour. These results correlated essentially with the foam drainage results.

Table X
Variation in Lauryl Alcohol Concentration-Triethanolamine Laurate Systems

Laurate ^a /Lauryl Alcohol Ratio (Mols)	Emulsion Properties		Foam Properties ^{b,c}	
	Viscosity	Stability	Drainage (60 min)	Stiffness (g)
1:0	Low	1-5 min	86.0	8
1:¼	Low	30-60 min	83.0	10
1:½	Low	>60 min	65.0	16
1:¾	Low	>16 hr	40.0	18
1:1	Low to medium	>16 hr	11.0	22

^a Triethanolamine laurate concentration = 0.10 *M*.

^b All discharges were quiet.

^c All foam densities ranged from 0.062 to 0.063 g/cc.

Table XI
Variation in Myristyl Alcohol Concentration-Triethanolamine Myristate Systems

Myristate ^a /Alcohol Ratio (Mols)	Emulsion Properties		Foam Properties ^b		
	Viscosity	Stability	Drainage (3 hr)	Stiffness (g)	Type of Discharge
1:0	Low	15-30 min	56	42	Quiet
1:¼	Low	>5 hr	2	45	Quiet
1:½	High	>5 hr	1	42	Slightly noisy
1:¾	High	>5 hr	0	52	Noisy
1:1	High	>5 hr	0	56	Noisy

^a Triethanolamine myristate concentration = 0.10 *M*.

^b Foam densities ranged from 0.064 to 0.069 g/cc.

Table XII
Variation in Propellant-Triethanolamine Laurate/Lauryl Alcohol Systems

Propellant	Emulsion Properties		Foam Properties			
	Viscosity	Stability	Drainage (60 min)	Stiffness (g)	Density (g/cc)	Type of Discharge
Freon-12	Low to medium	>5 hr	4	18	0.052	Quiet
Freon-12/Freon-114 (40/60)	Low to medium	>5 hr	4	21	0.065	Quiet
Freon-114	Low to medium	>5 hr	2	26	0.067	Quiet—semi-liquid
Freon-12/Freon-11 (50/50)	Low to medium	>5 hr	44	8	0.053	Quiet
Propellant 142b	Low	>5 hr	65	12	0.042	Noisy
Propellant 152a	Low to medium	>5 hr	3	14	0.036	Noisy

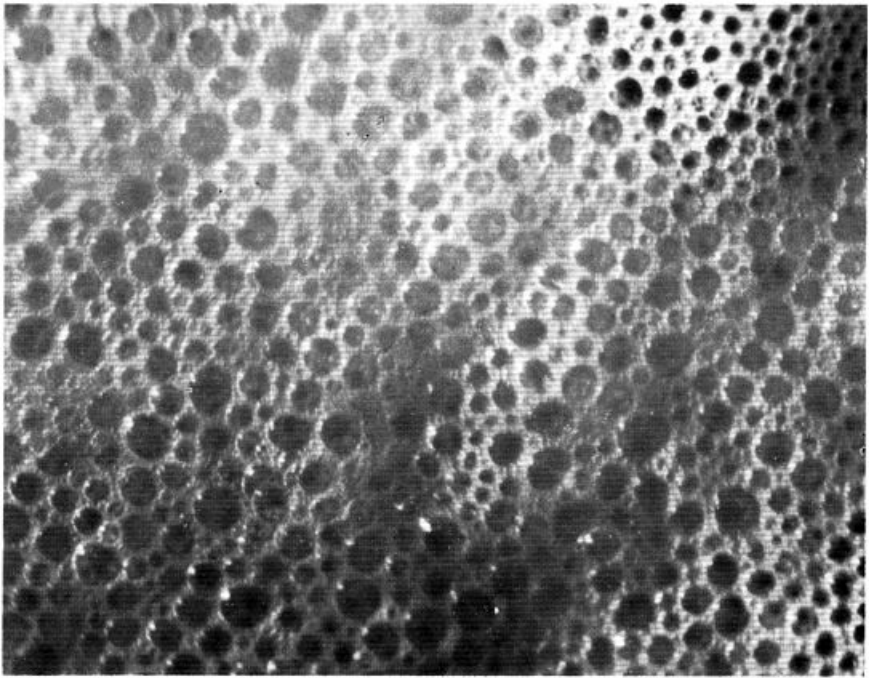


Figure 6. Photomicrograph of a triethanolamine stearate foam

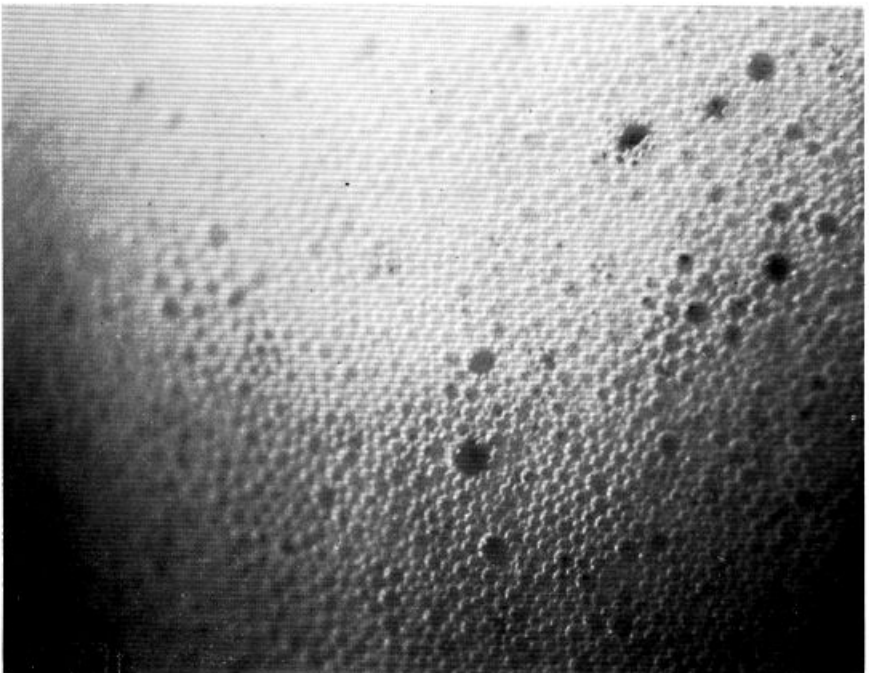


Figure 7. Photomicrograph of a triethanolamine stearate/stearyl alcohol foam

The same order occurred with foam persistence. The foam with no alcohol disappeared in about 30 minutes, and that with a soap/alcohol ratio of 1:¼ disappeared in one hour. The remainder became thin but retained most of their structure for over an hour.

In the triethanolamine myristate/myristyl alcohol series, the first increment of myristyl alcohol had a pronounced effect upon emulsion stability, foam drainage, and foam stability but subsequent additions of myristyl alcohol had much less effect. The foam with no myristyl alcohol wetted paper in about 25 minutes, while those with myristyl alcohol did not wet paper in an hour.

After two hours, the triethanolamine myristate foam had disappeared; but the remaining foams maintained most of their structure although the foams with the lower concentrations of alcohol became very thin.

Variation in Propellant

The effect of variation in propellants upon the properties of triethanolamine laurate/lauryl alcohol systems is shown in Table XII. All of the emulsions were quite stable, and differences in emulsion stability due to propellant variations were not detected. Freon-12/Freon-11 (50/50) and Propellant 142b gave the most rapidly draining foams, and Propellant 142b and Propellant 152a gave foams with the lowest density.

The foams with Freon-12/Freon-11 (50/50) propellant and Propellant 142b wet paper immediately after discharge, while foams with the other propellants did not wet during an hour after discharge. These results therefore correlate with the foam drainage data.

The foams with Freon-12/Freon-11 (50/50), Propellant 142b and Propellant 152a collapsed almost completely within 30 minutes after discharge. Those with Freon-12, Freon-12/Freon-114 (40/60), or Freon-114, retained their structure for over an hour after discharge, although they showed surface decomposition and thinning.

Variation in Soap/Alcohol Concentration

The properties of triethanolamine laurate/lauryl alcohol and triethanolamine myristate/myristyl alcohol systems at concentrations of 0.025 and 0.100 *M* in the aqueous phase are shown in Table XIII. Increasing the soap/alcohol concentration in the triethanolamine laurate/lauryl alcohol system increased emulsion viscosity and emulsion stability but decreased the rate of foam drainage. Foams at both concentrations showed some thinning after two hours but retained their shapes.



Figure 8. Photomicrograph of a triethanolamine palmitate foam

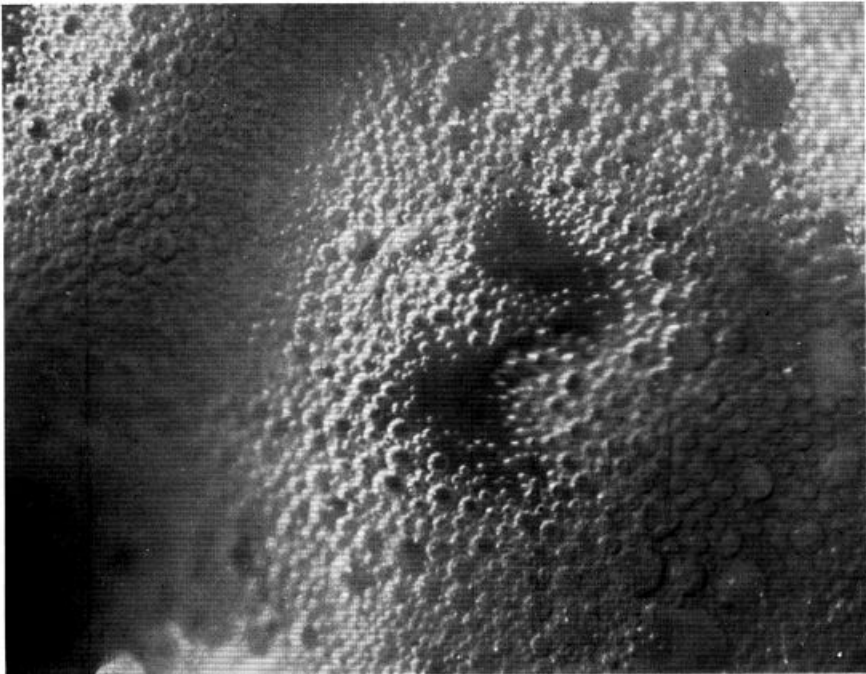


Figure 9. Photomicrograph of a triethanolamine palmitate/cholesterol foam

Increasing the concentration of the triethanolamine myristate/myristyl alcohol complex increased emulsion viscosity, emulsion stability, and foam stiffness. The foams with either soap/alcohol concentration were fairly stable and, except for a slight surface crazing, changed very little in two hours.

Variation in Fatty Acid/Triethanolamine Ratio

Free fatty acids are normally present in solutions of the salts of fatty acids as a result of hydrolysis. These free fatty acids have been reported to form molecular complexes with the salts under certain circumstances. As previously mentioned, sodium stearate and stearic acid have been shown to form such complexes. The triethanolamine salts of the fatty acids, which are salts of weak bases and weak acids, would also hydrolyze to form free fatty acids. Complexes between the free fatty acids and the triethanolamine salts might be formed in the aerosol systems.

It was hoped to obtain evidence for the existence of such complexes in the triethanolamine-fatty acid systems by changing the concentration of free fatty acid. Samples were prepared in which the ratios of fatty acid to triethanolamine were 1:1.5 and 1.5:1. In the first system, there was an excess of the triethanolamine, and in the second system there was an excess of the fatty acid. If the aerosol system containing the higher concentration of fatty acid exhibited the usual properties

Table XIII
Effect of Variations in Soap Alcohol Concentrations^a

	Salt Concentration in Aqueous Phase	
	0.025 <i>M</i>	0.100 <i>M</i>
Triethanolamine Laurate/Lauryl Alcohol		
Emulsion viscosity	Low	Low to medium
Emulsion stability	<1 min	>5 hr
Foam drainage (60 min)	20	6
Foam stiffness (g)	20	20
Type of discharge	Quiet	Quiet
Density (g/cc)	0.06	0.06
Triethanolamine Myristate/Myristyl Alcohol		
Emulsion viscosity	Low	High
Emulsion stability	1-5 min	>5 hr
Foam drainage (60 min)	2	0
Foam stiffness (g)	24	56
Type of discharge	Liquid—noisy	Noisy
Density (g/cc)	0.13	0.07

^a Soap/alcohol ratio (molar) = 1:1.

associated with complex formation, this would be considered evidence for the formation of the complexes.

The data obtained with lauric, myristic, and palmitic acids in combination with triethanolamine are given in Table XIV. In the triethanolamine laurate system, the addition of excess lauric acid had essentially no effect upon the properties of the system. There also was little effect upon foam stability. Foams from both mixtures wetted paper almost immediately after discharge and started to collapse. These results indicated that molecular complex formation was negligible in the triethanolamine laurate systems.

The addition of excess myristic acid to the triethanolamine myristate system had a noticeable effect upon the properties, however. Emulsion viscosity, emulsion stability, and foam stiffness increased, and the rate of drainage decreased. Foam stability was affected similarly. The foam with an excess of triethanolamine started to wet paper within 10 minutes, became very thin, and started to collapse. The foam with an excess of myristic acid showed little change after an hour. This effect of myristic acid upon the properties of the triethanolamine myristate system are typical of complex formation.

In the triethanolamine palmitate system, excess fatty acid resulted in an increase in emulsion stability and in foam stiffness. The rate of drainage was low regardless of the acid/base ratio, and the foam stability was high. Foams with both acid/base ratios showed little change after two hours. It seems likely that strong molecular complexes between palmitic acid and triethanolamine palmitate were formed, regardless of the acid/base ratio.

Table XIV
Variation in Fatty Acid/Triethanolamine Ratio

Acid	Acid/Base Ratio (Mols)	Emulsion Properties		Foam Properties ^{c,d}	
		Viscosity	Stability	Drainage (60 min)	Stiffness (g)
Lauric	1:1½ ^a	Low	<1 min	85	9
	1:1½ ^b	Low	<1 min	86	10
Myristic	1:1½ ^a	Low	<1 min	71	21
	1½:1 ^b	Low to medium	>1 hr	5	37
Palmitic	1:1½ ^a	Low to medium	15-30 min	0	23
	1½:1 ^b	Low to medium	>1 hr	0	42

^a 1:1½ ratio = 0.10 M acid/0.15 M base.

^b 1½:1 ratio = 0.15 M acid/0.10 M base.

^c All discharges are quiet.

^d All densities range from 0.060 to 0.069 g/cc.

DISCUSSION OF RESULTS

The addition of many of the long-chain alcohols to aerosol emulsions based either on sodium lauryl sulfate or the triethanolamine salts of the fatty acids has a pronounced effect upon such properties as emulsion viscosity and stability and foam drainage, stiffness, and stability. These effects are similar to those observed previously in nonaerosol systems and indicate that complex formation occurs between the surfactants and the alcohols in the aerosol systems. The aerosol systems used for the study were relatively simple. In aerosol products, where there may be many more ingredients, the effects of the added alcohols might be modified by the other components present, particularly if they were surface active.

The molecular complexes generally had an observable effect on the properties of both the aerosol emulsions and the resulting foams. Complex formation, therefore, occurred initially at the propellant/water interface in the aerosol emulsions and subsequently influenced the properties of the foams when the emulsion was discharged. Complex formation probably occurred in the bulk phase of the emulsion by solubilization of some of the alcohol molecules in the surfactant micelles as well as at the propellant/water interface.

The wetting properties of the foams on paper correlated well with the drainage rates and, in many cases, with foam persistence. The effect of the complexes in decreasing foam drainage was very marked and was consistent with the results reported on the effect of molecular complexes in nonaerosol foams. The effect of the complexes in decreasing foam drainage is considered to result from an increase in surface viscosity. In the present work, there were many cases in which an obvious decrease in foam drainage and an increase in foam stiffness could be interpreted on the basis of complex formation. In other cases, a decrease in foam drainage occurred, but there was no apparent increase in foam stiffness. It is probable that the foam stiffness measurements are much less sensitive than drainage tests and do not show increases in foam viscosity unless the increase is fairly large.

Cholesterol had little effect upon the properties of sodium lauryl sulfate systems and apparently did not form strong complexes with sodium lauryl sulfate in aerosol systems. Previous work indicated that cholesterol did form complexes with sodium alkyl sulfates in nonaerosol systems.

In triethanolamine palmitate and stearate systems, cholesterol increased foam drainage slightly and decreased foam stiffness. It also

increased the bubble size of the foams. It is possible that these effects, which are opposite those of the long-chain alcohols, are due to the formation of liquid complexes with cholesterol. Previous work showed that cholesterol formed liquid complexes with sodium cetyl sulfate, while cetyl alcohol formed solid complexes (3). The addition of cholesterol to the triethanolamine-fatty acid systems may have resulted in the formation of a film which had a lower viscosity than that of the triethanolamine salt-fatty acid complex. This would produce a foam with lower stiffness. The increased bubble size would also account for the slight increase in the drainage. Miles and his co-workers showed that the flow of liquids through foams decreased with a decrease in bubble size in the foam (4). The increased bubble size resulting from the presence of cholesterol might be accounted for by the increased fluidity of the liquid films. Such films would be expected to expand more during discharge of the product and subsequent vaporization of the propellant than more solid films. The greater expansion should produce large bubble sizes.

Another interesting effect that occurred with the addition of many alcohols was the change from a quiet discharge to a noisy, sputtery discharge. There probably are a number of factors involved in this effect. If combinations of alcohols and surfactants form strong, solid complexes at the propellant/water interface in the emulsion, these complexes might resist expansion when the product was discharged and the propellant vaporized into a gas. The fact that triethanolamine palmitate or stearate emulsions also gave noisy discharges without any alcohols present is an indication that fairly strong complexes between the free fatty acid and the triethanolamine soap are formed in these systems.

Another factor may be the droplet size of the dispersed propellant in the aerosol emulsion or possibly the uniformity of the droplet size. Emulsions containing large-size droplets might produce a noisier discharge than those with smaller droplets. There is no direct evidence for this, but a larger droplet size might explain why some of the cholesterol emulsions gave noisy discharges and also why some propellants gave a product with a noisier discharge than other propellants.

SUMMARY AND CONCLUSIONS

The effect of various alcohols upon the properties of aerosol emulsions and foams was studied to determine if the alcohols formed molecular complexes with the surfactants. In many cases, the addition of an

alcohol had a marked effect upon the aerosol system. Emulsion viscosity and stability were increased, foam drainage was decreased, and foam stability was increased. Foam stiffness was increased in some systems. On the basis of these results, it was concluded that molecular complexes were formed in aerosol systems. The effect of these complexes upon the properties of the systems was similar in many respects to that previously reported with nonaerosol systems.

The use of molecular complexes is an effective method for varying the properties of aerosol foams. By the proper choice of surfactant, alcohol, and propellant, foams may be obtained which wet immediately after discharge and then collapse or which wet immediately but retain their foam structure. Foams may also be obtained which are quite stable and show no wetting or collapse for extended periods. Aerosol emulsions can be formulated to give an immediate foam discharge or a liquid discharge which subsequently expands into a foam.

The aerosol emulsions were prepared with sodium lauryl sulfate or the triethanolamine salts of lauric, myristic, palmitic, and stearic acid as the surfactants and fluorinated hydrocarbon propellants as the dispersed phase. The effect of alcohols upon the emulsions and foams was studied with lauryl, myristyl, cetyl, stearyl and oleyl alcohols and cholesterol.

The extent to which any alcohol affected the properties of a specific aerosol emulsion or foam depended upon such factors as the type and concentration of the alcohol, the surfactant, and the propellant. The saturated fatty alcohols formed complexes in both sodium lauryl sulfate and triethanolamine-fatty acid systems. Microscopic observation showed that complex formation usually reduced the bubble size of the foams. In some instances, the addition of an alcohol resulted in a product which had a noisy or sputtery discharge. This was attributed to the formation of a solid molecular complex which resisted expansion when the liquefied propellant vaporized during discharge.

Cholesterol had little effect in sodium lauryl sulfate systems but formed fluid complexes in the triethanolamine-fatty acid systems. These complexes expanded easily during discharge, and this increased bubble size and decreased foam stiffness. Oleyl alcohol likewise had little effect in sodium lauryl sulfate systems but appeared to form weak complexes in some of the triethanolamine-fatty acid emulsions.

The type of propellant had a considerable influence on the properties of surfactant/alcohol systems. In general, the most stable emulsions and foams were obtained with Freon-12, Freon-12/Freon-114 (40/60)

or Freon-114. Freon-12/Freon-11 (50/50), Propellant 142b, and Propellant 152a gave less stable foams. The latter two propellants gave foams with the lowest density.

Triethanolamine-fatty acid systems with an excess of fatty acid were investigated to a limited extent. The data indicate that fatty acids also form complexes with the triethanolamine salts.

The results of the present study show that molecular complex formation can vary the properties of aerosol emulsions and foams over a wide range. These data were obtained with simple aerosol systems. The extent to which the present findings can be applied to modify the properties of practical aerosol products remains to be determined. Possible applications include the formulation of more heat stable foams, resulting from a potentially higher film drainage temperature with the foams containing molecular complexes, and the preparation of aerosol emulsion systems with powder suspensions. The increased viscosity of the aerosol emulsion systems with molecular complexes might retard settling and agglomeration of the powder sufficiently so that a practical product could be obtained.

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