arrangement since only such disaturated components give $\beta$-3 in the pure state (9) and since $\beta$-2 has been observed for nearly pure 2-oleyl samples (12); in addition $\beta$-2 has been observed for 50-50 binary mixes of disaturated glycerides (12) only when one component was a 2-oleyl glyceride but the other a 1-oleyl compound.

While agreeing with the general conclusion of Kartha (5) (and Hilditch) that animal fats are not randomly arranged, present results as shown in Table VI do not agree entirely with his conclusions that in animal fats $S_3$ is less and $S_2U$ is more than the corresponding "chance value."

The nature of the evidence presented is not such as to establish within extremely close limits the glyceride composition of the various fats, but it does indicate:

a) that animal fats are non-random in their fatty acid distribution.

b) that tallows differ sharply from lard in fatty acid distribution; the latter definitely is composed largely of 2-palmityl glycerides, the former probably of 1-palmityl glycerides.

c) for a given animal fat there is considerable constancy of palmityl position throughout its $S_3$, $S_2U$, and $SU_2$ glycerides.

## Summary

In agreement with comments of Hilditch but in contrast with certain other statements in the literature it is concluded that lard, beef tallow, and mutton tallow are non-random in distribution of fatty acid chains among their glycerides. From thermal and x-ray diffraction techniques applied to $S_3$, $S_2U$, $SU_2$, and $U_3$ fractions of these fats and to the various products of complete hydrogenation it is concluded that lard is composed largely of 2-palmityl glycerides as proposed by Hilditch while the tallows are composed largely of 1-palmityl glycerides.

## Acknowledgment

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### REFERENCES

1. Hilditch, T. P., "The Chemical Constitution of Natural Fats," 2nd Ed., John Wiley and Sons Inc., N. Y. (1947). Chapter VI, pp. 231-287.
2. Doerschuk, A. P., and Daubert, B. F., J. Am. Oil Chem. Soc., *24*, 274 (1947).
3. Hilditch, T. P., *loc. cit.*, p. 315.
4. Norris, F. A., and Mattil, K. F., J. Am. Oil Chem. Soc., *24*, 274 (1947).
5. Kartha, A. R. S., *ibid.*, *29*, 109 (1952).
6. Riemenschneider, R. W., Luddy, F. E., Swain, M. L., and Ault, W. C., *ibid. 23*, 276 (1946).
7. Collin, G., Hilditch, T. P., and Lea, C. H., J. Soc. Chem. Ind., *48*, 46 (1929).
8. Lutton, E. S., Jackson, F. L., and Quimby O. T., J. Am. Chem. Soc., *70*, 2441 (1948).
9. Lutton, E. S., *ibid.*, *73*, 5595 (1951).
10. Hilditch, T. P., *loc. cit.*, p. 300, 301, 302, 315.
11. Malkin, T., and Meara, M. L., J. Chem. Soc., 103 (1939).
12. Lutton, E. S., unreported.

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# Some Factors Influencing Foam Stability

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IT is evident that the foaming power of liquids does not depend on the surface tension alone. A liquid hydrocarbon of surface tension about 25 dynes/cm at 25°C. foams no more readily than water of surface tension about 72 dynes/cm at 25°C. Gibbs (1) points out that for persistence a liquid film must have a means of withstanding shock, a sort of elasticity. Stated succinctly, for stability a film must have an elastic property so that if the film is increased in area by an external agency, a force will arise in the film tending to oppose this increase of area and if the film is decreased in area, a force will arise to resist the change. Only if this compensatory reaction can be elicited from the film, can the shocks to which by chance it is subjected be prevented from destroying the film. This elasticity can be provided for liquid films between two gas masses only if the film contains at least two components (water is conventionally considered the first component).

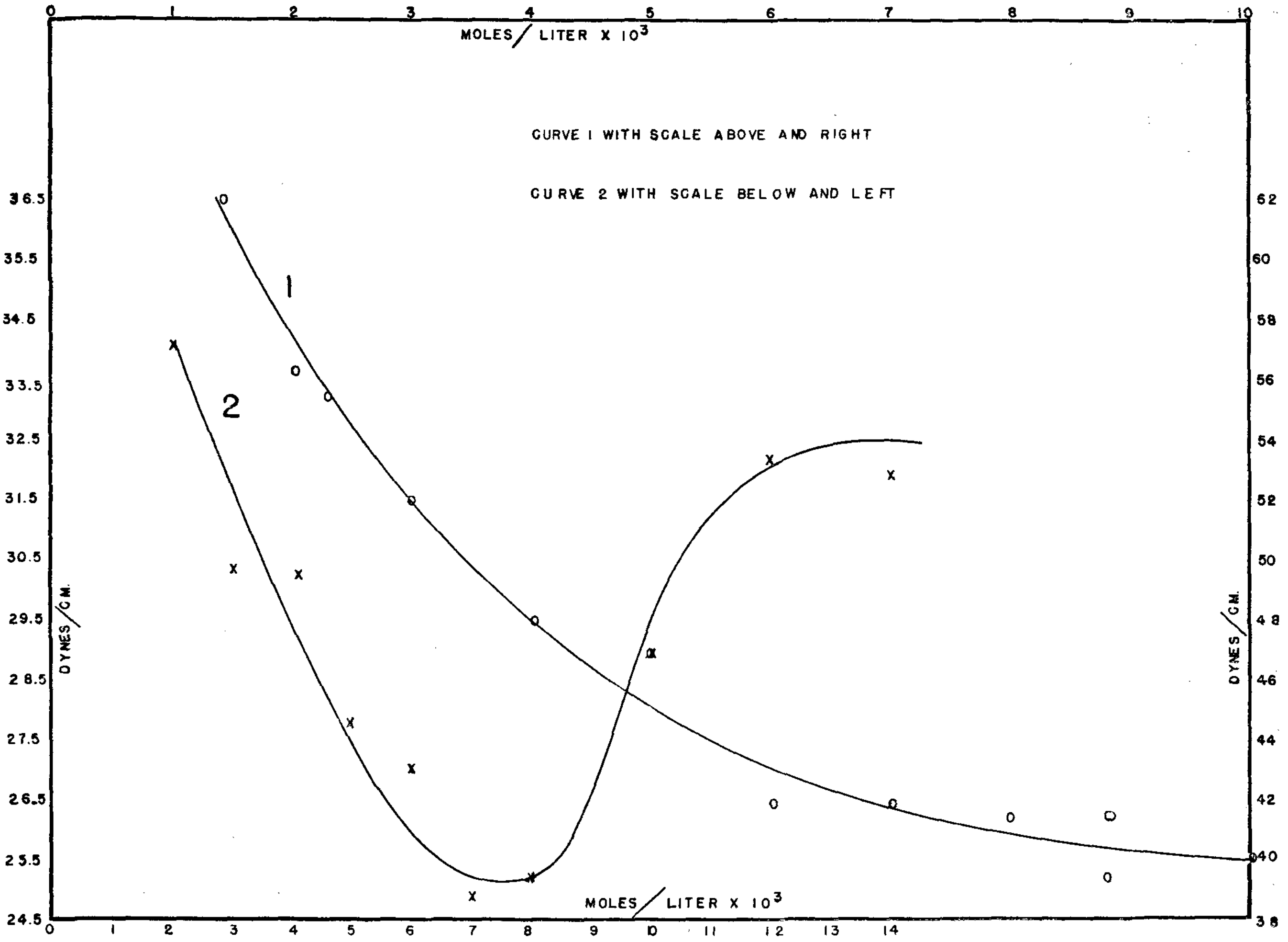
Now there are two cases to be considered, A and B:

A. The second of the two components may be a component of the surface alone, being insoluble in the bulk.

B. This case may arise in two ways:
   1. The second component may be a component of the surface and the bulk phases, but the bulk phase may be not large enough to constitute a reservoir. Therefore it cannot fix the chemical potential in the surface of component two as the surface phase changes its extent.
   2. The bulk phase may be large enough to act as a reservoir, but the time required for adjustment of the chemical potential of component two in the surface after a disturbance may be long compared to the duration of the disturbance.

The physical picture implicit in the above is clear. In general, in two component aqueous solutions the surface tension decreases as the Gibbs surface excess increases and increases as the surface excess decreases. If the surface-active component is confined to the surface alone, (Case A) a contraction or extension of total surface area causes an increase or decrease of surface concentration which causes a decrease or increase in surface tension. Hence we have a force which always resists a change in surface area whether this change is an increase or decrease. With the surface-active component confined to the surface and bulk liquid phases (Case B1) i.e., a compound of low vapor pressure, the situation is similar. If the adjustment to equilibrium is slow after change in surface area as in Part 2 of Case B above, the elasticity is even greater than the equilibrium value.

To illustrate the importance of this last point we may most effectively use a three-component system.



We cite the three-component system consisting of water, sodium lauryl sulphate, and lauryl alcohol, some data for which are given in the graph. Curve 2 gives the surface tension versus concentration curve for this three-component system. Curve 1 gives the data on pure sodium lauryl sulphate in water. It can be seen that this system when containing a weight ratio of lauryl alcohol to sodium lauryl sulphate of .02 has a surface tension minimum at 7 × $10^{-3}$ sodium lauryl sulphate. Consider for a moment a plane film containing water, sodium lauryl sulfate, and lauryl alcohol in a definite amount. The surface-active components are distributed between the two outer surfaces and the intersurface volume. As the surface is diminished, some of the material distributed over the surface goes into the bulk volume, but this volume does not change. Hence the bulk concentration increases. The surface composition must now adjust itself to the bulk concentration. This new bulk concentration may call for either an increase or decrease of surface tension, depending on the type of surface tension vs. concentration curve. The effect of a surface extension can be followed through in an analogous manner.

Now returning from our explanatory digression, we should expect that films of the three-component system at this minimum mentioned above would be unstable with respect to any displacement tending to decrease the total surface since such a displacement would tend to increase the concentration in the bulk liquid between the surfaces, and this would give rise to a greater tension in the film as Graph I shows. Yet this film is more stable in practice than that of pure sodium lauryl sulphate at the same concentration, which has a normal surface tension curve and should be stable. This behavior can be understood if at least one of the components, presumably lauryl alcohol, has its chemical potential in the surface adjusted to the equilibrium value slowly. In other words, the elasticity called into play is a non-equilibrium value.

Of course, it would be desirable to have data on the Gibbs surface excesses from surface tension, concentration measurement in these systems. However, except in solutions of two components, this method is prohibitively difficult. We have consequently resorted to concentration determination by foam fractionation, using an apparatus described by Abribat (2). This consists essentially of a glass chamber through which stock solution from a large reservoir is pouring and in which foam is generated by blowing nitrogen through a jet. The foam rises from the foamer into a long tube about 9 ft. in length. Provision is made at the bottom of this column for a tap to allow withdrawal of liquid draining out of the foam as it rises. The foam then passes over the top and is led down another tube into a trap where it is allowed to condense.

Observations were made on the rising bubbles, and it was found that after a short period of time the bubbles in the rising tube were of very closely equal size and that there was not observable breakage. The size of a bubble was estimated with a centimeter ruler. The rate of rise of the foam is measured at 10-minute intervals and, if necessary, adjusted by changing the rate of nitrogen flow if it had departed from the initial rate. Solution from a large stock was run through the foamer so as to prevent change in the original solution concentration. The liquid draining out of the rising foam was collected. The condensed foam was collected and its volume determined.

We chose the system sodium lauryl sulphate, lauryl alcohol in weight ratio of lauryl alcohol to sulphate of .02, because the curve of surface tension against concentration has the interesting minimum shown in Curve 2. It is further found that the films in the range from 7 $\times$ $10^{-3}$ to $10^{-2}$ sodium lauryl sulphate are slow (3) draining and above this concentration fast. We hoped to get some information by studying this range of concentrations. The concentration of sodium lauryl sulphate was determined in these three solutions. The total time of the run was recorded.

TABLE I

*Data on Bubbles and Foam and Residue Fractions from Foam Fractionation Experiments*

| | | | |
|---|---|---|---|
| Original concentration,* moles/liter | $1.10\times10^{-2}$ | $7.24\times10^{-3}$ | $1.51\times10^{-2}$ |
| Volume per bubble, $cm^2$ | $4.77\times10^{-2}$ | $4.77\times10^{-2}$ | $4.77\times10^{-2}$ |
| Bubbling rate, cm/min | 9.94 | 9.87 | 9.93 |
| Duration of run, min | 300 | 310 | 254 |
| Volume of foam, $cm^3$ | $3.05\times10^{4}$ | $3.10\times10^{4}$ | $2.56\times10^{4}$ |
| Number of bubbles | $6.15\times10^{5}$ | $6.50\times10^{5}$ | $5.37\times10^{5}$ |
| Area of bubble, $cm^2$ | .64 | .64 | .64 |
| Total foam area, $cm^2$ | $4.02\times10^{5}$ | $4.14\times10^{5}$ | $3.42\times10^{5}$ |
| Volume of condensed foam, $cm^3$ | 6.36 | 4.38 | 5.74 |
| Thickness of film, cm | $1.58\times10^{-5}$ | $1.06\times10^{-5}$ | $1.68\times10^{-5}$ |
| Foam bulk concentration, moles/liter | $3.91\times10^{-2}$ | $4.38\times10^{-2}$ | $4.52\times10^{-2}$ |
| Draining concentration,** moles/l. | $1.14\times10^{-2}$ | $8.39\times10^{-3}$ | $1.45\times10^{-2}$ |
| Surface concentration in Å$^2$/mole | 38 | 44 | 32 |

The cross-sectional area of the tube through which the foam rise was 10.2 $cm^2$.

* The word concentration occurring in the table refers to sodium lauryl sulphate.

** This refers to the concentration in the liquid which has drained out of the regions between the bubble faces as the foam rises in the tube.

From these data the results presented in Table I were computed. The surface concentration was calculated from the following relation:

$$\Gamma = v/s\ (\gamma' - \gamma) \qquad (1)$$

where $\Gamma$ is the surface concentration in moles/$cm^2$

$v$ = volume of condensed foam in $cm^3$

$s$ = area of foam in $cm^2$

$\gamma'$ = concentration in condensed foam in moles/$cm^3$

$\gamma$ = concentration in drainage liquid in moles/$cm^3$

The surface concentrations reported are approximately what one would calculate from the surface tension concentration curve for pure sodium lauryl sulphate, using the Gibbs equation at these concentrations. Unfortunately we have no analytical data as yet for the alcohol concentration in the interface. The foam fractionation method of determination would be tedious since large quantities of film would have to be generated in order to obtain enough to make an extraction with an organic solvent practicable. We have thought it more convenient to resort to radiochemical techniques in order to determine the alcohol concentration in the interface. A stock solution of $1.5\times10^{-2}$ M sodium dodecyl sulphate was prepared, containing dodecanol in weight ratio to the sulphate of .02, the dodecanol containing $C^{14}$.

If counts at constant geometry of a fixed volume of solution of concentration C moles/$cm^3$ are made, the counting rate $J_\infty$ (this symbol is used because the absorption of the beta particles is so complete in short distances that a thickness of a few millimeters gives nearly all the count that could be obtained from an infinite thickness) is given by

$$J_\infty = a\,Ac/k \qquad (2)$$

$J_\infty$ is the count per second of a solution of (for practical purposes) infinite depth. $a$ is a constant. A is the area of the solution cross section. k is the absorption coefficient. $k/\rho$ given by Solomon *et al.* (4) for barium carbonate is 290 $cm^{-1}$. $\rho$ here is the density of barium carbonate. Since $\rho$ is 1 for water, k = 290 $cm^{-1}$ for water. Equation (1) is valid if there is no surface concentration of radioactive species. If there is such a concentration and if we assume the same geometrical factor for such surface concentration, which would probably be sufficient in this case, the count could be written

$$J_\infty = a\,Ac/k + a\,A\,\Gamma \qquad (3)$$

where $\Gamma$ is expressed in moles/$cm^2$.

From counting of a solution in which $\Gamma = o$ we can obtain a value for $a$. This value of $a$ can then be used in solutions in which $\Gamma \neq o$. Now the surface tension concentration curve for this lauryl alcohol containing solution approaches that of pure sodium lauryl sulphate above 1.2 $\times$ $10^{-2}$ molar (see graph).

If we assume that this means the lauryl alcohol concentration in the surface in the first solution approaches zero above 1.2 $\times$ $10^{-2}$, we can proceed as follows: A solution of sodium lauryl sulphate, lauryl alcohol is counted, then enough sodium lauryl sulphate is added to make the total concentration 1.5 $\times$ $10^{-2}$ molar and counted again. The second counting rate is used in *(2)* to determine $a$. This value of $a$ is used with the first counting rate to calculate $\Gamma$ in *(3)*. Or if we designate the $J_\infty$ in *(2)* as $J^\circ_\infty$, we can write

$$\Gamma = (J_\infty - J^\circ_\infty)/a\,A \qquad (4)$$

We have made a series of measurements on solutions in which the additional sodium lauryl sulphate had been added. At each concentration of lauryl alcohol at least four measurements were made. These sub-averages were tabulated, and then a grand average for all concentrations was obtained. We do not wish to discuss the experimental difficulties encountered here, however certain facts must be mentioned. The data on most concentrations before the additional sodium lauryl sulphate was added showed an irreproducible time dependence, the count increasing to very high values. The values are so high that they could be understood only in terms of phase separation. Only in the case of the solution of sodium lauryl sulphate of 3.879 $\times$ $10^{-3}$ moles/cm was the count found to be fairly stable. From the results we can calculate a concentration of about 80Å$^2$ per molecule in this case. At this point we attempted to obtain an estimate of the solubility of lauryl alcohol in water, using a technique first used by Langmuir (5), starting with the known data on hexyl, heptyl, and octyl alcohols. We estimate a solubility of about $10^{-5}$ moles/l. Then even in the most dilute solution in which the lauryl alcohol was in weight ratio .02 to 3.879 $\times$ $10^{-3}$ moles sodium lauryl sulphate/liter or about $10^{-4}$ moles/l., the concentration of lauryl alcohol was about 10 times greater than the maximum permissible if sodium lauryl sulphate below the c.m.c. has no effect on the solubility.

Any theory of film stability, however sketchy, must be able to explain the difference between fast and slow draining films. Let us consider first a two-component system, one of which is surface-active. In a gravitational field the upper portion of a film must be under higher tension than the lower. Consequently in accordance with the general rule, a lower surface concentration will be required in the upper portion. Then some stretching of the upper portions of the film surface must take place to produce the decreased surface concentration and consequently elevated tension. If the film is of the gaseous type, quite a deal of stretching may be necessary to yield the appropriate increase in tension. Consequently the walls will descend and the film thinning will be accelerated. This film will be fast draining. If, on the other hand, the film is of the condensed type, this will, in general, mean that the surface active agent is but sparingly soluble and the film will behave toward any shocks of short period like a pure water film which is, of course, unstable. Thus it would seem that we could not obtain slow draining films in two-component systems.

In three-component systems the film will still have higher tension in its upper region, but we cannot say much about the surface concentrations except that a surface concentration readjustment must take place on film stretching. If one of the two surface-active components is present in small amount and is able with the other surface-active component to form a condensed film, only a small extension may be necessary to provide the required vertical tension gradient. Consequently the walls will not descend rapidly. This film will be slow draining.

## Summary

It is believed that liquid films owe their stability to the Gibbs elasticity. How this elasticity may arise is discussed, and it is concluded that in some cases a nonequilibrium value may be the important concern. Some data on surface composition from radiochemical experiments and foam fractionation are presented. Finally an explanation of the origin of the slow and fast draining films of Ross, Miles, and Shedlovsky is offered.

### REFERENCES

1. Gibbs, J. W., Collected Works, Vol. 1, p. 300 ff.
2. Abribat, M., *Actualities Scientifiques et Industrielles*, 1942, p. 123.
3. See Ross, Miles, and Shedlovsky, J. Am. Oil Chem. Soc., *27*, 268 (1950).
4. Solomon, A. K., Gould, R. G., and Anfinson, C. B., Phys. rev., *72*, 1097 (1947).
5. Langmuir, I., Colloid Symposium Monographs, Vol. III (1925).

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# Viscosities and Solubilities of Synthetic Detergent Mixtures Containing Soluble Silicates

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SOLUBLE silicates have long been used as builders for soaps, and their advantages are well known (1). In synthetic detergents sodium silicate shows similar advantages and has recently assumed added importance, due to its inhibiting effect on corrosion. However attempts to incorporate silicate in synthetic detergents in many cases have resulted in difficulties due to increased viscosity of the slurries, with trouble in pumping and handling and in the formation of insoluble matter on drying, with subsequent formation of turbid solutions. The present investigation was undertaken to study this problem.

## Materials

The detergents used were: Sodium Oronite (Oronite Chemical Company), the sodium salt of an alkyl aryl sulfonate, received in the form of a paste containing 40.6% sodium alkyl aryl sulfonate, 49.6% water, and 9.7% sodium sulfate; Ultrawet 45 KX (Atlantic Refining Company), also the sodium salt of an alkyl aryl sulfonate, and containing 40.6% sodium alkyl aryl sulfonate, 5.1% sodium sulfate, and 54.3% water; Orvus WA Paste (Procter and Gamble), a sodium alcohol sulfate containing 29.6% sodium alcohol sulfate and 1.4% sodium sulfate. In order to produce mixtures comparable with those with the other detergents, the Orvus Paste was concentrated by evaporation to 52% solids and 2.5% sodium sulfate was added.

The phosphates used were: Tetrasodium pyrophosphate (TSPP) and sodium tripolyphosphate (STPP). In many cases a mixture of equal weights of the two phosphates (MP) was used. Compositions of the silicates used are:

| | % $Na_2O$ | % $Si_2O$ | Wt. ratio Alkali: silica | Mole ratio |
|---|---|---|---|---|
| N | 8.9 | 29.8 | 1:3.22 | 1:3.32 |
| RU | 13.8 | 33.1 | 1:2.40 | 1:2.48 |
| BW | 19.5 | 31.2 | 1:1.60 | 1:1.65 |
| Metso Granular | 30.0 | 28.7 | 1:1.02 | 1:1.04 |
| Potassium silicate | 19.0<br>($K_2O$) | 30.8 | 1:1.62 | 1:2.53 |

## Experimental

The mixtures were prepared to contain 25% detergent (including sodium sulfate), 25% builder, and 50% water. The detergents and builders are reported on an anhydrous basis. Any water present in the original materials is included in the 50% water. In most cases the builder consisted of phosphate and silicate and sometimes other additives. Mixtures were prepared by adding the phosphate slowly, in small portions, to the warm (60°C.) detergent slurry, followed by the warm (60°C.) silicate solution, diluted with the remaining water. Other orders of mixing resulted in lumps or mixtures too thick to be used. The other additives were either added to the deter-