SURFACE FILMS OF FATTY ACIDS, ALCOHOLS, AND ESTERS[1]

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CONTENTS

I. INTRODUCTION

Important information concerning the molecular structure of fats and oils has been obtained by the use of x-rays, of electron diffraction, and of surface films. In the applications of these substances in industry and in everyday life the intermolecular structure, that is, the pattern according to which the molecules are fitted together, is fully as important as the structure of each individual molecule. While the x-ray method gives remarkable results if applied to crystalline material in bulk, and some information of value with liquids, the investigation of two-dimensional systems reveals the superiority in this case of the use of electron diffraction and the study of surface films. Beams of slow electrons are best suited to the study of extremely thin films, but unfortunately no investigator has as

yet mastered both the technique and the theory of the use of slow electrons, that is, of energies from 10 to 1000 electron volts (e.v.), for this purpose. What has been revealed by x-rays, by electrons of energies of the order of 40,000 e.v., and by the study of surface films shows that within the limits of our power of interpretation all three methods agree with each other whenever they have anything in common.

II. THE SPREADING OF OIL FILMS ON WATER

A. Oxidized oils

If a drop of fresh Nujol, a heavy hydrocarbon oil, is put on a clean surface of water it does not spread, but remains as a thick lens. If the Nujol has been oxidized by air by stirring it in an evaporating dish over a flame, it is found to spread as a uniform polymolecular film over a considerable area. If, for example, the area of the surface of the water in a rectangular trough is 5×10^3 cm.^{2}, a small drop of this oil spreads over the surface to form an invisible film, which, on moderate decrease of area on compression by the use of a movable barrier, exhibits a uniform light yellow color in white light. On compression the color changes to dark yellow, gold, red purple, blue, and green, and these colors then repeat themselves as the spectrum moves through four or more orders, but in the higher orders the colors red and green become much the most prominent. On further thickening, the film becomes colorless. An experiment such as is described involves films of a uniform optical thickness between a few hundred and several thousand Ångström units. The limits of thickness are much greater than this.

Such polymolecular liquid films may be designated as duplex, since their upper and lower surfaces are far enough apart to make their surface energies entirely independent of each other. Thus the total free energy, γ_d, of unit area of the duplex film of a liquid b on a liquid a is given by the expression:

$$\gamma_d = \gamma_b + \gamma_{ab} \tag{1}$$

Such a duplex film is, in general, unstable. Thus an oil film on water which exhibits a single diffraction color is always found to segregate into regions of varied thickness, and therefore of varied colors, at the end of a period which varies from a few seconds to a few weeks. In order to understand what occurs, a knowledge of the thermodynamics of films is essential.

If a crystal of an organic acid, an alcohol, or an ester is placed on the surface of clean water, it is found to spread as a monolayer. Oleic acid seems to spread to some extent as a duplex film, but the monolayer spreads

more rapidly and therefore ahead of the duplex film, which changes rapidly to a monolayer and lenses.

B. General theories

There are three theories of the spreading of oil on water which should be considered.

1. Rayleigh's theory (18, 22, 23): All liquids spread on the surface of clean water. To prevent spreading, it is necessary to have a foreign substance on the surface.

2. Langmuir's theory (16, 17): Non-polar liquids, such as the hydrocarbons, do not spread on water, but if the molecules contain a polar group and a non-polar group, the liquid will spread.

3. The general thermodynamic theory of Harkins (8, 11), which is not limited, but applies to all liquids, to the spreading of solids on liquids, and to the spreading of mobile films on solids. The theory is based on the concept that there are two types of spreading:[2] (A) Duplex (D) spreading: a liquid, such as benzene or the oxidized Nujol already considered, may spread as a duplex film. The thermodynamic relations indicate that this is unstable and always transforms into a non-duplex film (a monolayer) and a lens or lenses. (B) Non-duplex (or M) spreading: a non-duplex film may spread directly from a three-dimensional solid or liquid, or it may be formed by the transformation of a duplex film. All non-duplex films of known thickness are monolayers.

Duplex spreading: The theory of the spreading of a duplex film may be stated in the following abbreviated form: If a drop of an insoluble oil (b) is placed on a clean water (a) surface, it may or may not spread. The condition which determines whether or not the oil spreads is exceedingly simple. *If the oil likes itself (W_{c_b}) better than water (W_A) it will not spread, while if it likes the water better than itself, it will spread.* In order to use this relation in a quantitative sense it is essential to express the term "likes" as a thermodynamic quantity, which is done in the following equation:

$$S_{b/a} = -(\partial F/\partial \sigma)_{p,T} = W_A - W_{c_b} \qquad (2)$$

Here $-(\partial F/\partial \sigma)_{p,T}$ is the rate of decrease of the free energy (F) of the system with increase of area (σ) of the duplex film, and the concomitant decrease in the area of the clean surface of the water. W_A is the work

[2] Hardy (5) also assumed two types of spreading: primary, which corresponds to non-duplex, and secondary, which corresponds to duplex. One of the principal differences is that Hardy assumed non-duplex films to be moderately thick, while here they are assumed to be monomolecular in general.

required to pull the oil and water apart over an area of 1 sq. cm., and W_c is that required to rupture a bar of oil with a cross section of 1 sq. cm. of surface of the oil (figures 1 and 2). A consideration of these processes gives values for W_A and W_c as follows:

$$W_A = \gamma_a + \gamma_b - \gamma_{ab} \quad \text{(Dupré's equation (3))} \tag{3}$$

$$W_{c_b} = 2\gamma_b \tag{4}$$

so

$$S_{b/a} = \gamma_a - (\gamma_b + \gamma_{ab}) \tag{5}$$
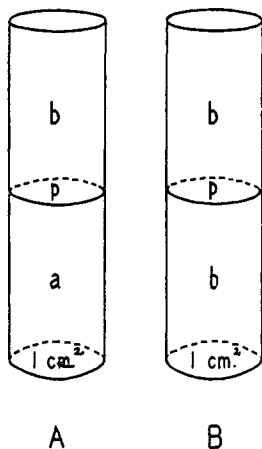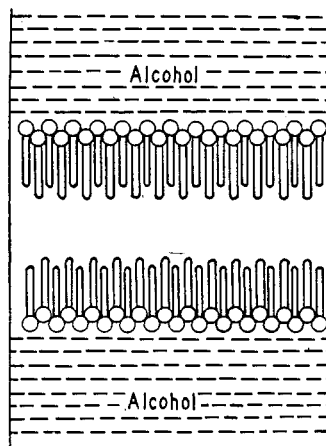

FIG. 1   FIG. 2

FIG. 1. (A) If the liquid b is pulled from the liquid a at the plane p, the increase in free energy is $\gamma_a + \gamma_b$ in the ideal case in which the liquids are completely separated from each other. There is a concomitant decrease of free energy equal to γ_{ab}, due to the destruction of the interface of ab. The work done (W_A) equals the net increase in free energy, or $W_A = \gamma_a + \gamma_b - \gamma_{ab}$. (B) If the liquid b is pulled apart at the plane p, the increase in free energy is $2\gamma_b$, or $W_c = 2\gamma_b$.

FIG. 2. Idealized diagram illustrating the separation of a bar of liquid alcohol into two parts. The molecules are represented as already oriented at the interface, since the break is well under way. This diagram indicates that in such an ideal case the energy of separation of a moderately long chain alcohol should be practically equal to that of a hydrocarbon of the same molecular size, except for the relatively small energy of orientation of the molecules at the interface before the actual separation has occurred.

C. *Benzene (figure 3)*

In order to obtain a better idea of the extent to which each of the three theories is valid, the discussion given below considers the spreading of
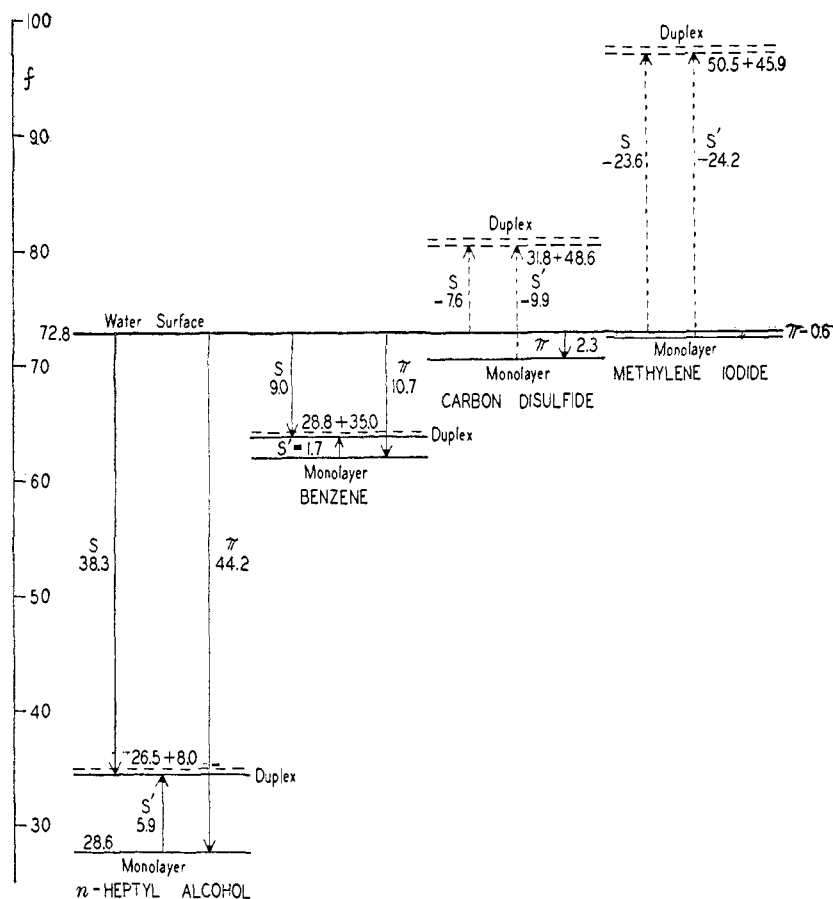
Fig. 3. Free-energy diagram for the spreading of oils on water. Any film the free-energy level of which is above that of water (72.8 ergs cm.$^{-2}$ at 20°C.) cannot spread, and any film the level of which is below that of water may spread spontaneously on water. Benzene, a non-polar liquid (isopentane has practically the same levels), should, according to the diagram, be able to spread either as a duplex film or as a monolayer, but only the latter is stable. For carbon disulfide, a non-polar liquid, the duplex film is at a free-energy level 7.6 ergs cm.$^{-2}$ higher than that of a clean water surface, so a duplex film is not formed by spreading. The free-energy level of the gaseous monolayer is, however, 2.3 ergs cm.$^{-2}$ below that of the water surface, which rapidly attains equilibrium with the lens and the vapor in a saturated atmosphere. The film pressure, as for benzene, is given by the difference in level between the clean water surface and that of the monolayer. Methylene iodide, even though it is highly polar, does not spread as a duplex film, and its monolayer gives only a small film pressure (0.6 dyne cm.$^{-1}$).

three liquids,—benzene, carbon disulfide, and a paraffin oil of high molecular weight.

For dry benzene on a clean water surface, what may be termed the initial spreading coefficient has the value

$$S_{b/a} = \gamma_a - (\gamma_b + \gamma_{ab}) = 72.8 - (28.9 + 35.0) = 8.9 \text{ ergs cm.}^{-2}$$

That is, if the area of the duplex film increases by 1 cm.² and that of the clean surface of the water decreases by this amount, there is a decrease in free energy of 8.9 ergs, which is a considerable decrease and indicates that benzene should spread readily to form a duplex film.

However, since the extremely thin duplex film of benzene becomes saturated with water very rapidly, the coefficient of spreading, which may be designated as the semi-initial coefficient, becomes

$$S_{b'/a} = \gamma_a - (\gamma_{b'} + \gamma_{a'b'}) = 72.8 - (28.8 + 35.0) = 9.0 \text{ ergs cm.}^{-2} \quad (6)$$

where the prime indicates that b is saturated with a. The value of this spreading coefficient indicates that wet benzene also spreads on a clean water surface to form a duplex film.

If b and a are mutually saturated, then

$$S_{b'/a'} = \gamma_{a'} + (\gamma_{b'} - \gamma_{a'b'})$$
$$= 62.2 - (28.8 + 35.0) = -1.6 \text{ ergs cm.}^{-2} \quad (7)$$

This may be designated as the *final spreading* coefficient. Its negative value indicates that benzene will not spread over the surface of water if the liquids are mutually saturated. An inspection of the numerical terms involved shows that the whole change between $S_{b'/a}$ and $S_{b'/a'}$ is due to a decrease of 10.6 ergs cm.$^{-2}$ in the free surface energy of the surface of water. Now if the free surface energy of the water saturated with benzene is subtracted from that of the clean water, there is obtained as the difference (π_e)

$$\gamma_w - \gamma_e = \pi_e \quad (8)$$

where, if surface tensions instead of free surface energies are considered, π is by definition the film pressure, and the subscript in π_e and γ_e indicates that the film of the oil b is in equilibrium with a lens of the oil.

Now equation 6 minus equation 7 gives

$$S_{b'/a} - S_{b'/a'} = \gamma_a - \gamma_{a'} = \gamma_w - \gamma_e = \pi_e \quad (9)$$

or the difference between the semi-initial and the final coefficients of spreading is equal to the film pressure. It is shown above that for benzene on water this difference is 10.6 ergs cm.$^{-2}$, which is therefore the value the film pressure of the non-duplex film of benzene on the water.

To obtain this thin film a clean surface of water in a large crystallizing dish may be partly covered with a layer, that is, a large lens, of benzene. If the curvature of the surface of the water is adjusted to give such a result, the lens or layer (*ca.* 2 mm. thick) will form an annular ring in contact with the outer edge of the dish, while in the center a circular hole will be formed. According to Langmuir there is no benzene film in this hole, but the vertical type of film balance, or the ring method, may be used to test this, and such a measurement gives a film pressure of 10.6 dynes cm.$^{-1}$ Thus the surface of the water in the hole is covered with a monolayer which gives this high pressure, corresponding to about 200 atmospheres. Obviously this monolayer is in equilibrium with the large lens.

D. Carbon disulfide (figure 3)

For carbon disulfide on water the semi-initial coefficient of spreading is

$$S_{b'/a} = \gamma_w - (\gamma_o' - \gamma_{wo}') = 72.8 - (31.8 + 48.6) = -7.6 \text{ ergs cm.}^{-2}$$

while the final coefficient is

$$S_{b'/a'} = 70.5 - (31.8 - 48.6) = -9.9 \text{ ergs cm.}^{-2}$$

or

$$\pi_e = S_{b'/a} - S_{b'/a'} = 2.3 \text{ ergs cm.}^{-1}$$

Thus the values of the initial and semi-initial spreading coefficients predict that carbon disulfide will not spread as a duplex film, but the difference between the semi-initial and final spreading coefficients indicates that it does spread as a monolayer, which has an equilibrium film pressure of 2.3 dynes cm.$^{-1}$ Presumably this monolayer is a gaseous film. Obviously it may have any film pressure less than 2.3 dynes cm.$^{-1}$ if it is not in equilibrium with a lens of the liquid and the vapor from the liquid.

Methylene iodide, a non-spreading oil in the sense that its spreading coefficient has a very large negative value ($S_{o'/w} = -23.6$ and $S_{o/w'} = -24.2$), nevertheless gives a non-duplex film or monolayer with a film pressure of 0.55 dyne cm.$^{-1}$

E. Paraffin oil of very high molecular weight

A paraffin oil may have a molecular weight so high that at 20°C. it gives almost no vapor pressure in three dimensions. Such an oil gives a high negative spreading coefficient, so it does not spread as a duplex film. Its cohesion is so large that it does not even spread as a gaseous monolayer, at least not sufficiently to give a measureable film pressure with the ordinary type of film balance. Such an oil may be considered as non-spreading.

III. TRANSFORMATION OF A DUPLEX FILM INTO A MONOLAYER AND A LENS

The examples given in section II show that in each case the free surface energy of the monolayer is less than that of the duplex film, provided the duplex film can spread at all. This is a general relation, so the duplex film always changes into a monolayer and a lens (or lenses if the time is not sufficiently long to give a single lens). If a duplex film cannot form, then if any film is produced it is a monolayer. Such a monolayer may be formed even if the initial spreading coefficient is negative, but may not

TABLE 1

A. Initial spreading coefficients of a few oils on clean water at 20°C.

MOLECULES WITH POLAR GROUPS	S	PARAFFINS	S	NON-POLAR AROMATIC HYDROCARBONS	S
n-Octyl alcohol	35.7	Isopentane	9.4	p-Cymene	10.1
Heptaldehyde	32.2	Hexane	3.4	Benzene	9.8
Oleic acid	24.6	Diisoamyl	3.7	o-Xylene	6.9
Ethyl nonylate	20.9			Toluene	6.8
o-Nitrotoluene	4.1			p-Xylene	6.7
Nitrobenzene	3.8			Mesitylene	5.6

LIQUIDS WITH NEGATIVE COEFFICIENTS	S	LIQUIDS WITR NEGATIVE COEFFICIENTS	S
Ethylene dibromide	−3.2	Monoiodobenzene	−8.7
o-Monobromotoluene	−3.3	Bromoform	−9.6
Carbon disulfide	−4.2	Acetylene tetrabromide	−15.6
Long-chain paraffins	−6.9	Methylene iodide	−26.5

B. Some final spreading coefficients of oils on water

OIL	S	OIL	S
Benzene	1.5	n-Heptyl alcohol	−5.9
Carbon disulfide	−10.0	Isoamyl alcohol	−2.6
Methylene iodide	−24.2		

give a measureable film pressure if the oil is non-polar and does not give a measureable three-dimensional vapor pressure.

If the atmosphere above an oil film is supersaturated with oil, the material condensed on the monolayer does not thicken it, but any excess deposited on the monolayer either evaporates or goes *into* the monolayer. As a result of this latter process, either the monolayer expands, or an equal amount of material in the monolayer is forced into the lens.

The rate of spreading of an oil on water increases with the magnitude of the spreading coefficient and with a *decrease* in the viscosity of the layer which spreads. The values of the initial spreading coefficients of a

few oils are given in table 1. The final spreading coefficient of an oil on water is always negative, so no oil will spread over its equilibrium mono-layer. The initial and final coefficients for water on oil are always negative, so water will not spread over the surface of an oil.

Since (1) many hydrocarbon oils, which do not contain polar groups, nevertheless spread on water to duplex films and then to monolayers, and (2) substances whose molecules contain a strongly polar group do not spread if the hydrocarbon fraction is too large, it is apparent that the presence or absence of a polar group is not the true criterion for spreading or non-spreading. Examples of the second type are arachidic acid (twenty carbon atoms) and acids having longer normal paraffin chains. These substances are solids on account of the higher cohesion due to the longer chains.

IV. PHASE RELATIONS OF MONOLAYERS

Monolayers are found to exhibit the three types of phases found in three-dimensional systems: (1) gas, (2) liquid, and (3) vapor. The charac-teristics of the phases of the two-dimensional systems may be exhibited by pressure-area ($\pi-\sigma$) diagrams (figures 4, 5A, and 5B), which exhibit relations similar to those represented in three dimensions by $p-v$ diagrams (10, 14).

Within a suitable temperature range many different polar–non-polar oils are found to give a $\pi-\sigma$ diagram of the type shown in figure 4. The temperatures in the figure are correct for pentadecylic acid (fifteen carbon atoms), but are lower for acids with a lower, and higher for those with a higher number of carbon atoms per molecule. With alcohols the tem-peratures are much higher. At very large molecular areas, of the order of 50,000 Å.^{2}, the film of pentadecylic acid obeys the law $\pi\sigma = kT$, where σ is the area and k is Boltzmann's constant. This is the law of a perfect gas. As the film is compressed to lower areas this two-dimensional gas becomes more and more imperfect, but the film remains homogeneous. This can be shown by the use of a small silver electrode, coated with polonium, placed a short distance above the surface of the water. This is connected through any type of electrometer to a calomel cell, the arm of which dips under the solution in the trough of the film balance.

The difference between the potential of the electrode when it is over a clean water surface, and when a film is on the surface underneath the electrode, is designated as the surface potential. The sign of this potential is taken as positive when films of organic acids, alcohols, etc. are present, but the salts of the acids exhibit a slight negative potential. With certain films the surface potential is as large as 950 millivolts.

The surface potential, if only a single organic substance is present, is

roughly proportional to the number of molecules per unit area, and since this number increases with the pressure, the surface potential also increases. It was found by Harkins, Ries, and Carman (13) that condensed films of tetrahydro-d-pimeric acid, a saturated compound, exhibit a normal increase of from 203 to 220 millivolts as the molecular area is decreased from 54 to 46 Å.^{2} The structure of d-pimaric acid is the same, except for two double bonds far from the carboxyl group.

With the film of this compound the same decrease of area *decreases* the film potential from 108 to 94 millivolts. The double bonds reduce the
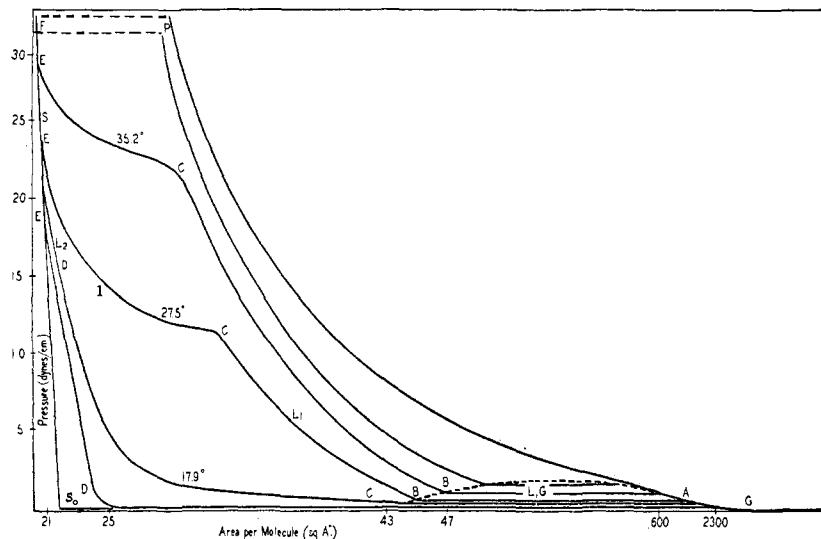
FIG. 4. General phase diagram of a monolayer at a temperature below the critical temperature for the formation of a liquid expanded (L_1) film. Phases: FE or S, solid; ED or L_2, liquid condensed; DC or I, intermediate; CB or L_1, liquid expanded; BA or L_1G, gaseous film and L_1 film in equilibrium; G, gaseous film.

potential due to the carboxyl group dipole by more than 50 per cent, which shows that their mutual dipole is opposed to that of the carboxyl group. The decrease of the potential on compression shows that a closer packing of the molecules, which presumably causes them to stand more upright on the surface, brings these dipoles more into opposition.

If at any given film pressure there are islands of liquid film in a sea of gaseous film, a survey of the surface, by moving the electrode over it, shows that the surface potential is much higher over an island than when there is only a gaseous film underneath. Such a survey may fail to reveal non-homogeneities, provided small islands are uniformly distributed over the whole area.

At 17°C. the gaseous film of myristic acid becomes entirely condensed to a liquid (L_1) state at a molecular area of 45 Å.^{2} At somewhat higher areas the film is heterogeneous (region L_1G of figure 4), and this is shown by an electrical survey of such a film made at a mean molecular area of 56.5 Å.^{2} The numbers represent the distribution of the film potential over an area about 25 x 50 cm. The values vary from zero, where only the gaseous film was present, to 199 millivolts in the region where the "island" was the most continuous. At an area of 37.1 Å.^{2} the film is in the inter-

TABLE 2

Surface potentials of myristic acid films at 23°C. (12)

AREA	SURFACE POTENTIALS IN MILLIVOLTS						
	Gaseous and liquid expanded (L_1) film						
56.5 Å.^{2}	10	22	31	43	90	165	158
	0	15	30	38	164	160	156
	5	35	51	165	167	165	165
	48	98	166	174	171	176	164
	145	148	170	169	170	103	199
	Liquid expanded film						
37.1 Å.^{2}			175	170	170	160	157
			172	165	168	160	155
			169	166	167	164	158
			166	169	188	165	155
			163	167	190	195	
	Intermediate film						
25.0 Å.^{2}				255	248	255	281
				255	248	255	245
				255	252	258	243
				254	277	261	238
				253	254	261	256

mediate state, and at 25.0 Å.^{2} it is still in the same state. Stearic acid in the L_2 or liquid condensed state gives a potential of about 410 millivolts at 17°C.

At 14.5°C. a monolayer of pentadecylic acid begins to condense to the liquid (L_1) state if compressed below 2300 Å.^{2}, or at 24°C. if below 800 Å.^{2} (figure 4).

The transition of a monolayer from a gaseous to an L_1 liquid state is an ordinary change of the first order, accompanied by a latent heat of phase transformation. Thus it is analogous to the condensation of a gas to a liquid in a three-dimensional system.
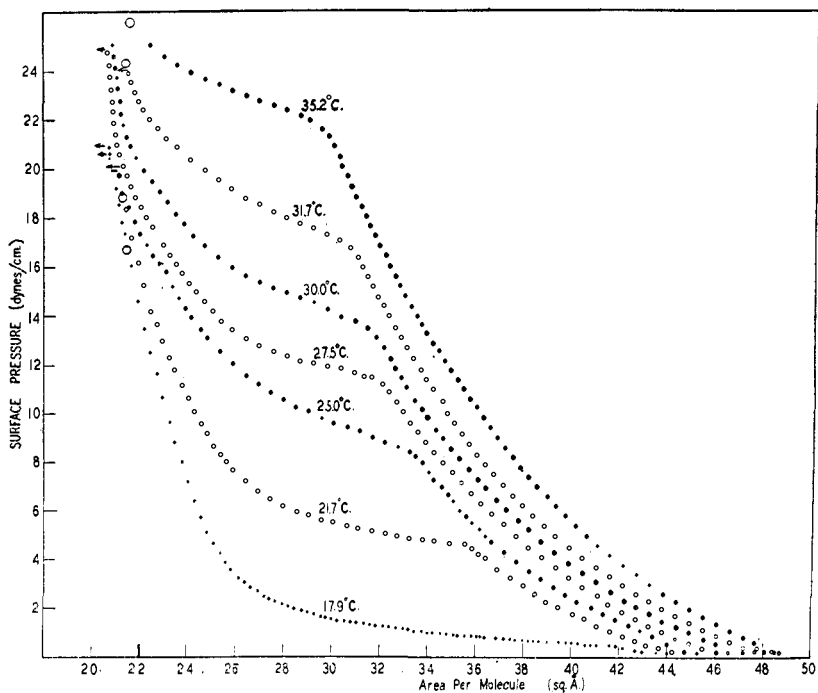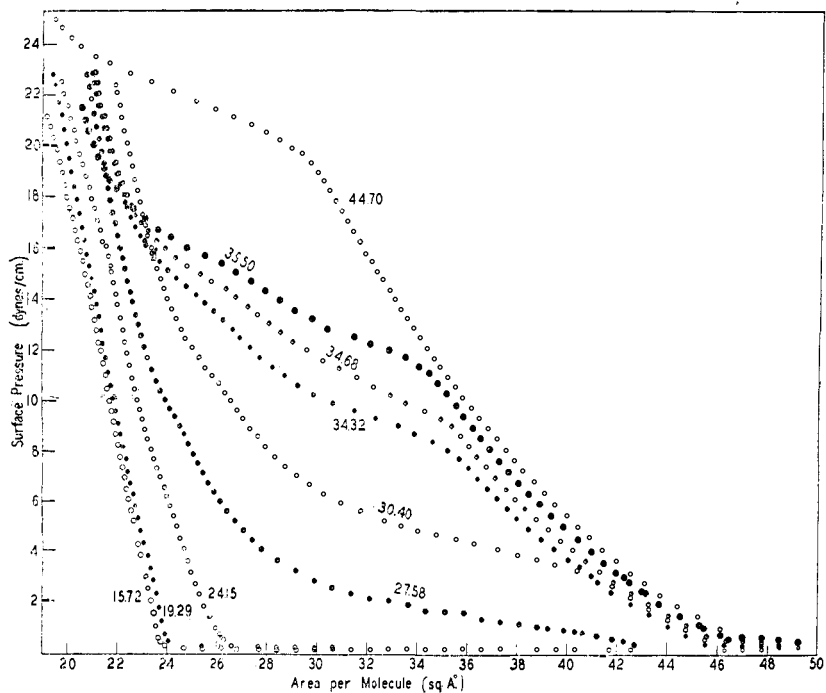
FIG. 5A. Liquid films of pentadecylic acid

FIG. 5B. Liquid films of palmitic acid. Above a pressure of 13 dynes some of the curves are affected by a slight collapse of the film.

TABLE 3

Two-dimensional phases and probable order of changes between them

PHASES	ORDER OF CHANGE BETWEEN THEM
Classification A	
I. Gas, *G*. Includes compressed vapors such as the "vapor expanded" film of Adam Perfect gas: $\pi\sigma = kT$ Imperfect gas: minimum of same order as for L_1 films: e.g., 0.04 for ethyl palmitate at 25°C., 34 Å.², and 14 dynes cm.$^{-1}$	
	I and II: first
II. Liquid, L_1 (*BC*). "Liquid expanded" of Adam. Liquid of high compressibility $-\kappa = 2$ to 7×10^{-2} $h_s = 50$ ergs cm.$^{-2}$	
	II and III: resembles diffuse first-order change of phase, but is probably second order
III. Intermediate (*I*) or transition (*CE*). Liquid of extremely high compressibility Intermediate, *I*. Maximum $-\kappa$ of order of 2 to 5×10^{-1} for normal long-chain acids 2.2×10^{-1} for normal long-chain esters Minimum same as $-\kappa$ of L_2 film: $h_s = 300$ ergs cm.$^{-2}$, which is nearly constant at the higher areas, but decreases rapidly to a low value as transition to next phase is approached	
	III and IV: third
IV. Liquid, L_2 (*DE*). "Liquid condensed" of Adam. Liquid of low compressibility $-\kappa = 5$ to 10×10^{-3} $\log \eta = \log \eta_0 - k\pi : h_s$ small	
	IV and V: second
V. Solid, *S* (*EF*) $-\kappa = 7$ to 9×10^{-4} $h_s = 200$ to 700 ergs cm.$^{-2}$	
Classification B: same as A, except as indicated below	
III. Intermediate (a) Transition, *T* (b) Liquid, L_2 IV. Solid	

A new, very highly condensed phase, designated as the *LS* phase (the *L* indicating that it has a much higher fluidity than the liquid from which it is formed, and the *S* that it has the compressibility of the solid phase) seems to be formed from the liquid L_2 phase by a first-order change. This is the only first-order change known in two-dimensional systems, except when a gaseous phase is condensed.

On compression the pressure of the liquid (L_1) film increases along a curve which has almost the form of an equilateral hyperbola, as may be seen more clearly in an enlarged section of figure 4, as in figure 5A.

At C (figure 4) there is a phase transformation of a peculiar type to the *intermediate* (I) liquid state. Whether this is a diffuse first-order change, or one of the second order, is not known. Just above the kink point the π–σ curve is almost, but not quite, horizontal. This is a region of considerable hysteresis.

At D (figure 4) there is a third-order transition to a condensed liquid (L_2) monolayer, and at E, a second-order transition to a solid.

Table 3 lists the five phases which may be formed on the compression of a monolayer, together with the probable order of the phase change between them. The compressibility (κ) is characteristic of the phase, as is the increase of enthalpy (h_s) which accompanies the spreading over unit area. This has almost the same value as the heat absorbed.

V. ESTERS AND METHYL KETONES (10)

The substitution of a methyl or an ethyl group for the acid hydrogen of a long-chain acid reduces the cohesion in the film. This gives a remarkable effect on the general phase diagram, since it may entirely eliminate the liquid expanded (L_1) phase, which is replaced by a gaseous monolayer, and this exhibits a hyperbolic π–σ relation. It is distinguished from the L_1 state only by the absence of the first-order transition from gas to liquid (L_1), and thus the heterogeneous region (L_1G) of figure 4 does not appear. Figures 6 and 7 represent the variation of the film pressure with molecular area of the ethyl esters of the normal acids from myristic to margaric at 25°C. and 15°C., respectively. According to Adam (1) the esters of all of these acids give high-pressure gaseous or *compressed vapor films* at 15°C. with the exception of ethyl margarate, which transforms from a low-pressure vapor directly to a condensed liquid state. If this is true, then at 25°C. every one of the four esters exhibits the compressed vapor state. In all cases increase of pressure causes the vapor phase to undergo a phase change into the intermediate state, provided it does not collapse, that is, if it does not exhibit instability with reference to the third dimension. At 25°C. this collapse occurs with the myristate and the pentadecylate at pressures of 16.5 and 17.5 dynes cm.$^{-1}$, respectively, and at a molecular area of about 32 Å.^{2} At 15°C. none of the gaseous films collapses. The myristate undergoes a phase change to the intermediate state at about 32 Å.^{2} and a film pressure of 16.2 dynes cm.$^{-1}$

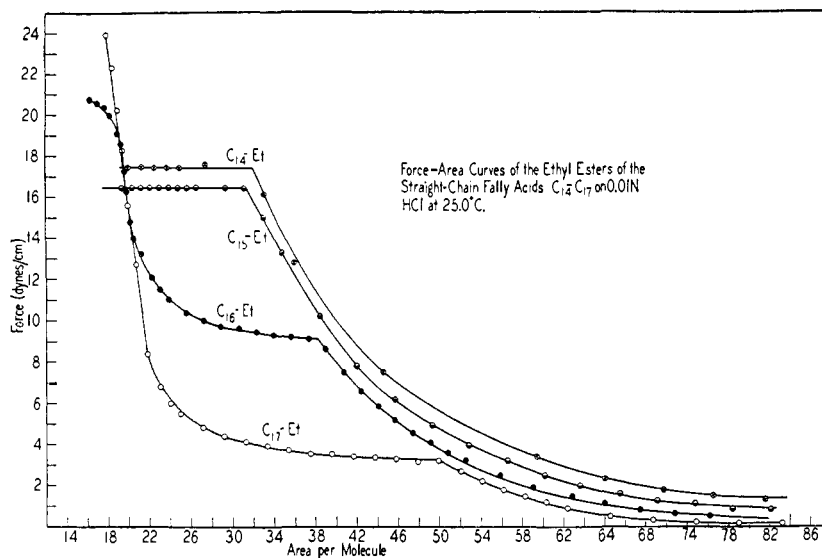With the exception of the margarate at 15°C., all of the esters are at

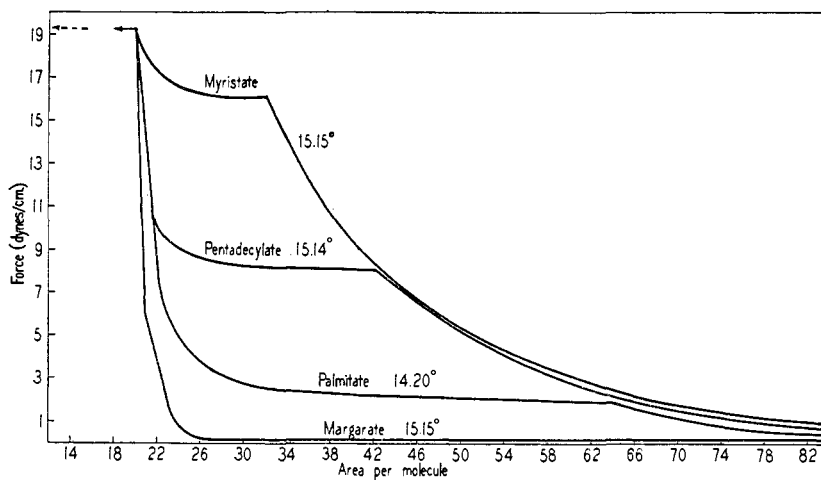FIG. 6. General phase diagram at temperatures above T_c for the L_1 phase: ethyl esters at 25°C.

FIG. 7. General phase diagram at temperatures above T_c for the L_1 phase: ethyl esters at about 15°C.

temperatures above the critical temperature for the phase transition from gaseous film to the liquid (L_1) state.

It is obvious, from the form of the curves, that in the relation

$$(\pi - \pi_0)(\sigma - \sigma_0) = kT$$

the value of π_0 is much smaller and that of σ_0 somewhat smaller for the compressed vapors than for expanded (L_1) liquids the molecules of which contain the same number of carbon atoms.

Langmuir (17) considers that these esters do not form a liquid condensed (L_2) phase, but the straight lines of figures 6 and 7, which when extrapolated to zero pressure give a molecular area of 24 Å.^{2}, seem to represent liquid phases. The extrapolated area for the solid phase is at zero pressure only about 21 Å.^{2}, and the determined value at 19 dynes cm.$^{-1}$ is 20 Å.^{2}

The compressed vapor films undergo a phase transformation to the intermediate phase *at a much higher molecular area* than with the acids. For example, at 14.2°C. ethyl palmitate undergoes this transition at a molecular area of 64 Å.^{2} ($\pi = 2$ dynes cm.$^{-1}$), while at even a much lower pressure the similar change for a long-chain paraffin acid does not occur much above 42 Å.^{2} Presumably this is due to the greater probability that the molecules of the ester lie flat on the surface, owing to the difficulty of making a sharp bend in the molecule at the polar group. In a condensed state the polar group is kept farther from the water by the ethyl group of the ester than by the proton which it replaces in the acid. When a greater molecular area is available, many of the polar groups of the ester can come in contact with the surface of the water, and thus orientation perpendicular to the surface becomes much less probable. If ethyl palmitate is in the compressed vapor state at 10°C., it should undergo the transition to the intermediate liquid state at about 80 Å.^{2}, or four times the area occupied in the condensed state. Even at this area, however, not all of the molecules can lie flat, since this requires 115 Å.^{2} per molecule.

The low area to which the compressed vapor state may persist is quite remarkable. Thus at 25°C. ethyl myristate remains as a vapor until its area is only 32 Å.^{2}, or not much above one-fourth that required for the flat orientation.

Another feature of the ester films is the very high compressibility (e.g., $-\kappa = 2.2$ for ethyl palmitate at 15.2°C.) exhibited at molecular areas slightly below that for the transition from vapor to intermediate film. Thus this transition is much more nearly of the first-order type than when long-chain acids are involved.

VI. CONDENSED LIQUID (L_2) FILMS OF ACIDS, ALCOHOLS, AND ESTERS (19)

As the molecular area of an intermediate surface phase is decreased its pressure rises more and more rapidly, until at a point D the π-σ curve begins to be linear. The linear region represents what is designated as

the condensed liquid phase. This has a relatively low compressibility, of the order of 0.008 for acids and 0.005 for alcohols, if the hydrocarbon chains are long.

The viscosity relations (2, 9) of these liquid monolayers are of considerable interest. Figure 8 exhibits the effect of pressure and of chain length upon the viscosity of the normal-paraffin-chain acids. For the eighteen-, nineteen-, and twenty-carbon-atom acids the logarithm of the
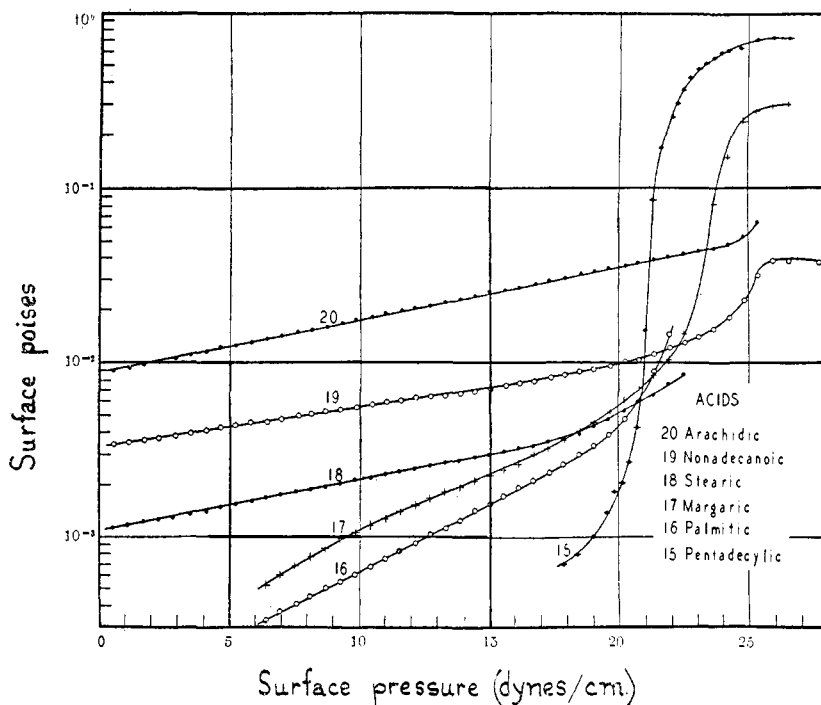
FIG. 8. Viscosity–pressure relations of monolayers of the normal long-paraffin-chain acids

viscosity of the liquid monolayers increases by a constant amount per carbon atom. The effect of pressure is given by the following equation:

$$\log \eta = \log \eta_0 + k\pi$$

where η represents the viscosity of the film. The viscosity increases much more rapidly than this as the pressure approaches that for the transition: Liquid (L_2) → Solid. At the freezing point the viscosity is increasing with great rapidity.

The relations for the alcohols (4) are much the same, except that the
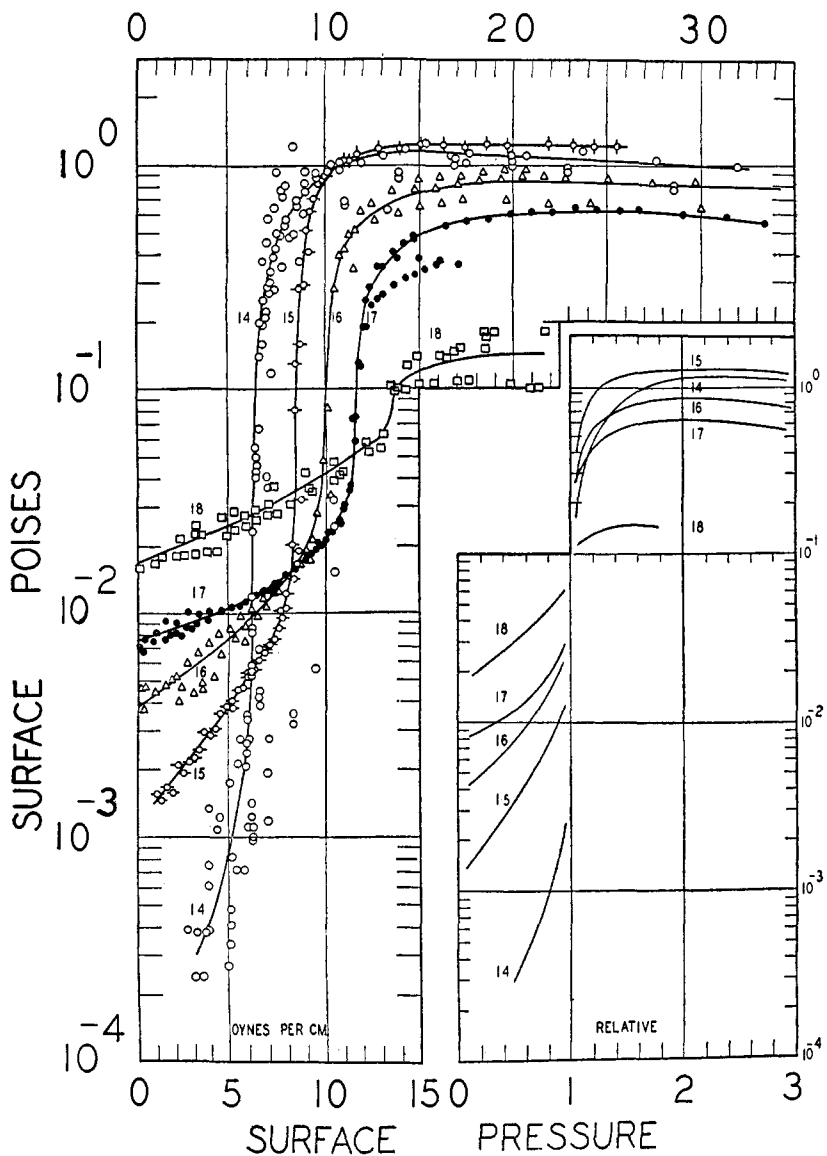
FIG. 9. Viscosity-pressure relations of normal long-chain alcohols. Ordinate, logarithm of surface viscosity; abscissa, surface pressure. In the insert the surface pressure scale is in multiples of the mean kink-point pressure.

viscosities are much higher if the number of carbon atoms is the same (figure 9). Since the pressure of solidification is much lower than with the alcohols, the linear part of the π–log η curve is very short. Thus
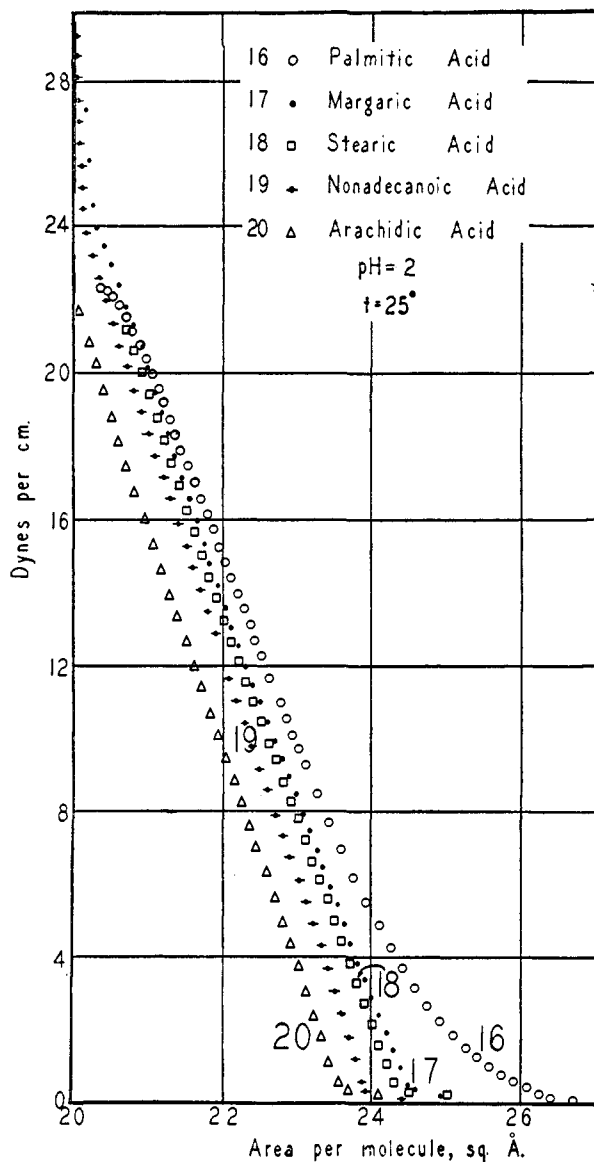
Fig. 10.   Pressure–area relations of liquid condensed films of normal
long-paraffin-chain acids

with the seventeen-carbon-atom alcohol the relation is linear up to only about a pressure of 7 dynes cm.$^{-1}$, since above this the viscosity is increased abnormally by the approach of the pressure to that of solidification (12 dynes cm.$^{-1}$).

The viscosity of the solid alcohol or acid *decreases* rapidly with the length of the hydrocarbon chain. As a result of this it is found that with long chains the viscosity of the solid is only slightly greater than that of

TABLE 4

Limiting areas (at $\pi = 0$) and compressibilities of long-chain acids and alcohols

A. Acids at 25°C.*

CARBON ATOMS PER MOLECULE	ACID	LIMITING AREA (SQ. Å. PER MOLECULE)	SLOPE (SQ. Å. PER DYNE)	COMPRESSIBILITY	
				At $\pi = 0$	At $\pi = 20$
14	Myristic	46.4			
15	Pentadecylic	45.6			
16	Palmitic	26.75			
17	Margaric	24.59	−0.180	−0.0073	−0.0086
18	Stearic	24.41	−0.177	−0.0072	−0.0085
19	Nonadecanoic	24.0	−0.163	−0.0065	−0.0075
20	Arachidic	23.64	−0.159	−0.0067	−0.0078

| CARBON ATOMS PER MOLECULE	ACID	CHANGE OF COMPRESSI- BILITY (PER CENT)	
14	Myristic		
15	Pentadecylic		
16	Palmitic		
17	Margaric	17.1	
18	Stearic	16.8	
19	Nonadecanoic	15.0	
20	Arachidic	16.2	

B. Alcohols at 20°C. Pressure-area data for alcohol monolayers

CARBON ATOMS PER MOLE- CULE	ALCOHOL	LIMITING AREA (SQ. Å. PER MOLE- CULE) AT $\pi = 0$		KINK-POINT PRESSURE (DYNES PER CM.)		SLOPE (SQ. Å. PER DYNE)		COMPRESSIBILITY	
		Liquid	Solid			Liquid	Solid	Liquid at $\pi = 0$	Solid at $\pi = 20$
14	Tetradecyl	22.02	21.1	6.2		0.226	0.084	0.0103	
15	Pentadecyl	21.91	21.0	8.2	2.0	0.138	0.030	0.0063	0.0015
16	Hexadecyl	21.85	20.9	10.2	2.0	0.121	0.021	0.0055	0.0010_2
17	Heptadecyl	21.76	20.6	11.8	1.6	0.117	0.021	0.0054	0.0010_4
18	Octadecyl	21.82	20.6	12.9	1.1	0.106	0.014	0.00485	0.0007_0

* At this temperature the fourteen-carbon-atom and fifteen-carbon-atom acids are in the L_1 state, and the acids containing from sixteen to twenty carbon atoms are in the condensed L_2 state.

the liquid, while with short chains it is very much greater. Thus the viscosity of the liquid monolayer tetradecyl alcohol is 10^{-3} poise at $\pi = 5$, but that of the solid is 1 poise at $\pi = 10$ dynes cm.$^{-1}$, i.e., there is a thou-

sandfold increase in viscosity. Very remarkable results on the pressure–area–temperature and pressure–viscosity–temperature relations of octadecyl alcohol in the neighborhood of 10°C. have been obtained in this laboratory by L. E. Copeland, but these are too complicated to discuss in this review.

It is usually stated that all normal long-chain paraffin acids occupy the same molecular area in the condensed liquid state, but actually (19), at a low film pressure, the molecular area decreases by about 0.3 Å.^{2} for each carbon atom added to the chain (figure 10) (reference 19, page 1186). The limiting areas and compressibilities of certain condensed liquid monolayers are given in table 4. The limiting area is the area obtained at zero pressure by extrapolation of the straight line which gives the pressure–area relation.

TABLE 5

Dependence of the compressibility on the state of the monolayer

PHASE	
I	Gas. Perfect gas: $\pi\sigma = kT$
	Imperfect gas: minimum of same order as for L_1 films: e.g., 0.04 for ethyl palmitate at 25°C., 34 Å.^{2}, and 14 dynes cm.$^{-1}$
II	Liquid expanded, L_1: $-\kappa = 2$ to 7×10^{-2}
III	Intermediate, I.
	Maximum $-\kappa$ of order of
	2 to 5×10^{-1} for normal long-chain acids
	2.2×10^{-1} for normal long-chain esters
	Minimum same as $-\kappa$ of phase IV = L_2
IV	Liquid condensed, L_2: $-\kappa = 5$ to 10×10^{-3}
V	Solid, S: $-\kappa = 7$ to 9×10^{-4}

The compressibility of the L_2 monolayer is of the order of ten times that of the solid, that for L_1 is of the order of six times that for L_2, and the maximum for the intermediate phase is of the order of eight times that for L_1, while its minimum compressibility is in the limit equal to that of L_2. Since the maximum compressibility of the intermediate phase is somewhat dependent upon the rate of compression, the value for any given substance and temperature is more uncertain than for the other phases.

VII. THE COMPRESSIBILITY OF MONOLAYERS

The compressibility of a monolayer is dependent upon the extent to which the film is already contracted by intermolecular forces, but is not always smaller at smaller areas, since it is also dependent on the phase involved.

Table 5 shows that each phase, as L_1, I, L_2, etc., is characterized by its own order of compressibility.

Table 6 lists the compressibilities of certain acid, alcohol, and ester monolayers.

TABLE 6

Compressibility (κ) of monolayers in different states

NUMBER OF CARBON ATOMS	SUBSTANCE	MOLECULAR AREA (σ)	PRESSURE (π)	TEMPER- ATURE, $t°C.$	COMPRESSIBILITY ($-\kappa$)
	Liquid (L_1) state expanded				
13	Tridecylic acid	26–31		12.5	0.019–0.027
	Tridecylic acid	32–41		12.5	0.026–0.06
14	Myristic acid	31–37.5		16.6	0.02–0.04
	Myristic acid	37.5–43.5		16.6	0.04–0.07
15	Pentadecylic acid	31.5–39.5		25.0	0.025–0.035
	Pentadecylic acid	39.5–44		25.0	0.035–0.045
57	Triolein	103	8–16	7	0.03
	Triolein	126	0–8	7	0.06
18	Ethyl palmitate (gas)	40	8.5	25	0.04
18	Octadecanenitrile	35.5–45	0.25–6.5	25.8	0.03–0.06
	Intermediate (I): nitriles				
18	Octadecanenitrile	35.5–27	6.5–16	25.8	0.02–0.06
	Intermediate state: acids				
14	Myristic acid	35	3	9.5	0.25
15	Pentadecylic acid	40		17.9	0.35
	Intermediate state: esters				
18	Ethyl palmitate	34.7	9.3	25	0.53
19	Ethyl margarate	47	3.5	25	1.2
	Ethyl margarate	58	2.1	15.2	2.2
	Liquid condensed (L_2): acids				
15	Pentadecylic acid	21–23.2		27.5	0.005–0.027
16	Palmitic acid	21–23.7		25	0.008–0.01
17	Margaric acid	21.6–25		25	0.007–0.0085
18	Stearic acid	21–24		25	0.0063–0.0095
19	Nonadecanoic acid	20.4–23.6		25	0.0063–0.0075
20	Arachidic acid	20.6–24.2		25	0.0065–0.0084
	Liquid condensed (L_2): alcohols				
18	Octadecanol	22.6–20.54	1.5–14	25.12	0.0055–0.008
		21.8–20.4	1.5–12.4	9.90	0.004 –0.016
		21.8–19.78	1.5–14.9	7.10	0.0055–0.008
19	Nonadecanol	22.7–20.7	1.5–15.3	21.73	0.0055–0.008
		22.6–20.5	1.5–14.7	14.83	0.0055–0.008
		22.3–20.0	1.5–17.4	10.35	0.0047–0.008
20	Eicosanol	22.3–20.33	1.5–16.2	24.76	0.004–0.009
		22.3–20.3	1.5–15.7	22.48	0.004–0.016
		21.9–19.92	1.5–19.3	18.34	0.004–0.009

TABLE 6—*Concluded*

Compressibility of monolayers in highly condensed states

NUMBER OF CARBON ATOMS	SUBSTANCE	MOLECULAR AREA (σ)	PRESSURE (π)	TEMPER-ATURE, $t°C.$	COMPRESSIBILITY ($-\kappa$)
"6"	LS state: alcohols (Compressibility of a solid state, but viscosity ranging from much less than for the L_2 state to the high values of the solid or S state: c = collapse)				
18	Octadecanol	20.54–c	14.05–c	25.12	0.0014–0.0017
		20.2–c	12.37–c	9.90	0.0007–0.0009
19	Nonadecanol	20.71–c	15.27–c	21.73	0.0008–0.0009
		20.36–c	14.7–c	14.83	0.0005–0.0009
20	Eicosanol	20.33–c	16.20–c	24.76	0.0005–0.0009
		20.24–c	15.70–c	22.48	0.0008–0.0011
"6"	S state (usually designated as the solid (two-dimensional) state) Alcohols				
18	Octadecanol	19.78–c	14.90–c	7.10	0.0006–0.0008
19	Nonadecanol	19.97–c	17.40–c	10.35	0.0007–0.0009
20	Eicosanol	19.92–c	19.30–c	18.34	0.0007–0.0010
"6"	Acids, esters				
17	Margaric acid	20	30	25	0.0008
18	Stearic acid	20	40	22.5	0.0009
18	Octadecyl alcohol	20.3	20	20	0.0007
18	Calcium stearate	20	0.5	22.7	0.0008
19	Ethyl margarate	20.5	19.5	20	0.0020

Section 2: Effect of a divided chain

Tertiary paraffin-chain compounds
$$R_1 \diagdown \atop R_2 \diagup \; CHCOOH$$

	R_1	R_2				
15	1 C	14 C	30	18	18	0.013
15	7 C	8 C	62	14	18	0.020
16	8 C	8 C	55	15	18	0.017
12	6 C	6 C	58	7.5	18	0.026

Section 3: Effect of orientation: molecules which lie flat on the surface

40 to 1480	ω-Hydroxydecanoic acid polymers	250 to 10,000	1.5–6	20	0.046–0.058

VIII. THERMODYNAMICS OF SPREADING AND EXTENSION OF FILMS

The expansion of a film may be brought about by two different processes which involve quite different amounts of energy: (1) Spreading may be defined as the process in which the area (σ_f) of a film, either duplex or monomolecular, increases by an amount $\Delta\sigma_f$, while the area of the surface of the subphase (e.g., water, mercury, etc.) decreases by $\Delta\sigma_f$. (2) Extension is the process in which the area of the film and of the subphase remains constant.

The maximum work (δW) done by a system when its area (σ) is increased or decreased is

$$\delta W = -\gamma\, d\sigma + p\, dv \qquad (10)$$

where γ is the surface tension. The zeta function of Gibbs is defined by him as

$$F = E - ST + pv \qquad (11)$$

The Helmholtz free energy is defined as

$$A = E - ST \qquad (12)$$

so

$$F = A + pv \qquad (13)$$

If a process is reversible and isothermal, $T\Delta S = Q$ is the heat absorbed, and

$$dA = -dW \qquad (14)$$

$$dF = -dW + p\, dv + v\, dp \qquad (15)$$

From equations 10 and 15

$$dF = \gamma\, d\sigma + v\, dp \qquad (16)$$

so if p is constant

$$(\partial F/\partial\sigma)_{p,T} = \gamma \qquad (17)$$

and

$$(\partial F/\partial\sigma)_{p,T}\, d\sigma = \gamma\, d\sigma \qquad (18)$$

For a saturated surface $\gamma = f(p,\, T)$ only, so

$$\Delta F = \gamma\Delta\sigma \qquad (19)$$

If a liquid b is to spread on the surface of a liquid a, $(\partial F/\partial\sigma)_{p,T}$ should be negative for the summation of all of the terms involved. Thus if b

spreads on a to form a duplex film, then the condition for this type of spreading to occur is

$$dF = \left(\frac{\partial F}{\partial \sigma_b}\right)_{p,T} d\sigma_b + \left(\frac{\partial F}{\partial \sigma_{ab}}\right)_{p,T} d\sigma_{ab} + \left(\frac{\partial F}{\partial \sigma_a}\right)_{p,T} d\sigma_a$$

$$= \gamma_b \, d\sigma_b + \gamma_{ab} \, d\sigma_{ab} + \gamma_a \, d\sigma_a < 0 \quad (20)$$

For a film of appreciable thickness the effects of gravitation must also be considered, but they may be neglected here. If it is assumed that

$$d\sigma_b = d\sigma_{ab} = -d\sigma_a \quad (21)$$

which is practically valid for a very thin layer, then

$$\frac{dF}{d\sigma} = \gamma_b + \gamma_{ab} - \gamma_a \quad (22)$$

Let

$$-(\partial F/\partial \sigma)_{p,T} = S_{b/a} \quad (23)$$

be defined as the spreading coefficient; then

$$-(\partial F/\partial \sigma)_{p,T} = S_{b/a} = \gamma_a - (\gamma_b + \gamma_{ab}) \quad (24)$$

If the liquids are pure and the surfaces clean, then $S_{b/a}$ may be designated as the initial spreading coefficient, and spreading will occur as a duplex film if this is positive.

If b is saturated with a, but a is entirely free from b, then $S_{b'/a}$ is the semi-initial spreading coefficient, while $S_{b'/a'}$ is the final spreading coefficient. The prime in b' indicates that the liquid b is saturated with the other liquid (a).

From equations 3, 4, and 5,

$$S_{b/a} = W_A - W_{c_b} \quad (25)$$

The pressure π_f of a non-duplex film or monolayer is defined by the equation:

$$\pi_f = \gamma_a - \gamma_f \quad (26)$$

where γ_f is the free surface energy of a when covered by the film f.

Now the final spreading coefficient $S_{b'/a'}$ indicates that the lens of b' is in equilibrium with the film f, so γ_f may be written γ_e to specify equilibrium. Thus

$$S_{b'/a'} = \gamma_e - (\gamma_{b'} + \gamma_{a'b'}) \quad (27)$$

The semi-initial coefficient is

$$S_{b'/a} = \gamma_a - (\gamma_{b'} + \gamma_{a'b'}) \qquad (28)$$

and equation 28 minus equation 27 gives

$$S_{b'/a} - S_{b'/a'} = \pi_e \qquad (29)$$

or, the film pressure is the difference between the semi-initial and the final spreading coefficients.

Since the final coefficient is always negative

$$\pi_e > S_{b'/a} \qquad (30)$$

or, the equilibrium film pressure of the monolayer is always greater than the semi-initial spreading coefficient.

IX. HEATS OF SPREADING AND EXTENSION

The heat content (H) is defined by

$$H = E + pv \qquad (31)$$

or

$$dH = dE + p\,dv + v\,dp \qquad (32)$$

and from equation 2

$$H = F - ST \qquad (33)$$

or

$$dH = dF + T\,dS + S\,dT \qquad (34)$$

In the treatment which follows, energy values designated by small letters refer to the change of energy for unit area. Thus in

$$h = (\partial H/\partial \sigma)_T$$

the h designates the increase of heat content of a film of very large area for unit increment of area.

Consider a trough filled with a body of water with a plane surface partly covered with a monolayer. The area of the film, together with that of the subphase, may be increased by 1 sq. cm. by the use of some mechanical device while the area of the water surface is kept constant. Thus a ring of suitable dimensions, already lying in the surface, may be pulled upward until there is a unit increase in the area of the film. If the

film area is thus increased by $d\sigma_f$, instead of unity, the equation for the process which may be designated as extension (e), may be written

$$dF_e = (\partial F/\partial \sigma_f)_{T,\sigma_w} \, d\sigma_f = \gamma \, d\sigma_f \tag{35}$$

or

$$\Delta F(\Delta \sigma = 1 \text{ cm.}^2) = (\partial F/\partial \sigma_f)_{T,\sigma_w} = f_e \tag{36}$$

which gives the free energy of extension of the film. The entropy of extension is

$$s_e = (\partial S/\partial \sigma_f)_{T,\sigma_w} = -(\partial \gamma_f/\partial T)_{\sigma_f} \tag{37}$$

The increment of heat content is given by

$$h_e = (\partial H/\partial \sigma_f)_{T,\sigma_w} = \left[\frac{\partial(\gamma_f/T)}{\partial(1/T)} \right]_{\sigma_f} \tag{38}$$

and the heat absorbed (q) by

$$q_e = T(\partial S/\partial \sigma_f)_{T,\sigma_w} = -T(\partial \gamma_f/\partial T)_{\sigma_f} = T s_e \tag{39}$$

Similar equations may be written for the energy of spreading of a film. This process (s) may be assumed to occur as follows: The surface of the water in the trough is separated into two parts by a movable barrier. On one side of the barrier the surface is covered by the film, on the other side the water surface is clean. Let the barrier be moved in such a way that the area of the film is increased by 1 sq. cm., and that of the water is decreased by this amount.

The equations for spreading are:

$$dF_s = (\partial F/\partial \sigma_f)_{T,\Sigma} \, d\sigma_f - (\partial F/\partial \sigma_w)_T \, d\sigma_w$$

$$= -(\gamma_w - \gamma_f) \, d\sigma_f = -\pi \, d\sigma_f \tag{40}$$

where $\Sigma = \sigma_w + \sigma_f$.

The increase in entropy which accompanies the spreading of the film over the water is, from equation 16,

$$S_e = (\partial S/\partial \sigma_f)_{T,\Sigma} = -(\partial^2 F/\partial T \partial \sigma_f)_\Sigma = -(\partial \pi/\partial T)_{\sigma_f} \tag{41}$$

Figure 11 shows the variation of π with T for two long-chain acids. The heat absorbed is

$$q_s = T s_s \tag{42}$$

and the increase in heat content

$$h_s = (\partial H/\partial \sigma_f)_T = -\left[\frac{\partial(\pi/T)}{\partial(1/T)} \right]_{\sigma_f \Sigma} \tag{43}$$

Equations 15 to 18, which give the energy and entropy of extension for the films, are also applicable to pure liquids. Thus, using equation 17, the increase in the heat content when the surface area of water is increased is found as $h = 116$ ergs per cm.$^{-2}$ at 20°C.
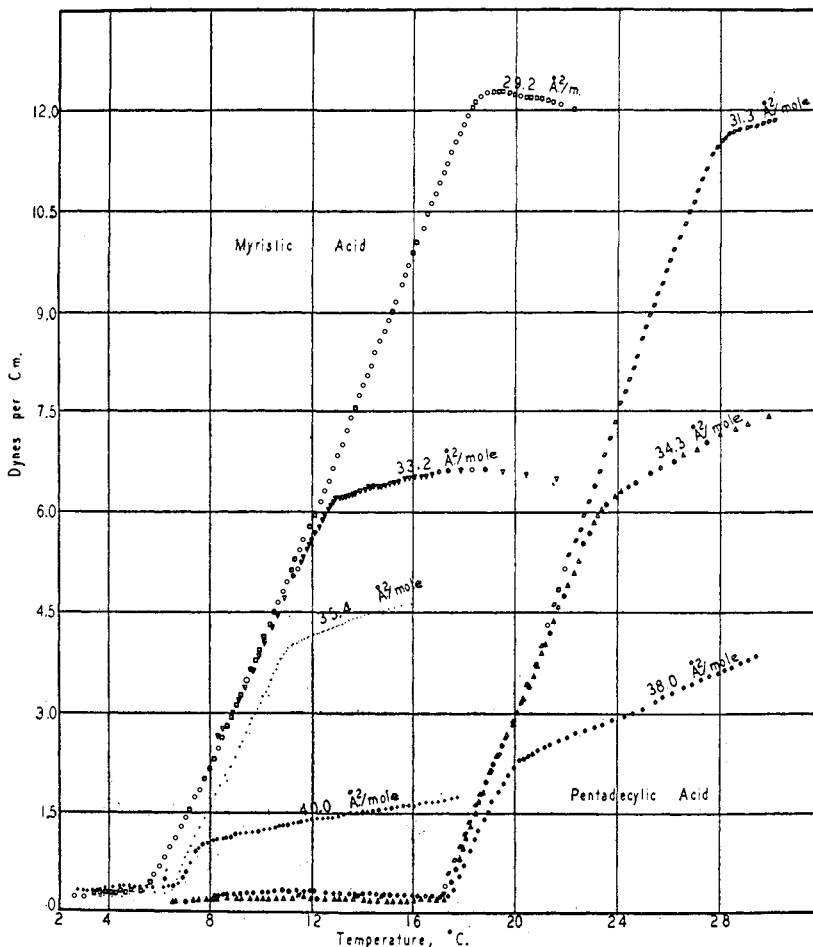

FIG. 11. Variation of the film pressure of intermediate and expanded films with temperature. The slope $(\partial \pi / \partial T)_{v,\sigma}$ is the entropy of the film.

In equation 26 π is defined as

$$\gamma_w - \gamma_f \tag{44}$$

and it can be shown that, in equation 16,

$$s_e = s_s + s_w \tag{45}$$

and in equation 17,

$$h_e = h_s + h_w \tag{46}$$

The energy changes of the greatest interest are those associated with the isothermal expansion (or compression) of a film between any molal area, σ_1, and any other molal area, σ_2. The heat content and heat absorbed may be calculated for either the spreading or the extension of the film. For one mole of material the increase of heat content is

$$\Delta H_m = \int_{\sigma_1}^{\sigma_2} (\partial H/\partial \sigma)_T \, d\sigma_m = \int_{\sigma_1}^{\sigma_2} h \, d\sigma_m \tag{47}$$

and the heat absorbed:

$$Q_m = T \int_{\sigma_1}^{\sigma_2} (\partial S/\partial \sigma)_T \, d\sigma_m = T \int_{\sigma_1}^{\sigma_2} s \, d\sigma_m \tag{48}$$

where ΔH_m and h of equation 23 and Q_m and s of equation 24 stand for $(\Delta H_m)_e$, h_e, $(Q_m)_e$, and s_e when the process is one of extension, and for $(\Delta H_m)_s$, $(Q_m)_s$, and s_s when the process is one of spreading.

The heat absorbed may readily be calculated from ΔH and ΔF of any process. For spreading:

$$(Q_m)_s = (\Delta H_m)_s - (\Delta F_m)_s = (\Delta H_m)_s + \int_{\sigma_1}^{\sigma_2} \pi \, d\sigma_m \tag{49}$$

For extension:

$$(Q_m)_e = (\Delta H_m)_e - (\Delta F_m)_e = (\Delta H_m)_e - \int_{\sigma_1}^{\sigma_2} \gamma \, d\sigma_m \tag{50}$$

X. ENERGY MAGNITUDES ASSOCIATED WITH THE SPREADING OR EXTENSION OF MONOLAYERS

The expansion of the surface of a pure liquid, or of a film-covered surface, may be considered to occur by the process which has been considered as *extension*. The energy of extension per square centimeter of surface formed may be considered in relation to any one of the following energy quantities: f, the increase of free energy; h, the increase of enthalpy or ϵ, the increase of internal energy, which is equal to h within the limits of error of their determination; q, the heat absorbed; and s, the entropy.

The value of h_e or ϵ_e for the extension of a water surface at 20°C. is 116 ergs cm.$^{-2}$, but for oils the values are small, and in the same units are: propane, 34; heptane, 50; octane, 50; propyl alcohol, 48; butyl alcohol, 48.5; heptylic acid, 52.5; octyl alcohol, 50.5.

It might be thought, in view of the above facts, that the increase in potential energy (ϵ_e) for the extension of a monomolecular film of oil and

the water upon which it lies, would be of the order of the above values, particularly if the principle of independent surface action is considered in this connection. However, this is very far from what is obtained by the application of the thermodynamic equations to the experimental data. This gives values of the increase of internal energy, in ergs per square centimeter of film produced by extension, as low as *zero* for long-chain alcohols in certain peculiar regions, 120 for condensed films of long-chain acids, 400 for some of their intermediate films, and as high as 900 for films, usually classed as solid monolayers, of the normal long-paraffin-chain alcohols.

A few representative values, which do not, however, include the minimum and maximum cited above, are given in table 7. This table shows that high values of the energy of extension or of spreading found for certain two-dimensional phases (intermediate and solid) are due to the abnormally large entropy of the monolayer, since the free energy of the oil film is in each case less than that of water. With solid alcohol monolayers the entropy (s_e) has been found to be as large as 2.6 ergs cm.$^{-2}$ deg.$^{-1}$ In the case of long-chain acids, the highest value of the entropy is found in the intermediate state. The highest values yet found are those for the solid long-chain alcohol monolayers, but values for the intermediate phase of the alcohols have not been obtained, on account of the high temperature required.

Let us consider the heat (q_s) absorbed by the spreading at 20°C. of a pentadecylic acid monolayer over 1 sq. cm. of the surface of water. On account of the instability of the solid film q_s is not known, but from the high values obtained for alcohols it may be expected to have a value of about 200 ergs. At E (figure 4) the solid monolayer melts with a *zero* heat of fusion, so the phase change is of the second order. The liquid condensed film thus formed absorbs practically no heat as it expands by spreading. At D there is a change, presumably of the third order, to the intermediate film for which q_s is also zero adjacent to D but rises rapidly to a nearly constant value of 280 ergs cm.$^{-2}$ At C there is a phase transformation to liquid expanded film, and the heat of spreading drops quickly to about 50 ergs cm.$^{-2}$

Let us suppose that we begin with a monolayer of pentadecylic acid at 21.7°C. and a molecular area of 20.0 Å.^{2} and allow it to expand by spreading to 20.5 Å.^{2} The heat absorbed is of the order of 0.15 kg.-cal. At E the monolayer melts without the absorption of heat, and it expands to (D) 20.8 Å. without absorbing any heat. The heat absorbed increases rapidly to a maximum per unit area, and the total heat absorbed in expanding by spreading through the whole intermediate state is 6.4 kg.-cal. At an area of 35.5 Å. per molecule the film changes to the liquid expanded state

TABLE 7

A. Energy (ε) and entropy (s) of extension and of spreading of monolayers on water

Energy in ergs cm.$^{-2}$; entropy in ergs cm.$^{-2}$ degree^{-1}

		f	ϵ	$q = Ts$	s
Liquid monolayers: pentadecylic acid	Expanded film at 22°C. and σ = 38 Å².				
	A. Clean water	72.46	116$_4$	44.00	0.14$_9$
	B. Film (extension)	69.80	161	91.6	0.31
	C = B − A (spreading)	−2.64	45	47.6	0.16
	Intermediate film at 20°C. and σ = 34.3 Å².				
	A. Clean water	72.75	116	43.25	0.148
	B. Film (extension)	69.75	394	324	1.106
	C = B − A (spreading)	−3.0	278	281	0.959
	Intermediate film at 18°C. and σ = 38 Å².				
	A. Clean water	73.05	115.5	42.49	0.146
	B. Film (extension)	72.32	367	295	1.014
	C = B − A (spreading)	−0.73	252	253	0.869
Liquid monolayers: hexadecyl alcohol at σ = 20.0 Å².	Condensed liquid film at 9°C. π = 7.7 dynes per cm.				
	A. Clean water	74.37	115.5	41.17	0.14$_6$
	B. Film (extension)	66.7	166	99.6	0.35$_3$
	C = B − A (spreading)	−7.7	50.$_7$*	58.4	0.20$_7$
Phase of low compressibility, usually designated as "solid"	At 16°C. π = 13.8 dynes per cm.				
	A. Clean water	73.34	116.1	42.77	0.148
	B. Film (extension)	59.5	508	449	1.55
	C = B − A (spreading)	−13.8	392	406	1.40$_4$

B. Effect of pressure on the energy relations of octadecanol at σ = 19.96 Å².

Phase	π	t IN °C.	ϵ_s	q_s	s_s
L_2	16	7.34	264	280	1.00
S	17	7.88	1528	1545	5.5
	18	8.06	1630	1648	5.9
	19	8.28	1062	1081	3.8
	20	8.57	760	780	2.8
	21	8.92	710	731	2.6
	22	9.29	617	639	2.3
	23	9.68	780	803	2.8
	24	10.05	845	869	3.1
LS	25	10.38	602	627	2.2
	29	12.95	385	414	1.45

* Values for the increase in internal energy on spreading (ϵ_s) of the condensed liquid (L_2) monolayer of a long-chain alcohol have been found in the range from 36 to 200 ergs cm.$^{-2}$, but with a long-chain normal acid the values lie in the vicinity of zero, so that the energy of extension of films of the acids is about 116 ergs cm.$^{-2}$, i.e., equal to the energy of extension of the water surface without the film.

and by further expansion to 44 Å.^{2} absorbs 2.1 kg.-cal if the process is spreading. The total heat absorbed in expansion from 20 to 44 Å. per molecule is 8.65 kg.-cal. *none* of which is used in melting the solid, and most of which is used in expansion in the intermediate state.

Table 8, taken from the work of Harkins, Young, and Boyd (14), gives the increase in enthalpy (ΔH) and the heat absorbed in the spreading and in the extension of a monolayer of pentadecylic acid. As the temperature rises, the amount of heat absorbed in the intermediate state decreases, while that in the expanded state increases. The total increase of enthalpy (ΔH), or of internal energy (ΔE), in passing through both the intermediate and the expanded state seems, if the process is one of extension, to decrease slowly as the temperature rises.

TABLE 8

Heat absorbed (Q_m) and increase of heat content (ΔH_m) for the spreading and extension of a pentadecylic acid film in the intermediate phase (EC) and the liquid expanded phase (CB)

Energy in kg.-cal. per mole; area (σ) in Å.^{2} per molecule; energy values calculated from those for ϵ_s in table 7

INTERMEDIATE PHASE							LIQUID EXPANDED PHASE					
			H_m		Q_m				ΔH_m		ΔQ_m	
σ_1	σ_2	$t°$	Spreading	Extension	Spreading	Extension	σ_1	σ_2	Spreading	Extension	Spreading	Extension
21.5	42.0	19.0	8.3	11.8	ΔH_m −0.080	9.6	42.0	43	Very small since $\Delta\sigma$ very small			
20.8	35.5	21.7	6.4	8.9	ΔH_m −0.160	7.4	35.5	44	0.7	2.1	ΔH_m −0.025	1.2
20.5	33.5	25.0	5.4	7.6	ΔH_m −0.0190	6.2	33.5	45	1.0	3.1	ΔH_m −0.054	1.8
20.5	31.5	27.5	4.6	6.5	ΔH_m −0.0195	4.9	31.5	46	1.3	3.7	ΔH_m −0.097	2.2

With esters the maximum value of h_s or q_s in the intermediate state is only about two-thirds that for the acids, but since the intermediate state persists to a much higher area than with the acids, the integral heat (ΔH_m) has about the same magnitude.

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