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Citation: [The Journal of Chemical Physics](#) **1**, 756 (1933); doi: 10.1063/1.1749243

View online: <http://dx.doi.org/10.1063/1.1749243>

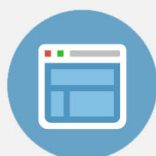
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Oil Lenses on Water and the Nature of Monomolecular Expanded Films

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(Received September 8, 1933)

A higher hydrocarbon, such as tetradecane, on the surface of water forms a circular lens. The condition for the formation of such stable lenses is that the spreading coefficient $F_S = \gamma_1 - \gamma_2 - \gamma_{12}$ shall be negative. As the volume of the oil lens is increased, the thickness t at the center slowly approaches a limiting value given by $t_\infty^2 = -2F_S\rho_1/g\rho_2(\rho_1 - \rho_2)$. Equations are given by which F_S can be accurately determined from measurements of the radii of large lenses of known volume. The magnitude of the linear tension at the lens boundary is also calculated. Experiments with tetradecane on water at 25°C give $F_S = -6.2$ dynes cm^{-1} and $\gamma = 26.9$. When hydrophilic molecules are introduced into the interface between the lens and the water, they give a spreading force F_{12} which causes a decrease in $-F_S$ and in t . When $t < 0.1$ mm gravitational effects are negligible and the lens degenerates into a *duplex film*. If such a film is confined by a movable barrier (piston), the force per unit length F exerted on

the barrier is equal to F_S . If the adsorbed molecules at the interface give a force F_{12} in accord with the gas laws, then $(F - F_0)(a - a_0) = kT$ gives the equation of state of the duplex film, where F_0 is the value of F_S in the absence of hydrophilic substances. It is shown that this equation applies to expanded oil films on water and that these are properly regarded as duplex films although they are monomolecular. The presence of a kink in the observed $F-a$ curves is attributed to the sudden appearance of micelles, each containing β -molecules when F_{12} rises to a critical value. For the fatty acids on dilute HCl, $\beta = 13$. This small value is due to the crowding apart of the heads because of hydration. The esters show little or no hydration and $\beta = 60$. The heat of formation of the micelles in the fatty acids is found to be $5.5 + 0.24n$ kg cal. per mole where n is the number of carbon atoms. The values of F_0 and a_0 for various substances are determined from data given by Adam.

FATTY acids and similar organic substances spread over the surface of water to form monomolecular films in which the active groups or heads are in contact with the water while the hydrocarbon chains or tails form a layer above the plane containing the heads. When such films are compressed by a force F (dynes per cm), they form condensed films having an area $20.5A^2$ for each molecule. This area is identical with the cross-sectional area of the molecules in stearic acid crystals in a plane parallel to that occupied by the heads of the molecules.¹ Since this plane makes an angle of $63^\circ 38'$ with the axis of the hydrocarbon chains, there is strong evidence that the hydrocarbon chains in these condensed films of normal fatty acids on water are inclined about 27° from the vertical.

With the lower fatty acids, such as lauric and myristic acids, when the films are only slightly compressed, they occupy much larger areas than $20.5A^2$. There are many different substances

which give, under these conditions, a rather definite area of about $50A^2$ per molecule. Adam has called these films liquid expanded films. The tendency to form these expanded films increases as the hydrocarbon chain is shortened, or as the temperature is raised, the effect of each additional CH_2 group in the chain being equivalent to a lowering of temperature of about 8°C .

In two papers^{2, 3} in 1925 I offered an explanation of the existence of these expanded films. I pointed out that in these films there are really two surfaces which form the upper and lower boundaries of the hydrocarbon part of the film. Since the thicknesses of these films are several times that of the hydrocarbon chain, the region between these boundaries must be regarded as essentially a typical hydrocarbon liquid in which the molecules possess all the natural freedom of motion of such liquids with the single restriction

² I. Langmuir, Colloid Symposium Monograph 3, 48 (1925).

³ I. Langmuir, an article, *The Effects of Molecular Dissymmetry on the Properties of Matter*, in a book entitled *Colloid Chemistry*, Jerome Alexander, 1, 525 (1926).

¹ Alex. Müller, Proc. Roy. Soc. (London) A114, 542 (1927).

that the molecules are constrained to keep one end in contact with the lower surface. A higher normal hydrocarbon liquid on a water surface does not spread; it must therefore require a definite spreading force F to pull a hydrocarbon liquid out over a water surface to form an expanded film. Such a force must have its origin in some property imparted by the heads. At the interface between the hydrocarbon liquid and the underlying water there are, in the case of a fatty acid film, carboxyl groups. Even if these do not exert repulsive forces on one another, they should at least tend to spread within the available surface as a two-dimensional gas, and thus exert a two-dimensional gas pressure F which will counteract the normal tendency of the hydrocarbon layer to draw together.

It was shown that this theory leads to an equation of state of the form

$$(F - F_0)(a - a_0) = kT.$$

By taking the values $F_0 = -13$ and $a_0 = 18$, this gave very satisfactory agreement with Adam's early data^{3a} for myristic acid at 32.5°. This theory as given in the papers referred to was presented briefly in about four pages and there was no detailed analysis of the experimental curves.

Adam has definitely rejected this theory.⁴ For example, in his book he says:

Langmuir suggested that the molecules adhere by their chains, and that the heads are in a state of constant agitation, the chains tending to make a condensed, and the heads a gaseous film. But since it is not the length of the chains, but the nature of the heads, which determine whether the films are liquid or vapor expanded, and since those heads which probably have the greatest attraction for one another laterally form liquid expanded films, a better suggestion seems to be the reverse of Langmuir's, *that the heads tend to hold the molecules together, while the chains try to disrupt the film.*

Adam considers, however, that "the detailed structure of the liquid expanded films is difficult to decide."

Rideal⁵ offers no explanation of expanded films

and does not accept those previously proposed by the writer.

The evidence in support of the theory proposed is, however, so striking that it needs to be presented in more detail than has been done previously. It is clear that Adam has misunderstood the theory and does not see its widespread application to his own experimental data. A recent more thorough examination of Adam's published results has led me to extend the theory that I proposed in 1925 so that it now seems to offer a nearly complete theory of all observed characteristics of expanded films.

CHARACTERISTICS OF TYPICAL MONOMOLECULAR FILMS

The complete curve giving F as a function of a , the area per molecule, such as that represented by Fig. 1, represents essentially an equation of state for a 2-dimensional system which may

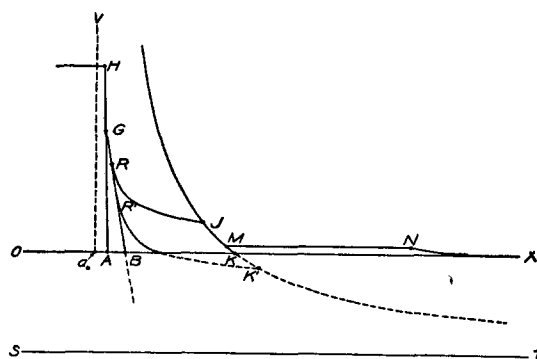


FIG. 1. Diagram of F - a curves for typical monomolecular films.

contain gas, liquid and solid phases. The lines shown in Fig. 1 may not all be observable with any single substance for reasons that will be discussed later. Since only positive values of F are directly observable, all those portions of the curves which correspond to negative values in Fig. 1 can be inferred only from theoretical considerations.

The line AGH corresponds to a typical condensed film such as that of stearic acid on pure water at room temperature. When such fatty acids are placed on water containing dilute hydrochloric acid, a break occurs at G so that the curve below G is given by BG . Adam believes

^{3a} N. K. Adam, Proc. Roy. Soc. **A101**, 516 (1922).

⁴ N. K. Adam, *Physics and Chemistry of Surfaces*, Clarendon Press (1930), page 75.

⁵ E. K. Rideal, *Introduction to Surface Chemistry*, Cambridge University Press, pp. 101-104.

that the area corresponding to B is that of the heads of the molecules.

With a liquid expanded film such as myristic acid on dilute hydrochloric acid, the observed F - a curve leaves the line GB near R and gradually flattens out as it approaches J where there is a sharp kink, and it then falls more rapidly along a line JK to a definite point M . It then extends horizontally along the line MN until at some point N it begins to fall again approaching the horizontal axis asymptotically as a continues to increase. The theory proposed in 1925 indicated that the line JK is part of a rectangular hyperbola in which the horizontal asymptote ST lies at a distance F_0 below the horizontal axis OX , and the vertical asymptote is represented by the dotted line at V corresponding to an abscissa a_0 .

It is the plan of the present paper to develop a theory which gives the mechanism underlying each part of the broken line shown in Fig. 1, and by which quantitative information regarding the fundamental properties of molecules may be obtained.

LARGE FREE LENSES OF OIL ON WATER

Let us consider the conditions for equilibrium between a pure water surface (I) and a thin layer of an oil (II) placed upon the water. We assume provisionally that the film, although of a thickness large compared to that of the oil molecules, is yet so thin that gravity plays no appreciable part in causing it to flow out over the surface. We are then surely justified in assuming that the oil film has an upper surface (surface tension γ_2) and a lower surface (interfacial tension γ_{12}) which do not influence one another.

For equilibrium between this thin oil film and the water it is necessary that the surface tension γ_1 of the water shall balance the sum of γ_2 and γ_{12} for the film. Let us put

$$F_S = \gamma_1 - \gamma_2 - \gamma_{12}. \quad (1)$$

If $F_S > 0$, that is, if γ_1 is greater than $\gamma_2 + \gamma_{12}$, the oil spreads over the water until it covers the whole surface or until the film becomes so nearly monomolecular that $\gamma_2 + \gamma_{12}$ increases to the value γ_1 .

If $F_S < 0$, the oil film contracts and gathers into one or more lenses of such thickness that

gravity can prevent any further contraction. Harkins has called F_S the spreading coefficient.

Harkins' data⁶ for normal chain hydrocarbons on water show that F_S is +3.3 for hexane, 1.7 for heptane, and 0.3 (dynes cm^{-1}) for octane. No data seem to be available for γ_{12} or F_S for the higher liquid hydrocarbons. If, however, the rate of decrease of F_S per CH_2 observed by Harkins continues beyond octane, the value of hexadecane should be $F_S = -11.7$. For paraffin oil (Squibbs' petrolatum) which probably consists mostly of saturated cyclic hydrocarbons, Harkins⁶ has found $F_S = -13.69$ at 20°C .

A simple direct method for determining F_S for nonspreading substances consists in measuring the diameters D of very large lenses formed when known volumes V of oil are placed on surfaces of water. Except when the density of the oil is very close to that of water, the curvature of the interface between the oil and the water becomes negligible at a distance of 2 or 3 cm from the edge of the lens. For lenses of a diameter greater than about 6 cm, the central part of the lens is thus of a uniform thickness. For a series of lenses of increasing radius R , the central thickness t slowly approaches a limiting value t_∞ which may be readily calculated by the following method.

Let z be a coordinate which measures vertical distances upward from the plane of the water surface (far from the boundary of the lens). Then since the oil is lighter than water (and only such oils can form large lenses), Z_2 , the level of the upper surface of the lens, will have a positive value. The pressure at the lower surface (the interface) at Z_{12} must be the same as in the water phase at the same level. This condition gives

$$Z_2 = t(\rho_1 - \rho_2)/\rho_1 \quad (2)$$

and

$$Z_{12} = -t\rho_2/\rho_1, \quad (3)$$

where ρ_1 is the density of the water and ρ_2 that of the oil.

Consider now a lens so large that the curvature of the boundary is negligible. The *total* force per unit length acting across a portion of a vertical plane cutting the lens far from the boundary consists of the surface tension forces $\gamma_1 + \gamma_{12}$ and

⁶ W. D. Harkins, Colloid Symposium Monograph 6, 26 (1928).

the hydrostatic liquid pressures. From the free surface down to the depth y in any liquid this latter force is the pressure integral $\int p \, dy$ and is thus equal to $(1/2)g\rho y^2$. Thus down to the interface at Z_{12} the total spreading force per unit length in the central part of the large lens is

$$F_2 = (1/2)g\rho_2 t^2 - \gamma_2 - \gamma_{12}. \quad (4)$$

For equilibrium, this must equal the spreading force F_1 in the water, remote from the lens boundary, down to the same depth Z_{12} . This force is

$$F_1 = (1/2)g\rho_1 Z_{12}^2 - \gamma_1. \quad (5)$$

Equating F_2 and F_1 , eliminating Z_{12} by Eq. (3), and combining with Eq. (1) we have

$$t_m^2 = -2F_S \rho_1 / g \rho_2 (\rho_1 - \rho_2). \quad (6)$$

From a knowledge of t_∞ we can thus calculate the spreading coefficient F_S . The actual thickness t at the center of a lens, however, often differs from t_∞ by as much as one percent even for lenses as large as 60 cm in diameter. This is due to the fact that there is a linear tension f (a one-dimensional analogue of pressure) along the perimeter of the lens acting to keep the lens in a circular form. This force, which is of considerable magnitude (6.5 dynes for paraffin oil on water) must be balanced by an increase in the spreading force $F_2 - F_1$ by means of an increase in t , just as the surface tension in a soap bubble is balanced by the increased air pressure within the bubble. This effect can be taken into account by subtracting a term f/R from the 2nd member of Eq. (4) before equating to F_1 . In this way we obtain

$$t^2 = t_{\infty}^2(1 - f/F_S R). \quad (7)$$

CALCULATION OF THE LINEAR TENSION OF A CYLINDRICAL LENS BOUNDARY

A plane through the vertical axis of symmetry of a large lens cuts the free surfaces and the interface in the manner illustrated in Fig. 2. As R is made to increase indefinitely, the surfaces represented by the meridian curves in this figure become noncircular cylinders with horizontal elements.

Consider now the horizontal forces acting across a vertical plane which is perpendicular to the meridian plane, but near the lens boundary. Let α be the angle which the tangent to any

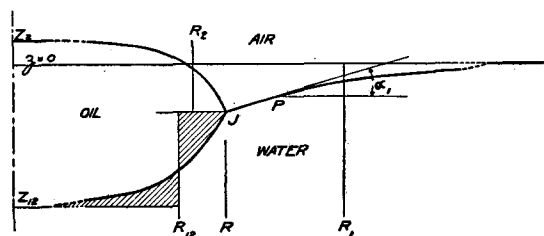


FIG. 2. Profile of a lens on water.

meridian makes with a horizontal plane and let y be the vertical distance of any point from the horizontal plane at which $\alpha = 0$.

If we take the spreading force F (associated with any surface) to be zero when the surface is horizontal ($\alpha=0$), then we have for the spreading force F_r in a radial direction

$$F_r = \gamma(1 - \cos \alpha) - \frac{1}{2}g\rho y^2. \quad (8)$$

For equilibrium, with a truly cylindrical lens boundary, F_r must be constant and hence equal to zero. Thus putting $F_r=0$ we obtain

$$y^2 = a^2(1 - \cos \alpha), \quad (9)$$

where a is the Laplace capillary constant defined by

$$a^2 = 2\gamma / g\Delta\rho \quad (10)$$

and $\Delta\rho$ is the difference of density on the two sides of a phase boundary. Eq. (9) may also be written

$$y = 2^{\frac{1}{2}} a \sin (\alpha/2). \quad (11)$$

An equation of this form holds for each of the three surfaces.

Now consider the horizontal forces acting across the meridian plane near a lens boundary. Here the surface tension force per unit of horizontal distance is $\gamma/\cos \alpha$ (instead of $\gamma \cos \alpha$ in the former case) and thus we have

$$F_T = \gamma(1 - 1/\cos \alpha) - \frac{1}{2}g\rho y^2. \quad (12)$$

Eliminating y by using Eq. (8) after putting $F_r=0$ we have

$$F_T = \gamma(\cos \alpha - 1/\cos \alpha) = -\gamma \sin^2 \alpha / \cos \alpha. \quad (13)$$

There is thus a negative spreading force (tension) in a horizontal direction which is perpendicular to that of the slope of the surface. The tension f corresponding to any one of the three surfaces that meet at the lens boundary at J

is obtained as an integral $\int F_T dx$. We may put

$$dx = (dx/dy) \cdot (dy/d\alpha) d\alpha,$$

in which $dx/dy = \cos \alpha / \sin \alpha$ and

$$dy/da = a \sin \alpha / a(1 - \cos \alpha)^{1/2}.$$

With the value of F_T from Eq. (13) we thus find

$$f = (\gamma a / 2) \int \sin^2 \alpha (1 - \cos \alpha)^{-1/2} d\alpha$$

or

$$f = (2(2)^{1/2}/3) \gamma a [1 - \cos^3(A/2)]. \quad (14)$$

Here the integration has been carried from $\alpha = 0$ to A , the angle α at the junction J where the three surfaces meet. The total linear tension acting along the perimeter of the lens is the sum of three terms

$$f = f_1 + f_2 + f_{12} \quad (15)$$

found from Eq. (14) by inserting the appropriate values of a and A . Since A is a rather small angle in most cases, it is useful to expand Eq. (14) in powers of A obtaining

$$f = (2^{1/2}/4) \gamma a A^2 [1 - (7/48)A^2 + \dots]. \quad (16)$$

THE MERIDIAN CURVES AT A LENS BOUNDARY

The effect of the linear tension in modifying the profile curves shown in Fig. 2 for lenses of moderate size may now be determined. A horizontal plane through the junction J allows us to apply our equations separately to the three phase boundaries. Consider, for example, the free water surface. For a lens of moderate size the spreading force F_R given by Eq. (8) is not everywhere zero as in the cylindrical case but at any point P where α differs appreciably from zero, it must have a value which balances the effect of the linear tension of the parts of the surface outside of P . We may thus put

$$F_R = f_1/R_1 \quad (17)$$

where R_1 is an effective radius at which the tension may be regarded as being concentrated. In Fig. 2 the positions of R_1 , R_2 , and R_{12} have been chosen so that the two shaded areas (shown only for R_{12}) are equal. This assumption gives for moderate values of A

$$R_1 = R + a_1/2^{1/2}. \quad (18)$$

Combining Eqs. (8), (17) and (10) we thus obtain⁷

$$z_1^2/a_1^2 = 1 - \cos \alpha_1 - f_1/\gamma_1 R_1 \quad (19)$$

in place of Eq. (9). It should be noted that the value of f_1 in this equation is to be obtained from Eq. (14) by replacing A by α_1 . Similarly for the other two surfaces we have

$$(z_2 - z_0)^2/a_2^2 = 1 - \cos \alpha_2 + f_2/\gamma_2 R_2 \quad (20)$$

and

$$(z_0 - z_{12})^2/a_{12}^2 = 1 - \cos \alpha_{12} + f_{12}/\gamma_{12} R_{12}, \quad (21)$$

where R_2 and R_{12} are obtained from equations like (18) except that the sign of the last term is reversed.

If we apply Eqs. (19), (20) and (21) to the junction J in Fig. 2, we obtain

$$z_0^2/a_1^2 = 1 - \cos A_1 - f_1/\gamma_1 R_1, \quad (22)$$

$$(Z_2 - z_0)^2/a_2^2 = 1 - \cos A_2 + f_2/\gamma_2 R_2, \quad (23)$$

$$(z_0 - Z_{12})^2/a_{12}^2 = 1 - \cos A_{12} + f_{12}/\gamma_{12} R_{12}. \quad (24)$$

Expanding the first members of the last two equations, combining with the first equation so as to eliminate z_0 , and eliminating Z_2 and Z_{12} by Eqs. (2) and (3) we obtain

$$\begin{aligned} \frac{1}{2} g t^2 (\rho_1 - \rho_2) \rho_2 / \rho_1 = & -(\gamma_1 - \gamma_2 - \gamma_{12}) \\ & + (\gamma_1 \cos A_1 - \gamma_2 \cos A_2 - \gamma_{12} \cos A_{12}) \\ & + (f_1/R_1 + f_2/R_2 + f_{12}/R_{12}). \end{aligned} \quad (25)$$

For equilibrium between the horizontal components of the surface tensions at the junction J we must have

$$\gamma_1 \cos A_1 = \gamma_2 \cos A_2 + \gamma_{12} \cos A_{12}. \quad (26)$$

Using this relation and introducing F_0 by Eq. (1) into Eq. (25) we find

$$\begin{aligned} t^2 = & [2\rho_1/g\rho_2(\rho_1 - \rho_2)] [-F_S \\ & + (f_1/R_1 + f_2/R_2 + f_{12}/R_{12})], \end{aligned} \quad (27)$$

which agrees with Eqs. (6) and (7) except that the effective radii R_1 , R_2 and R_{12} are now no longer identified with R .

⁷ If the values of f_1 and R_1 by Eqs. (14) and (18) are inserted in these equations they may readily be shown to be identical with a rather complicated equation given by Poisson in his book *Nouvelle Theorie de l'Action Capillaire* as quoted in the Handb. der Exp. Physik VI, 98 (1928).

VOLUME OF LENS

If the lens is of sufficient size to give a uniform thickness t in the central part then the volume V is

$$V = \pi R^2 t - \pi R(a_{12}^2 \sin A_{12} - a_2^2 \sin A_2). \quad (28)$$

This may be understood readily from the fact that the vertical component $\gamma \sin A$ of the surface tension at the junction multiplied by the perimeter $2\pi R$ must be the buoyant force $\rho g \Delta V$ of the displaced volume ΔV resulting from the deviations of the surface from the horizontal.

CONTACT ANGLES AND THE VALUES OF A

The relation of the angles A_1 , A_2 and A_{12} at the junction J to the contact angles is given in Fig. 3. The angles subtended by the three phases at the

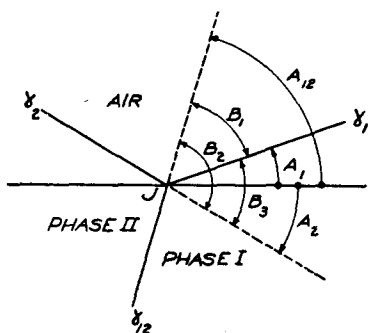


FIG. 3. Contact angles at a lens boundary.

junction J are $\pi - B_1$, B_2 and $\pi - B_3$. These angles are related to the three surface tensions by

$$\cos B_1 = (\gamma_1^2 - \gamma_2^2 + \gamma_{12}^2) / 2\gamma_1\gamma_{12}, \quad (29)$$

$$\cos B_3 = (\gamma_1^2 + \gamma_2^2 - \gamma_{12}^2) / 2\gamma_1\gamma_2, \quad (30)$$

$$B_2 = B_1 + B_3. \quad (31)$$

Combining these equations with Eq. (1) we have

$$\sin^2 (B_1/2) = -F_S(2\gamma_2 + F_S) / 4\gamma_1\gamma_{12}, \quad (32)$$

$$\sin^2 (B_3/2) = -F_S(2\gamma_{12} + F_S) / 4\gamma_1\gamma_2. \quad (33)$$

Thus the angles approach zero as $-F_S$ decreases to zero. From Fig. 3 we see that

$$A_2 = A_1 - B_3, \quad (34)$$

$$A_{12} = A_1 + B_1. \quad (35)$$

The value of A_1 may be obtained from Eqs. (22) to (24). Taking A to be a sufficiently small angle so that $(1/24)A^2$ can be neglected in comparison with unity, we may expand $1 - \cos A$ in Eqs. (22) and (23). Introducing the values of f from Eq. (16) after inserting the value of R_1 , etc., from Eq. (18) and eliminating Z_2 and Z_{12} by Eqs. (2) and (3), we may obtain from Eqs. (22) and (23) the following

$$b_1 A_1 = -2^{1/2} z_0, \quad (36)$$

$$b_2 A_2 = -2^{1/2} [(\rho_1 - \rho_2 / \rho_1) t - z_0], \quad (37)$$

where

$$b_1 = a_1 [1 - (2^{1/4}) a_1 / R + (3/16) a_1^2 / R^2] \quad (38)$$

and

$$b_2 = a_2 [1 + (2^{1/4}) a_2 / R + (3/16) a_2^2 / R^2]. \quad (39)$$

Eliminating z_0 we obtain a single equation in A_1 and A_2 . By Eq. (34) we may then eliminate A_2 and obtain

$$A_1 = \frac{b_2 B_3 - (\rho_1 - \rho_2) 2^{1/2} t / \rho_1}{b_1 + b_2}. \quad (40)$$

MEASUREMENTS OF THE DIAMETERS OF LENSES

By placing measured volumes (or weights) of oil on a water surface and measuring the diameters of the circular lenses that are formed, a series of values of V and R in Eq. (28) are obtained. By inserting the values of t from Eq. (7) or (27) and dividing by πR^2 , this equation may be put in the form

$$V / \pi R^2 = t_\infty - C_1 / R + C_2 / R^2, \quad (41)$$

where C_1 and C_2 can be expressed in terms of the angles $A_{1\infty}$ and $A_{2\infty}$, the values of A_1 and A_2 for a lens of very large diameter. Experimentally we may thus obtain t_∞ by plotting the average lens thickness $V / \pi R^2$ against $1/R$ and extrapolating back to the intercept t_∞ at $1/R = 0$. This extrapolation may be greatly facilitated by knowledge of the theoretical values of C_1 and C_2 that can be obtained by the foregoing methods, from even approximate values of γ_1 , γ_2 and γ_{12} . From the values of t_∞ thus obtained, F_S may be calculated from Eq. (6). If γ_1 and γ_2 are known, γ_{12} can then be determined from Eq. (1), and in this way new values of A_1 , C_1 and C_2 can be obtained for more accurate calculations of t_∞ .

The measurements of the diameters of lenses thus provide a method of determining the interfacial surface tension γ_{12} . The method becomes increasingly accurate as F_S approaches zero. Instead of calculating A_1 by Eq. (40) from surface tension data, it is very easy to make direct accurate measurements of A_1 and A_2 by an optical goniometer sighted at the junction J of large lenses. Of course such measurements by themselves give B_3 by Eq. (34) and thus by Eq. (30) give γ_{12} when γ_1 and γ_2 are known, but when F_S is small, still greater accuracy can be obtained by combining these measurements with determinations of the lens diameters.

It is also a simple matter to measure directly the linear tension f_∞ for a boundary of zero curvature and thus determine the relation of t and t_∞ . This may be done by inserting two parallel vertically placed metal strips into a lens on water. One of these strips is attached to the vertical pointer of a balance (a balance to measure horizontal forces). The second strip may then be moved away from the first one so that the lens becomes so distorted as to become approximately rectangular with parallel sides. The force exerted on the other strip as indicated by the balance, is thus $2f_\infty$.

If such measurements of f_∞ are combined with direct measurements of t , t_∞ and thus F_S may be determined by Eqs. (7) and (6) without needing to know the angles A . By using two sharp points attached to micrometers arranged so that one point can be brought in contact with the upper and the other with the lower surface, accurate measurements of t can be made.

These various methods thus provide us with accurate determinations of γ_{12} . They have the advantage over the drop weight method usually used, that they are purely static methods and that they permit us to study the effects of known amounts of adsorbed substances at the interface by the methods which will be described in a later section.

EXPERIMENTAL DATA ON THE DIAMETERS OF LENSES

Weighed amounts of Squibb's Petrolatum were placed on a large tray (45×75 cm) full of distilled water at 24°C, which was then covered by a sheet of glass to eliminate air currents. The

diameters of the lenses were measured to 0.1 mm. The values of $V/\pi R^2$, plotted as a function of $1/R$, are indicated in Fig. 4 by small circles.

The family of curves in this figure represent the calculated relation of $V/\pi R^2$ to $1/R$ according to Eq. (28) based upon the various assumed values of γ_{12} which are given on the curves. It is seen that the experimental points, except for lenses of small diameter, agree with the curve for $\gamma_{12}=53.0$ dynes cm^{-1} . The value of $t_\infty=0.4806$ cm, given by the intercept of this curve on the $V/\pi R^2$ axis, corresponds to $F_S=-11.37$.

Harkins⁶ found for this oil at 20°C, by the drop weight method, $\gamma_2=31.12$; $\gamma_{12}=55.32$, $F_S=-13.69$. This high value of γ_{12} is incompatible with our measurements on lenses. To find whether impurities were present in the oil which could lower γ_{12} , a portion was shaken with Fuller's earth and centrifuged, but the lens diameter remained unchanged. We have checked Harkins' value of γ_2 by Wilhelmy's method obtaining $\gamma_2=30.8$ at 23.5°C, which should correspond to 31.1 at 20°C.

The method of calculating the curves in Fig. 4 may be illustrated by the curve for $\gamma_{12}=53.0$. Taking $\rho_2=0.8849$ (measured at 20°C), $\rho_1=0.9982$, $\gamma_1=72.75$ we find by Eq. (1), $F_S=-11.37$ and by Eq. (6) $t_\infty=0.4806$. By Eq. (10) we get $a_1=0.3949$; $a_2=0.2681$; $a_{12}=0.9768$. Eqs. (32) and (33) give $B_1=0.3894$; $B_3=0.7039$ radians. By Eq. (40) for $R=\infty$ we find $A_1=0.1682$ and Eqs. (34) and (35) give $A_2=-0.5337$; $A_{12}=0.5576$. By Eq. (16) we obtain $f_1=0.29$; $f_2=0.81$; $f_{12}=5.44$, and by Eq. (15) $f=6.54$. Substituting these values into Eq. (27), taking the square root and expanding as a series in powers of $1/R$ we have

$$t=0.4806(1+0.288/R+0.127/R^2).$$

From this, by Eqs. (40), (38) and (39) we find

$$A_1=0.1676(1+0.0063/R)$$

and similar expressions for A_2 and A_{12} by Eqs. (34) and (35). Finally Eq. (28) gives

$$V/\pi R^2=0.4806-0.4029/R+0.0602/R^2,$$

which is the equation of the uppermost curve in Fig. 4.

Some measurements were also made of lenses of purified tetradecane on water at 25°C. The

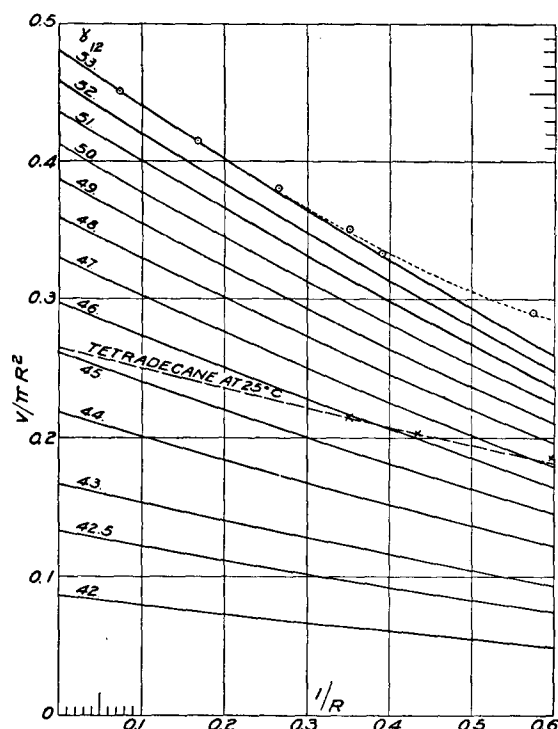


FIG. 4. Calculated curves giving $V/\pi R^2$ (in cm) as a function of $1/R$ (in cm^{-1}) for lenses of petrolatum on water at 20°C taking $\gamma_2 = 31.12$ and the values of γ_{12} marked on the curves. The dashed line is calculated for tetradecane on water at 25°C with $\gamma_2 = 26.9$, $\gamma_{12} = 51.3$. The experimental data for petrolatum are marked by circles and for tetradecane by crosses.

tetradecane from Eastman was found to spread actively on water indicating the presence of hydrophilic substances equivalent to about one percent of stearic acid. Purification was tried by shaking with fuming sulphuric acid and washing with water. About 6–8 treatments gave a sample that did not spread. Agitation with Fuller's earth, and removal of the latter by centrifuging, was found to be far more convenient and effective. The purified material behaves markedly different when placed on water: it does not spread and a large lens shows extraordinary tendencies to break up into small lenses, for example, when touched by a clean wet stirring rod. The points marked by crosses in Fig. 4 give the results of these measurements.

The surface tension γ_2 of tetradecane at 23.5°C by Wilhelmy's method was found to be 27.0 corresponding to 26.9 at 25°C . By choosing various values for γ_{12} and calculating curves for

$V/\pi R^2$, it was found that best agreement with the data was obtained with $\gamma_{12} = 51.3$. This curve is shown as a dashed line in Fig. 4. The data for tetradecane on water at 25°C are: $\rho_1 = 0.9970$; $\rho_2 = 0.7615$; $\gamma_1 = 72.0$; $\gamma_2 = 26.9$; $\gamma_{12} = 51.3$; $F_s = -6.2$; $a_1 = 0.3840$; $a_2 = 0.2690$; $a_{12} = 0.667$; $B_1 = 0.2846$; $B_2 = 0.5626$; $A_1 = 0.0908$; $A_2 = -0.4718$; $A_{12} = 0.3754$; $f_1 = 0.080$; $f_2 = 0.53$; $f_{12} = 1.66$; $f = 2.30$; $A_1 = 0.0908 (1 - 0.004/R)$; $t = 0.265 (1 + 0.187/R + 0.053/R^2)$; $V/\pi R^2 = 0.265 - 0.147/R + 0.0141/R^2$.

EFFECT OF ADSORBED HYDROPHILIC MOLECULES AT THE INTERFACE OF A FREE LENS

It is possible by the following technique to introduce known numbers of molecules of certain hydrophilic compounds into the interface between the lens and the water. A large lens (about 10 to 20 cm in diameter) is placed on the surface of water in a wide tray equipped with a horizontal balance to measure surface forces.⁸ The movable barrier is pushed back and a definite amount of a benzol solution of a spreadable substance, for example, stearic acid, is placed on the water, taking care that the amount added is insufficient to cover the available water surface. By advancing the barrier, the monomolecular stearic acid film can be compressed and pushed into the lens while the force F can be measured by the balance. If an equilibrium state is reached, measurements of the total area (determined by the barrier), the area of the lens, and the surface concentration of the film on the water give data for calculating the number of molecules introduced into the lens.

Instead of attempting to obtain equilibrium between the hydrophilic molecules on the water surface and those in the interface, it is usually better after introducing a desired number of molecules into the interface to remove the excess of hydrophilic material from the water surface (so that $\gamma_1 = \gamma_w$). The escape of these molecules from the lens is usually such a slow process that it does not cause appreciable loss during measurements of the lens diameter.

The molecules thus introduced into the lens, if their number is not too great, distribute them-

⁸ I. Langmuir, J. Am. Chem. Soc. 39, 1848–1906 (1917). See especially p. 1869.

selves uniformly over the interface under the lens, and lower the interfacial tension γ_{12} (without changing γ_2) and thus cause a change in the radius of the lens. From a family of curves such as that shown in Fig. 4, it is then possible from measurements of R and V to determine γ_{12} .

The lowering of the surface tension of pure water by the presence of adsorbed molecules may be usefully regarded as being due to a spreading force F of the two-dimensional gaseous or liquid adsorbed film. Similarly at the interface between water, w , and a hydrocarbon oil, R , we may put

$$F_{12} = \gamma_{wR} - \gamma_{12}, \quad (42)$$

where γ_{wR} represents the interfacial surface tension between pure water and pure hydrocarbon when no hydrophilic substances are present in the interface.

In this way the two-dimensional equation of state of adsorbed molecules at a water-oil interface can be studied in much the same way as has previously been done at the air-water surface.

If the applied surface pressure is sufficiently increased, the molecules can be crowded into the lens in such numbers that some of them leave the interface and become dissolved in the hydrocarbon phase. The distribution of the molecules between the hydrocarbon phase and the interface for changes in γ_{12} should thus be in accord with Gibbs' equation. In a later paper it is planned to report on these investigations.

Let us consider a hydrocarbon lens which is surrounded by water having an uncontaminated surface, but at whose interface with water there is a known surface concentration σ_{12} of adsorbed hydrophilic molecules. The spreading coefficient F_S , as given by Eq. (1) is then

$$F_S = \gamma_w - \gamma_R - \gamma_{Rw} + F_{12}. \quad (43)$$

Let us denote by F_0 the spreading coefficient for the lens on water when hydrophilic substances are absent so that

$$F_0 = \gamma_w - \gamma_R - \gamma_{Rw}. \quad (44)$$

Thus from Eqs. (43) and (44)

$$F_S = F_0 + F_{12}. \quad (45)$$

We have seen that for a paraffin oil, lenses are formed which are about 5 mm thick. As σ_{12} is

increased by adding hydrophilic molecules to the interface so that F_{12} increases, the thickness of the lens, as given by Eqs. (6) and (45), decreases and must approach zero when F_{12} becomes nearly equal to $-F_0$. Thus at a certain critical concentration of adsorbed molecules, free lenses can no longer exist, for the oil spreads out as a film over the whole of the available water surface (unless it thereby becomes monomolecular in thickness).

CONFINED OIL LENSES

Let us consider a large free oil lens with an interface containing adsorbed hydrophilic molecules upon an area of clean water in a tray, this area being limited by a movable barrier and a piston. By advancing the barrier the free water surface can be made to disappear so that the lens covers the whole available area. The lens may then be said to be a *confined* lens. If the area is still further decreased, a force F (dynes cm^{-1}) is exerted against the piston. By the same method as was used in the derivation of Eq. (6) and by using Eq. (45) we see that

$$F = F_0 + F_{12} + (1/2)g\rho_2 t^2(\rho_1 - \rho_2)/\rho_1. \quad (46)$$

By this method of the confined lens it is thus possible to determine F_{12} as a function of σ_{12} . To avoid having the oil creep up onto the piston, it has been found useful to construct a boat-like piston with its edge slightly raised above the water surface. This method for the study of the equation of state of adsorbed molecules at an interface has the following advantages over the free lens method:

(1) It is not limited (as is the free lens method) to the determination of values of F_{12} which are less than $-F_0$.

(2) It permits σ_{12} to be easily and reversibly changed by the movement of a barrier instead of requiring separate experiments involving the production of lenses of different diameters or containing different numbers of hydrophilic molecules.

(3) Because it possesses one more degree of freedom than the free lens method, it permits an independent variation of the film thickness t and so allows any effects dependent on t to be measured.

DUPLEX OIL FILMS $F_s > 0$

If the thickness of the oil film used in the confined lens method is less than about 0.1 mm, the last term in Eq. (46) becomes less than about $0.005 \text{ dyne cm}^{-1}$ and is therefore negligible. The gravitational effect of film thickness thus disappears. We shall call such films *duplex films*. For these films we then have by Eq. (46)

$$F = F_0 + F_{12}. \quad (47)$$

Since F becomes zero when $F_{12} < -F_0$, we see that by the study of duplex films F_{12} can be determined only when $F_{12} > -F_0$.

The concept of duplex films must evidently be restricted to cases where we are justified in considering that the film has an upper surface and a lower surface (interface) which are distinct from one another. However, in view of the small range of molecular forces, it is to be expected that this condition will be fulfilled until the film becomes at least approximately monomolecular. In a later section we shall discuss the conditions under which monomolecular films may be usefully regarded as being duplex films.

EQUATION OF STATE OF ADSORBED ACTIVE GROUPS AT THE INTERFACE

The active groups or heads of the molecules of hydrophilic substances present at low concentration in a liquid hydrocarbon on water tend to occupy positions in the interface. The hydrocarbon chains of these hydrophilic molecules, however, being in an environment of other hydrocarbon chains, have no tendency of their own to go to the interface; they are free to move except that one end of the chain must remain attached to the active group at the interface. The thermal agitation of the heads should tend to cause them to become uniformly distributed over the interface. This tendency must manifest itself as a spreading force F_{12} which could be measured by any agent, such as a piston, which interferes with this indefinite spreading. For sufficiently low surface concentration σ_{12} of the heads in the interface, this force F_{12} should be given by the ideal two-dimensional gas law

$$F_{12} = \sigma_{12} kT. \quad (48)$$

In studies of monatomic caesium films on

tungsten⁹ it has been shown that the finite area occupied by each atom or molecule can be taken into account by modifying this equation to

$$F_{12} = \sigma_{12} kT / (1 - \sigma_{12} / \sigma_M), \quad (49)$$

where σ_M is the maximum concentration corresponding to a close-packed film. If we rewrite this equation in terms of a , the area per molecule instead of the concentration σ we have

$$a = 1 / \sigma_{12} \quad (50)$$

and

$$F_{12}(a - a_0) = kT, \quad (51)$$

where a_0 for our present purposes may be regarded as an empirical constant.

It should be noted that this equation is based upon the assumption that there are no attractive or repulsive forces between the heads except those that prevent any two from occupying the same place at the same time.

Of course at higher concentrations (σ_{12}) it is conceivable that attractive forces between the heads might produce large deviations from Eq. (51) and might even cause the heads to condense into a liquid two-dimensional phase within the interface. Let us therefore estimate the magnitude of the forces between the heads and see if they are large enough to cause deviations from Eq. (51).

The dipole moment of the carboxyl group on an aliphatic chain is¹⁰ about 1.4×10^{-18} e.s.u. The vertical component of the dipole moment per molecule for films of fatty acids on water has been found^{11, 12} to be about 0.2×10^{-18} e.s.u.

Since the force between electrically charged bodies in a medium of dielectric constant ϵ is only $1/\epsilon$ th as great as in free space, the forces between dipoles immersed in water are only $1/80$ th as great as those given by applying Coulomb's law. This decrease is, of course, due to the orientation of the water molecules, each of which has a dipole moment 1.8×10^{-18} . It is the resulting

⁹ I. Langmuir, J. Am. Chem. Soc. **54**, 2798-2832 (1932). See Eq. (59).

¹⁰ Smyth and Rogers, J. Am. Chem. Soc. **52**, 1824 (1930).

¹¹ N. K. Adam and J. B. Harding, Proc. Roy. Soc. **A138**, 411 (1932).

¹² J. H. Schulman and A. H. Hughes, Proc. Roy. Soc. **A138**, 430 (1932).

large attractive force between the water molecules and the carboxyl group that causes the spreading of films of fatty acids on water. Similarly the decrease in the observed dipole moment of the carboxyl group from 1.4 to 0.2×10^{-18} when brought into contact with water is to be looked upon as the effect of the orientation of water molecules, rather than being due principally to an orientation of the carboxyl group itself with respect to the surface as has been suggested by Adam and Harding.

In connection with studies of caesium films on tungsten a general equation has been derived for the spreading force F' resulting from the dipole forces between adsorbed molecules.⁹ The equation there given (Eq. (81)) relates to fictitious dipoles resulting from adsorbed ions and their induced images. For the real dipoles of oil films we should multiply the coefficients by 2 and divide by ϵ the dielectric constant so that the equation becomes

$$F' = (2/\epsilon)(3.34\sigma^{5/2}M^2 + 1.53 \times 10^{-5}\sigma^2T^{1/3}M^{4/3}I), \quad (52)$$

where $I < 0.89$. If we put $M = 1.4 \times 10^{-18}$, $\sigma = 3.3 \times 10^{14}$ corresponding to $a = 30A^2$, $T = 300$ and $\epsilon = 80$, we obtain $F' < 0.7$ dyne cm^{-1} as the effect of the spreading force in modifying F_{12} given by Eq. (51) as a result of the dipole attractions or repulsions between the heads. The value of F_{12} for $a = 30$ and $a_0 = 10$ is 20 dynes cm^{-1} . Considering that the dipoles are probably not so oriented as to produce the maximum attractive or repulsive forces, it appears reasonably certain that the dipole forces in oil films have little effect in modifying Eq. (51) until the heads of the molecules are practically in contact.

EQUATION OF STATE FOR DUPLEX FILMS

If we ignore the distinction between the upper and lower surfaces of a duplex film and consider the spreading force F for the whole film as given directly by the observed force on the piston, we obtain by combining Eqs. (47) and (51)

$$(F - F_0)(a - a_0) = kT. \quad (53)$$

Taking F and a as variables, this is the equation of a rectangular hyperbola with asymptotes at $F = F_0$ and at $a = a_0$. It should be noted

that since negative values of F cannot be observed by the balance method, the portion of the hyperbola below the a -axis cannot be obtained experimentally in the case of duplex films. If, however, we are willing to add a sufficient thickness of pure hydrocarbon to the film to obtain the gravitational effects characteristic of confined lenses, we may determine values of F_{12} less than $-F_0$ by use of Eq. (46) and from these by Eq. (47) can calculate the negative values of F that we cannot observe directly.

EXPANDED FILMS OF MYRISTIC ACID AS EXAMPLES OF DUPLEX FILMS

Fig. 5 contains a family of F - a curves for myristic acid films on 0.01N HCl solution obtained by Adam and Jessop.¹³ The ordinates represent the spreading force F in dynes cm^{-1} , and the abscissas are the areas per molecule in A^2 . The figures marked on each of the curves give the temperatures at which the measurements were made.

Each curve shows a kink which corresponds to the point J in Fig. 1. The curves to the right of these points J are almost exactly rectangular hyperbolas. The constants F_0 and a_0 in Eq. (53) have been chosen separately for each of these curves to obtain as good fit as possible. The values of F_0 so obtained are found to be practically the same over the whole temperature range, the average value being

$$F_0 = -11.2 \text{ dynes cm}^{-1}. \quad (54)$$

The values of a_0 are found to vary with the temperature in accord with the equation

$$a_0 = 12 + 0.178t, \quad (55)$$

where t is the temperature in degrees Centigrade.

Introducing the values of F_0 and a_0 into Eq. (53), F has been calculated as a function of a for each temperature, and the resulting values have been plotted in Fig. 6. In view of the fact that only three adjustable parameters are involved in Eqs. (53), (54) and (55), the agreement between the curves in Figs. 5 and 6 is remarkably good.

The largest discrepancies between the two families of curves are those for the curve at 34.4°

¹³ N. K. Adam and G. Jessop, Proc. Roy. Soc. A112, 362 (1926).

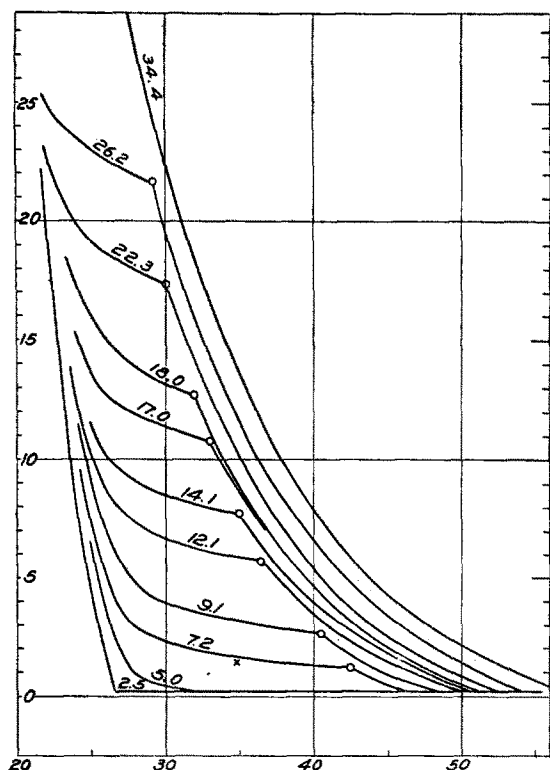


FIG. 5. Experimental F - a curves for myristic acid films on 0.01 N HCl.

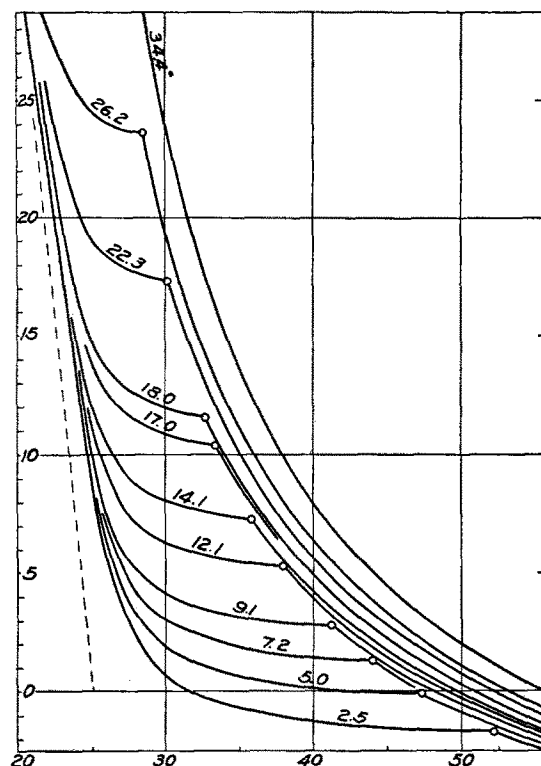


FIG. 6. Calculated F - a curves for myristic acid films.

at values of F greater than 20; these may well be the result of experimental error for these high temperature measurements are difficult. For very low values of F , $F < 2$, the slopes of the curves for the observed data are definitely less than those of the calculated curves. With these exceptions the root-mean-square deviation of the observed and calculated curves is only $0.21 \text{ dyne cm}^{-1}$.

A striking feature of these curves is that the F - a curves cut the horizontal axis at a rather definite angle indicating that any horizontal asymptote must lie at negative values of F .

On the whole the agreement seems to be sufficiently good to justify the belief that these expanded films of myristic acid are essentially duplex films. The thickness of the films varies from 14.6\AA at $a=30$ to 8.8\AA at $a=50$. These thicknesses are far greater than the range of molecular forces exerted by nonpolar molecules. Since the films are liquid and of a thickness much less than the length of the extended molecule, 22\AA , the molecules must be inclined at an average

angle of about 50° from the vertical when $a=30$ and 66° when $a=50$. The molecules are probably just as free to move as they are in the interior of any liquid except that one end of each molecule is constrained to remain at the interphase. It seems reasonable to assume that this constraint is a matter of minor importance which would lead, at most, to an alteration in F_0 , but would not change the character of the phenomenon.

This hypothesis that a liquid monomolecular film of molecules containing long hydrocarbon chains is essentially a duplex film having distinct upper and lower surfaces may be tested in many different ways. In the first place the value of F_0 given by Eq. (54) is in reasonable accord with the value -5.7 which we found for tetradecane. Another test consists of adding to the myristic acid before it is mixed with benzol and spread on water, various proportions of a pure hydrocarbon such as tetradecane. If we are right in considering the film to be a duplex film, the shapes of the F - a curves should remain practically unchanged

except for a small modification due to a slight alteration of F_0 . Some preliminary experiments to test this point have shown that the addition of an equal weight of tetradecane to myristic acid produces no appreciable change in the F - a curves. Some variation in F_0 upon the addition of tetradecane may, however, result from the fact that the CH_3 group at both ends of the tetradecane molecule can occupy positions on the upper surface, while in the myristic acid molecule there is only one CH_3 that could take a position in the upper surface. This should have the effect of reducing γ_R in Eq. (43). This conclusion is based on several lines of evidence that the field of force around a CH_3 group is less than that for a CH_2 radical. For example, the surface tensions of the isohydrocarbons is less than the n -hydrocarbons; the cleavage of crystals of stearic acid, etc., lies along the planes separating the CH_3 groups rather than those separating the CH_2 groups.

TWO PHASE DUPLEX FILMS

Adam's curves for myristic acid in Fig. 5 show a sharp kink at a definite area a_J and at a force F_J , these points corresponding to the point J in Fig. 1.

Such an abrupt change in the direction of a curve must be due to the appearance of a new element in the system such as a new phase.

By measurements of the electric surface potentials Schulman and Hughes* have found some evidence that the film is often observably heterogeneous for areas less than a_J , while for areas less than a_R (see Fig. 1) the film is again homogeneous.

With two phases of constant composition in equilibrium with one another, F should remain constant. It is seen, however, from Fig. 5, that when a is less than a_J each curve has a slope which is definitely not zero. At sufficiently low temperatures, for high values of F , the myristic acid forms condensed films giving curves such as HGB in Fig. 1. It would seem probable, therefore, that the new phase which appears at a is a phase of this type consisting of close-packed molecules. A difficulty with this hypothesis, however, is that this new phase should then be one of constant composition with definite

properties. This would require that the curve RJ should be a horizontal line.

Adam has demonstrated beyond any reasonable doubt that in condensed films of substances containing long hydrocarbon chains which give curves like HA in Fig. 1, the chains are close-packed just as they are in crystals of stearic acid. Myristic acid, however, at low temperatures and especially on pure water gives a break in the curve at G so that the F - a characteristic follows the line GB . Adam regards the area at the point B as being that of the heads.

The strong spreading tendencies of the fatty acids prove that the carboxyl group attaches itself very firmly to water. In the preceding section it was seen that the agreement of the data with Eq. (53) indicates that the forces acting between the carboxyl groups in the expanded films are very weak. This must mean that some of the water molecules become so oriented so as to neutralize the moment of the carboxyl group. Very strong forces must then exist between these carboxyl groups and the water molecules. From this point of view as the film is compressed to an area less than a_B , the decrease in area is due to the progressive squeezing out of these water molecules until at the point G all the water has been removed from the spaces between the carboxyl groups. A suggestion of this kind has also been made by Schulman and Hughes.*

The tendency of fatty acid films to form condensed films increases as the chain length increases. We may assume that the energy involved per molecule, when the chains become close-packed, as at the point G , is proportional to the length of the chain. This energy is a kind of heat of fusion and should be of the same order of magnitude as that involved in the solidification of such substances as stearic acid.

With these facts in mind we may now understand the nature of the curve JR . At the point J the chains of the fatty acid molecules in the film begin to assume the close-packed arrangement in which the molecules have a cross-sectional area of 20.5\AA^2 . The heads of the molecules, however, because of their hydrated carboxyl groups, cannot space themselves on the surface of the water closer than 25.4\AA^2 . The solidification process,

* Reference 12, p. 443,

* Reference 12, p. 449.

therefore, can only proceed to a small extent by forming groups of molecules or micelles of the type represented diagrammatically in Fig. 7.

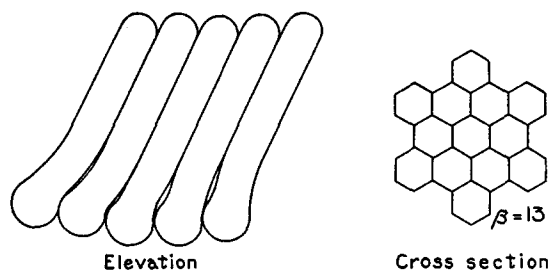


FIG. 7. Diagrammatic representation of a micelle.

The crowding apart of the lower ends of the molecules cannot prevent the upper parts of a few adjacent molecules from arranging themselves as in condensed films, but no large number of molecules can gather together in this way because of the crowding apart of the heads. The new phase that appears at the point J , therefore, consists of micelles containing relatively few molecules. Because the molecular weight of these micelles is not indefinitely large, they therefore exert a pressure which adds itself to that of the phase of single molecules. Strictly speaking, the film between R and J is not a two-phase system, but is a mixture of two two-dimensional gases, one consisting of normal molecules and the other consisting of micelles, each of which contains β molecules. The kink at J is due to the sudden appearance of the micelles at this point. On the basis of these hypotheses we may readily calculate the shape of the curve that we should expect between R and J .

THE SPREADING FORCE F_β DUE TO THE MICELLES

Consider an interface having a total area S between a hydrocarbon liquid and water and let n be the total number of molecules in the interface which act as molecules in a two-dimensional gas, then the area per molecule is given by

$$a = S/n. \quad (56)$$

Now let us consider that the n molecules in the surface exist partly as single molecules and are partly gathered into micelles, each of which contains β -molecules. Let us assume further that

an equilibrium exists between the micelles and the single molecules such that the partial spreading force F_1 of the single molecules remains constant as long as the micelles are present. Let S_J be the total area at which the micelles first appear as the area is decreased. We may thus put

$$a_J = S_J/n, \quad (57)$$

where a_J is the area per molecule at the point J (Fig. 1) when the whole surface is covered with single molecules giving a spreading force F_1 . Let S_R be the area of the film when it is compressed to such a point that the single molecules disappear so that all the molecules are present as micelles. The number of micelles is then n/β , and each of these covers the area $\beta S_R/n = \beta a_R$. Let us now consider the intermediate stages where $S_R < S < S_J$. Let n_1 be the number of single molecules and n_β the number of micelles. We then have the equation,

$$n_1 + \beta n_\beta = n. \quad (58)$$

We may derive a second equation involving the areas covered by the molecules and by the micelles. Since the partial pressure F_1 remains constant, each of the n_1 single molecules requires the same area a_J as it does when the film area is S_J , whereas each micelle covers the area βa_R . The total surface areas, according to Eq. (56), gives an , and this must be equal to the area required by the single molecules and the micelles. We thus have

$$n_1 a_J + \beta n_\beta a_R = an. \quad (59)$$

Let σ_1 and σ_β be the surface concentrations of the single molecules and of the micelles. We then have

$$\sigma_\beta = n_\beta/S; \quad \sigma_1 = n_1/S. \quad (60)$$

Combining these equations with Eqs. (58), (59) and (56) and then dividing by S we obtain

$$\sigma_1 + \beta \sigma_\beta = 1/a, \quad (61)$$

$$\sigma_1 a_J + \beta \sigma_\beta a_R = 1. \quad (62)$$

Solving these equations for σ_1 and σ_β we find

$$\sigma_\beta = (1/\beta a)(a_J - a)/(a_J - a_R), \quad (63)$$

$$\sigma_1 = (1/a)(a - a_R)/(a_J - a_R). \quad (64)$$

The partial pressure F_β of the micelles in accordance with Eq. (49) may be written

$$F_\beta = \sigma_\beta kT / (1 - \sigma_\beta / \sigma_{\beta R}), \quad (65)$$

where $\sigma_{\beta R}$ is the concentration of micelles at the point R . Since the number of micelles is then n/β we have by Eq. (56)

$$\sigma_{\beta R} = n / \beta S_R = 1 / \beta a_R. \quad (66)$$

Substituting the values of $\sigma_{R\beta}$ and σ_β from Eqs. (66) and (63) into Eq. (65) we obtain

$$F_\beta = kT(a_J - a) / \beta a_J(a - a_R). \quad (67)$$

Thus between J and R the curves should be given by

$$F = F_J + F_\beta, \quad (68)$$

where F_β is given by Eq. (67).

Examination of the curves in Fig. 5 shows that they are of the type required by this theory. There is a sharp kink at J as the theory would indicate but there is no kink at R where the curve joins the line GB , the approach to this line being asymptotic because of the denominator in the second member of Eq. (67).

The values of β have been calculated from Adam's data of Fig. 5. For this purpose the values of a_R were assumed to lie along a straight line like GB in Fig. 1 with a value of a_B of $25A^2$. Thus

$$a_R = 25 - 0.156F. \quad (69)$$

The values of β obtained in this way from the experimental data on F and F_J by Eqs. (67) and (68) varied from about 9 to 18. For values of a only slightly greater than a_R the accuracy of these determinations of β is naturally not large for it depends too much on the rather arbitrarily assumed value of a_R .

If we may assume that the molecules tend to arrange themselves in a hexagonal lattice like a honeycomb, each molecule should be surrounded by six others and the next ring of molecules should also contain 6. The number of molecules in a micelle may thus naturally be assumed to be 7 or 13. The value $\beta = 13$ is approximately the average of the values found from the data of Fig. 5.

TWO-DIMENSIONAL VAPOR PRESSURE OF THE MICELLES

The points J in Fig. 5 thus correspond to the two-dimensional vapor pressures of the micelles, that is, to the value F_1 , the spreading force due to the single molecules in equilibrium with micelles. If we examine Fig. 5 we see that the points corresponding to J decrease steadily as the temperature is lowered and become zero at a definite temperature of about 6° . This is a very unreasonable behavior for a vapor pressure. When we consider, however, that the true vapor pressure is exerted at the interface, we see that the observed spreading force F does not measure this pressure. The value of F_1 is thus given by

$$F_1 = F_J - F_0. \quad (70)$$

With the data for F_J in Fig. 5 and by using the value of F_0 from Eq. (54) the logarithms of $(F_J - F_0)$ have been plotted against the reciprocals of the absolute temperature. As is usual for vapor pressure curves, a straight line was obtained; this corresponded to the equation

$$\log_{10} (F_J - F_0) = 8.058 - 1950/T. \quad (71)$$

The fact that these vapor pressures measured from F_0 agree with the Clapeyron equation, whereas the uncorrected values do not, affords further justification for regarding these myristic acid films as duplex films.

The values of F_J calculated from Eq. (71) have been used to fix the points J given in Fig. 6 which are marked by small circles. Comparing Figs. 6 and 5, it will be seen that the agreement is probably nearly within the experimental error.

With these values of F_J and a_R , as given by Eq. (69) and by taking $\beta = 13$, the curves in Fig. 6 to the left of points J have been calculated by Eqs. (67) and (68). The general agreement between the slopes of these portions of the curves and those given by the experiments indicates that the value of β is approximately constant and equal to 13. The reasonableness of this value of β thus helps justify the hypothesis that in this two-phase system the condensed phase consists of micelles.

Comparing the curves of Figs. 6 and 5 we see that there are considerable discrepancies at temperatures of 5 and 2.5° and in general at very

TABLE I. Expanded films of fatty acids on dilute HCl at $F=1.4$ dynes cm^{-1} .

Acid	1 No. of C atoms n	2 $a_{1.4}$	3 t_0 $^{\circ}\text{C}$	4 $t_{\frac{1}{2}}$ (obs.)	5 a_0	6 $-F_0$	7 $(-F_0)$ (calc.)	8 $t_{\frac{1}{2}}$ (calc.)
Lauric	12	47.6	14.7	$<0^{\circ}\text{C}$	14.6	10.4	10.8	-9.0
Tridecylic	13	44.6	13.5	<0	14.4	11.4	12.1	+0.2
Myristic	14	43.7	21.0	9	15.7	13.0	13.4	9.6
Pentadecylic	15	42.1	23.9	19.5	16.2	16.2	14.7	18.8
Palmitic	16	41.5	34.8	28.5	18.1	16.5	16.0	28.2
Margaric	17	42.2	42.2	37.5	19.4	17.5	17.3	37.4
Stearic	18	43.0	52.8	46.	21.3	19.2	18.6	46.6
Heneicosoic	21	46.7	78.0	65.5	25.8	21.6	22.5	74.2
Behenic	22	46.0	75.0	72.5	25.3	21.6	23.8	83.2

low values of F . The probable reason for these deviations will be discussed later.

ADAM'S DATA FOR OTHER FATTY ACIDS

For the other saturated fatty acids Adam has not published full curves such as those of Fig. 5 for myristic acid, but gives merely the area $a_{1.4}$ of the expanded films at a standard small compression of $F=1.4$ dynes cm^{-1} and at some temperature t_0 distinctly above the range at which expansion at this compression occurs. He also gives the temperature $t_{\frac{1}{2}}$ at which half the expansion from the condensed to the expanded film has occurred at $F=1.4$. The data of the first four columns in Table I are those of Adam.¹⁴ The value of $a_{1.4}$ for myristic acid is about 9 percent lower than the value given in his later papers, as shown in Fig. 5, so that exact comparison with our foregoing analysis is not possible.

Taking a_0 as given by Eq. (55) and as tabulated in column 5, we may calculate F_0 by means of Eq. (53) from Adam's data on a and T after placing $F=1.4$. These values, which are given in the 6th column, when plotted against n , lie roughly along a straight line corresponding to

$$F_0 = 4.8 - 1.3n. \quad (72)$$

The 7th column gives the values of $-F_0$ calculated by this equation. It is seen that $-F_0$ increases 1.3 dynes cm^{-1} for each additional carbon atom. This agrees approximately with the increment of 1.5 which Harkins⁶ found for $-F_S$ between hexane and octane.

The temperatures $t_{\frac{1}{2}}$ as given in the 4th column may be used to generalize Eq. (71) for all

saturated normal fatty acids. Referring to Fig. 5, the point marked by a cross just below the curve for 7.2° represents half expansion at $F=1.4$ for it lies about halfway between the intersections with the curves corresponding respectively to JM and GB in Fig. 1. These data thus give about 7.0 for the temperature of half-expansion. The value of F_J at this temperature is evidently about 0.4 lower than $F=1.4$, so that the spreading force F_1 of the micelles, as defined by Eq. (70) is to be taken as $1 - F_0$.

Eq. (71) may be written

$$\log_{10} F_1 = 8.058 - B_n/T, \quad (73)$$

where B_n is a constant which depends upon n , the number of carbon atoms in the fatty acid molecule. Taking the values of $-F_0$ from the 7th column of Table I, adding 1 to get $-F_1$, substituting this in Eq. (73) together with the value of T corresponding to $t_{\frac{1}{2}}$ enables us to determine B_n for each acid. These values plotted against n give roughly a straight line corresponding to

$$B_n = 1208. + 53.n. \quad (74)$$

To show how well these values agree with the experimental data, they have been used in Eq. (73) to calculate (from F_0 in column 7) the temperatures of half-expansion which are given in the 8th column. The agreement with the data of the 4th column is good except for the last two acids where, as Adam points out, the experimental accuracy is much less. The values of B_n in Eq. (74) correspond to a heat of "evaporation" for the micelles of $5.52 + 0.242n$ kg cal. per mole or $(3.82 + 1.67n)10^{-14}$ erg per molecule.

The large value for the constant term in these expressions (5.52 kg cal.) suggests that more than

¹⁴ N. K. Adam, Proc. Roy. Soc. A101, 521 (1922).

half of the energy of formation of the micelles is due to attractive forces between the carboxyl groups when they are in contact. The increment of 0.242 kg cal. per mole for each CH_2 should correspond roughly with the heat of fusion of the hydrocarbons which is 0.60 kg cal. per CH_2 .^{14a} Referring to Fig. 7 we see that when 13 hexagons are closely packed, 30 out of the original 78 hexagonal faces are still free. The contribution to the heat of formation of the micelle should thus only be 48/78ths of 0.60 or 0.37 kg cal. per CH_2 , even if the solidification were as complete as in a large crystal. The experimental increment 0.242 which is thus 2/3 of the heat of fusion helps justify our hypothesis of the cause of the micelle formation.

It is possible by the methods we have given for myristic acid, applied to the data contained in Eqs. (55), (72), (73) and (74), to construct the whole family of F - a curves for any saturated normal fatty acid. When experimental data are available, it will be interesting to compare them with these predicted curves.

For unsaturated fatty acids on dilute HCl, Adam¹⁴ gives the data contained in the first four columns of Table II. For oleic acid on dilute

TABLE II. *Unsaturated fatty acids.*

Acid	1 n	2 $a_{1.4}$	3 t	4 t_1	5 $-F_0$	6 a_0	7 B_n
Iso-oleic	18	46	35°C	25	18.6	24.9	2016
Oleic(trans)	18	52.5	10	<0	(11.2)	21.7	(1700)
Elaidic(cis)	18	47	10	-0.5	14.0	(21.7)	1875
Erucic(trans)	22	47	10	4.5	16.4	25.2	1892
Brassicic(cis)	22	45	40	34.	19.2	22.6	2073

HCl at 15° Adam and Jessop have given a complete curve¹⁵ which agrees within a standard deviation (S.D.) of 0.24 dyne cm^{-1} with Eq. (53) if we take $a_0=19.9$ and $F_0=-11.2$. For the corresponding saturated acid (stearic) at this temperature, we should have, by Eqs. (55) and (72), $a_0=14.7$ and $F_0=-18.6$. Thus the effect of introducing the double bond in the middle of the hydrocarbon chain has been to increase a_0 by 5.2 and to decrease $-F_0$ by 7.2. The increase in

a_0 indicates that the double bond tends to occupy a position on the water surface in accord with the known fact that the effect of a double bond is to increase the solubility of a hydrocarbon derivative in water.

Although for the other unsaturated acids, since only $a_{1.4}$ is given, we cannot determine a_0 and F_0 separately, we may draw certain tentative conclusions.

Taking F_0 for oleic acid to be -11.2 from the more complete later data, we calculate, by Eq. (53), $a_0=21.7$. The difference in $a_{1.4}$ for oleic and elaidic acids is probably due to a change in F_0 rather than to one in a_0 . We thus take $a_0=21.7$ for elaidic acid and find the value of F_0 given in the 5th column. For the corresponding acids with 22 carbon atoms, assuming the increment of 1.3 per CH_2 as in Eq. (72), we take a value of $-F_0$ 5.2 units greater than for the 18 carbon acids. For iso-oleic acid with the double bond between the α , β -atoms, F_0 has been taken to be the same as for stearic acid. The variations in the resulting values of a_0 are probably of no significance, since the data for $a_{1.4}$ are uncertain by about 2 units (Adam), but that they are on the average 7.5 ± 2.5 larger than the values given for the saturated acids by Eq. (55) indicates that the general effect of the double bond is to raise a_0 .

The values of B_n in the 7th column have been calculated from t_1 and $1-F_0$ by Eq. (73). They should be compared with the values of 2162 for stearic and 2374 for behenic acid given by Eq. (74) for $n=18$ and 22, respectively. The effect of the double bond near the carboxyl group in iso-oleic acid is to lower B_n by 146 which is equivalent to a decrease in n of 2.8. A double bond near the middle of the chain lowers B by an average of 294 (equivalent to a decrease of 5.6 in n) in the case of the cis-compounds elaidic and brassicic acids, while in the trans-compound erucic acid the decrease is 482 which corresponds to the effect of shortening the chain by 9.1 CH_2 groups.

These very large and specific effects of the double bonds near the middles of the chains are in striking contrast with the small changes produced on the JK part of the curve as derived from the data for $a_{1.4}$. This latter part depends only on F_0 and a_0 , whereas the value of F_J at any temperature (which determines B) involves all the factors that determine the stability of the

^{14a} W. E. Garner, K. Van Bibber and A. M. King, J. Chem. Soc. (1931), 1533.

¹⁵ N. K. Adam and G. Jessop, Proc. Roy. Soc. A120, 473 (1928).

micelles. Any irregularity in the chain naturally affects the ease with which the molecules can pack into a micelle.

COMPOUNDS WITH MULTIPLE CHAINS

In condensed films of such substances as tristearin, glycol dipalmitin, etc., which have two or more chains of equal lengths, each chain occupies the area $20.5A^2$ so that the area for a whole molecule increases in proportion to the number of chains. With expanded films, however, the area depends only on a_0 and F_0 and thus, according to Eq. (53), should not be expected to increase in proportion to the number of chains even if a_0 does so. Adam finds that the area at no compression is 135 for triolein at 15°C, while for tristearin and tripalmitin at 60°C it is 115. He notes that these areas are about 2.4 instead of three times the areas of the "corresponding compounds with single chains."

Adam¹⁶ has given a complete curve for glycol dilaurate at 15°C which agrees within about $SD=0.2$ dyne cm^{-1} with Eq. (53) if we take $a_0=39$ and $F_0=-8.5$. Comparing this with the data for lauric acid in Table I we see that the value of a_0 has been increased very greatly, from 15 to 39, while $-F_0$ has decreased by 2 units. Adam and Jessop's curve for triolein¹³ gives best agreement with Eq. (53) (rather poor) with $a_0=90$ and $F_0=-8.5$.

THE EFFECT OF UNEVEN UPPER SURFACE

Films prepared from mixtures of cholesterol and myristic acid¹⁵ on dilute HCl give areas less than the sum of those obtained from the constituents separately.

Cholesterol consists of large compact molecules that form a condensed film with an area of 40.8 and a thickness of 15.3 \AA . An expanded myristic acid film of an area $a=47$ has a thickness of 9.3. In the mixed film the large molecules thus extend through the film and tend to produce humps in the upper surface. If the total area of the upper surface is increased, for example, 10 percent, from this cause, and the surface tension of the upper surface is 50 dynes cm^{-1} , the effect is to increase $-F_0$ by 5 dynes cm^{-1} . This may

perhaps be the main cause of the decrease in area of the expanded films containing cholesterol. Similar effects were observed when tripalmitin and other large molecules were used instead of cholesterol. The three chains in tripalmitin being attached at one end must lie closer than if unattached and produce a local thickening of the film.

The micelles present in the *JR* portion of the curves of expanded films should also tend to cause an uneven upper surface. This effect should be especially marked when F_J is small, that is, at low temperatures, for then the film of single molecules is so thin that the micelles rise above it. It appears probable that the deviations between the curves in Figs. 5 and 6 at low values of a and at low temperatures are due to this cause.

THE EFFECT OF LARGE HEAD GROUPS IN DECREASING β

For para-dodecyl-phenol a family of curves have been obtained¹⁷ like that for myristic acid. The area at no compression is, however, unusually small ($a=36$). The *JK* part of the curves at 30°C gives $a_0=16.3$, $F_0=-20$. This large value of $-F_0$ explains the small value of a at $F=0$. The *JR* portions are far steeper than those of myristic acid and are found to correspond to micelles for which $\beta=5\pm 1$. This low value is in accord with the presence of the phenyl group in the head which should restrict the number of chains that can unite in a micelle. The value of B_n is 1970.

A similar example of the effect of a large head group in reducing the value of β is furnished by the data¹³ on the α -bromo-fatty acids. For the acid containing 17 carbon atoms, at 15° the *JR* portion of the curve gives a value $\beta=7$. The *JK* portion gives $a_0=17.1$; $F_0=-13.7$.

FILMS OF ESTERS AND VAPOR EXPANDED FILMS

A family of curves is also given for mono-palmitin.¹⁷ The *JK* portions agree well with Eq. (53) ($SD=0.3$) when $a_0=22$ and $F_0=-8.8$. The area at no compression, in accord with these

¹⁶ N. K. Adam, Proc. Roy. Soc. A126, 366 (1930).

¹⁷ N. K. Adam, W. A. Berry and H. A. Turner, Proc. Roy. Soc. A117, 532 (1928).

values, is large ($a=67$). The values of $F_J - F_0$ furnish, by Eq. (74), the value $B_n = 2052$. When the values of F_J are then calculated by this equation at the four temperatures (from 16 to 37°) at which the experiments were made, the calculated and observed values agree with an S.D. of 0.13 dyne cm^{-1} , although only one adjustable parameter is available in these calculations.

The *JR* portions of the curve are fairly flat. Calculation shows that $\beta = 13.5 \pm 2$. The magnitude of β seems to depend very largely on whether or not the F - a curve for the condensed film possesses a *GB* branch (Fig. 1). We have concluded that the line *GB* is due to the hydration of the heads. If there is little or no hydration, the F - a curve follows the line *GA*. The fatty acids and particularly the α -bromo acids show a very distinct *GB* line with values of a_B of about 26 which indicate that the carboxyl group has a strong tendency to be hydrated and then occupies an area distinctly greater than 20.5. With the alcohols the point *B* lies at about $a = 22$. Thus the larger size of the head in the mono-palmitin as compared to the acids is offset by a lower degree of hydration.

The effect of replacing the hydrogen atom in the carboxyl group of the fatty acids by a methyl group is to lower the expansion temperature t_4 by one or two degrees, while an ethyl group produces a lowering of 15°. This indicates that the tendency to form micelles is decreased very greatly by the presence of an ethyl or higher group in the ester chain. The condensed films of these esters show, however, an area of 20.5 so that the fact that the —COO— group must be pulled away from the water in the formation of the micelles (as in the condensed films) explains the lesser stability of the micelles.

Another interesting feature of these ester films is that the *GB* section of the curve is wholly absent in the condensed films and as a result of this lack of hydration the values of β are very large (the *JR* lines are flat). This means that the expanded film passes to the condensed state more nearly as a definite change of phase instead of by the growth of micelles. The curves for propyl palmitate give $a_0 = 12$, $F_0 = -4.8$, $B_n = 2000$, and $\beta = 60$. For ethyl palmitate¹³ similar data give $a_0 = 12$, $F_0 = -5.7$, $B_n = 2059$ and $\beta = 55$.

The small values of $-F_0$ for these esters are presumably due to a lack of sufficient flexibility of the molecule in the neighborhood of the —COO— group to allow both chains to assume a steep angle to the water surface. With glycol dilaurate and triolein the larger value of $-F_0 = 8.5$ results from the additional linkages between the two chains by which greater flexibility can be attained.

The marked effect of attachment to the water in the middle of a chain in decreasing $-F_0$ is best illustrated by the data which Adam and Jessop have given¹³ for films of oleic acid on acidulated water containing potassium permanganate. The oxidation of the double bond gives strong attachment to the water near the middle of the chains. The curve at 15° yields $a = 27.1$ and $-F_0 = 2.2$, which is the lowest value derivable from any of Adam's curves.

The films which Adam has called *vapor expanded* films are evidently merely those which are characterized by very low values of $-F_0$. At low compressions the curve then extends to such large values of a that the film becomes so thin that the molecules lie nearly flat on the surface before F falls to zero. Thus the films can no longer be considered duplex films and it is not surprising that they should merge into true gaseous films without the abrupt change of slope that characterizes typical (liquid) expanded films.

FACTORS WHICH DETERMINE a_0

In the foregoing analysis of the experimental data a_0 has been treated as an empirical constant, although its derivation from Eq. (49) would suggest that a_0 should have the value of a which corresponds to a close-packed film. The empirical values of a_0 are usually less than this.

The fact that no two molecules in a monomolecular film can be in the same place at a given time indicates the existence of repulsive forces of very short range. Such forces yield a term a_0 which should correspond to the value of a for a condensed film (at least for fairly concentrated films).⁹

We have seen, however, particularly in our discussion of Eq. (74) that in the formation of the micelles there is evidence of short range attractive forces between carboxyl groups. Such forces

should tend to counteract the effect of the repulsive forces at contact and thus tend to *decrease* the value of a_0 . We should therefore not attach too much significance to the actual values of a_0 but may well interpret the differences in a_0 for different substances as indications not only of the relative sizes of the active groups, but also of the magnitude of the forces between them.

FLEXIBILITY OF HYDROCARBON CHAINS

Adam has summarized¹⁶ the evidence that the chains are flexible. The fact that the upper and lower surfaces of duplex films of a thickness of only 5–10 \AA ² can act nearly independently just as in a thicker film of liquid is perhaps still more convincing evidence.

In a series of papers Staudinger¹⁸ and his coworkers have developed a theory of the viscosity of solutions of high polymeric compounds which is based on the assumption of long rigid molecules. It would seem that such theories require revision. Perhaps it is the shearing stress in a liquid during viscosity measurements that pulls a very long molecule into a nearly straight line and thus, in part, justifies the theoretical derivation of the equations.

NOTE ON ANTONOFF'S RULE

Antonoff's rule¹⁹ states that for true equilibrium $F_s = 0$. As Harkins and others have pointed out, this cannot be true in general. For example, for a pair of liquids A and B there are two spreading coefficients: for lenses of A on B , $F_{SA} = \gamma_B - \gamma_A - \gamma_{AB}$, while for lenses of B on A , $F_{SB} = \gamma_A - \gamma_B - \gamma_{AB}$. Both spreading coefficients can be zero only when $\gamma_{AB} = 0$, i.e., when the liquids are miscible.

It is nevertheless a fact that F_s is extremely close to zero for very large numbers of organic liquids placed on water and *in equilibrium* with it, so that as a useful empirical rule Antonoff's rule is justified.

If the molecules of a vapor of an organic liquid, when they strike a water surface, form an adsorbed film which nearly completely covers the surface, then some molecules must condense on

top of those already adsorbed. We then have two cases to consider:

(1) The molecules in the 2nd layer may have a shorter life t (before evaporating again) than the life t_0 of molecules on the surface of the organic liquid.

(2) The life t of the molecules may be equal to or greater than t_0 .

In the 1st case the 2nd layer of molecules will not become complete so that $F_s < 0$, while in the 2nd case the 2nd layer and therefore presumably a 3rd and 4th layer, etc., will grow in presence of saturated vapor until the water is covered by a liquid film and therefore $F_s = 0$.

According to the principle of independent surface action²⁰ which the writer has so often employed, the properties of a surface depend primarily on the atoms or groups of atoms actually forming the surface and depend on the underlying layers only insofar as they alter the actual surface atoms. Thus in general the properties of the upper surface of an adsorbed monomolecular film are nearly the same as those of the substance in bulk. This may be illustrated by some examples.

Carbon tetrachloride vapor forms an adsorbed monomolecular film on water which tends to become nearly complete before the vapor becomes saturated. The properties of the upper surface of the film thus approximate to that of liquid carbon tetrachloride, so that the life t of molecules of CCl_4 which may condense on the film is about the same as that of molecules on liquid CCl_4 . Thus the film grows in thickness which means that $F_s = 0$.

Orientation of the molecules in the adsorbed film may make t for the second layer very different from t_0 . Thus lenses of molten palmitic acid on water, although in equilibrium with it, do not spread indefinitely. This is due to the fact that the orientation and tight packing of the molecules in the film on the water has the effect of preventing the carboxyl groups of any vapor molecules incident on the surface from coming into contact with other carboxyl groups. On the other hand a molecule striking a surface of liquid palmitic acid can more easily penetrate the less tightly packed surface layer and thus its carboxyl

¹⁸ H. Staudinger and E. Ochial, *Zeits. f. physik. Chemie* **A158**, 35 (1931).

¹⁹ Antonoff, *J. Chim. Phys.* **5**, 372 (1907). Bartell, Case and Brown, *J. Am. Chem. Soc.* **55**, 2769 (1933).

²⁰ I. Langmuir, *Chem. Rev.* **6**, 467 (1929); also *Colloid Symposium Monographs* **3**, 48 (1925).

can meet other carboxyls. Thus t for molecules in the 2nd layer of the adsorbed film is less than t_0 and therefore $F_s < 0$.

A corollary of this point of view is the conclusion that if, for two immiscible liquids A and B , A is strongly adsorbed (from a saturated vapor) on B then the vapor of B cannot be strongly adsorbed on A (since both F_{sA} and F_{sB} cannot be zero).

The frequency with which strong adsorption occurs and the relatively small effects on the lives t produced by orientation is thus the fundamental reason that Antonoff's rule is so often applicable.

Of course there are numerous cases such as that of the higher hydrocarbons and water where only a negligible adsorption of either vapor by the other liquid occurs. Such cases are usually those yielding large negative values for F_s .