Molecular Interaction in Monolayers: Viscosity of Two-Dimensional Liquids and Plastic Solids. V. Long Chain Fatty Acids

BY EDWARD BOYD AND WILLIAM D. HARKINS

1. Introduction. Viscosity and Molecular Packing

The viscosity of liquid fatty acid monolayers on an aqueous subsolution is highly dependent upon the pH and the closeness and type of packing of the molecules in the film. One of the important uses of surface viscosity measurements is to prove the existence of phase transitions which are not revealed by other forms of measurement, such as those of pressure–area, or potential. Thus earlier work on surface viscosity in this Laboratory[1] indicated that above a pressure of about 23 dynes per cm. a film of pentadecylic acid is a "plastic" solid. Transitions of this type had not been observed previously in a substance of this class, which at the same temperature gives an expanded film. It seemed important to confirm this observation by an investigation of the form of the pressure–viscosity relation in the neighborhood of the indicated transition. Another purpose to be served by this investigation is the determination of the effect on the viscosity of the change from the hydroxyl groups of the alcohols studied by Fourt and Harkins[2] to the carboxyl groups of the corresponding straight chain acids.

The preceding paper of Nutting and Harkins[3] shows that the area per molecule of stearic acid at a low film pressure is 24.41 sq. Å., while that of stearyl alcohol is 21.82 sq. Å. The square roots of these values, 4.94 and 4.67 Å., give some idea of the relative distances between the molecules. A calculation based upon a model of hexagonal close packing for the molecules gives 5.57 and 5.27 Å. for the intermolecular distances. On account of the greater distance between the hydrocarbon chains of the molecules of acid in the film it is to be expected that films of the acids will be very much less viscous than those formed by the corresponding alcohols. In the high pressure regions of the force–area diagram the areas are more nearly the same. Thus, with margaric acid (C_{17}) at pressures above 24 dynes per cm. the

area per molecule is in the neighborhood of 20.4 sq. Å.; for heptadecyl alcohol at this pressure the area is of the order of 20.3 sq. Å. The square roots of these values, 4.51 and 4.50 Å., indicate that the molecular distances are nearly identical. Hence, in this region of high film pressure it might be expected that the non-Newtonian viscosities of the acid and corresponding alcohol films may be nearly the same. It is not meant to imply, however, that the nature of the polar group has no other effect than that which it exerts through its influence on the spacing of the hydrocarbon chains.

2. Apparatus, Materials and Methods

The surface balance and torsion system were the same as those previously used in this Laboratory by Fourt,[4] where, essentially, a measure of the surface viscosity is given by the dampening of the vibrations of a torsion pendulum oscillating in the film. The logarithmic decrement of the oscillations is proportional to the viscosity. Letting λ_{10} stand for the common logarithm of the ratio of successive amplitudes, and σ for the surface viscosity in C. G. S. units, we have

$$\sigma = \Delta\lambda_{10} \frac{2.3I}{2\pi P} \left(\frac{1}{a^2} - \frac{1}{b^2} \right)$$

where I is the moment of inertia, P is the period, a is the radius of the oscillating body, and b the radius of the bounding vessel. The value of $\Delta\lambda_{10}$ gives the change of decrement between the clean surface and that covered by the film, that is, applies a correction for the water resistance on the assumption that all of the change in resistance is caused by the film.

The fatty acids employed were prepared by Reid and Meyer and were the same as those used by Nutting and Harkins with the exception of the nonadecanoic acid which was purified by vaporization and condensation at very low pressure.

All of the acid films were spread on 0.01 N hydrochloric or sulfuric acid solutions made up with redistilled water.

(1) W. D. Harkins and R. J. Myers, *Nature*, **140**, 465 (1937); R. J. Myers and W. D. Harkins, *J. Chem. Phys.*, **5**, 601 (1937).

(2) L. G. Fourt and W. D. Harkins, *J. Phys. Chem.*, **42**, 897 (1938).

(3) G. C. Nutting and W. D. Harkins, THIS JOURNAL, **61**, 1180 (1939).

(4) L. G. Fourt and W. D. Harkins, *J. Phys. Chem.*, **42**, 897 (1938).

Table I

Viscosity of Monolayers of the Normal Saturated Fatty Acids in Surface Poises at a Few Surface Pressures

No. of C atoms	2	5	7	10	15	18	20	25
15	. . . .	. . . .	. . . . .	. . . . .	. . . . .	0.00070	0.00190	(0.700)
16	. . . .	. . . .	0.00037	0.00063	0.00152	.00262	.00440	. . . . .
17	. . . .	0.00040	.00061	.00109	.00222	.00360	.00520	(.270)
18	0.00123	.00150	.00174	.00212	.00298	.00378	.00420	. . . . .
19	.00382	.00421	.00473	.00550	.00705	.00840	.00995	(.0250)
20	.01000	.01230	.01420	.01780	.02530	.03100	.03580	.05700

Values contained within parentheses are non-Newtonian viscosities.

3. Viscosity Relations of the Long Chain Acids

The viscosities of monolayers produced on an aqueous subphase of pH 2 are given at a few pressures in Table I, and for all of the pressures that were investigated in Fig. 1.

The most important relations exhibited are:

(1) From the lowest pressures investigated up to 18 dynes per cm. or more the logarithm of the surface viscosity is proportional to the film pressure, or

$$\log \sigma = \log \sigma_0 + Kf \qquad (1)$$

for all of the acids from 16 to 20 carbon atoms.

(2) The viscosity of the liquid films increases rapidly with the length of the hydrocarbon chain.

(3) The liquid or low pressure condensed films exhibit a Newtonian viscosity.

(4) The viscosity of the "plastic" (or high pressure condensed) films decreases with the length of the hydrocarbon chain.

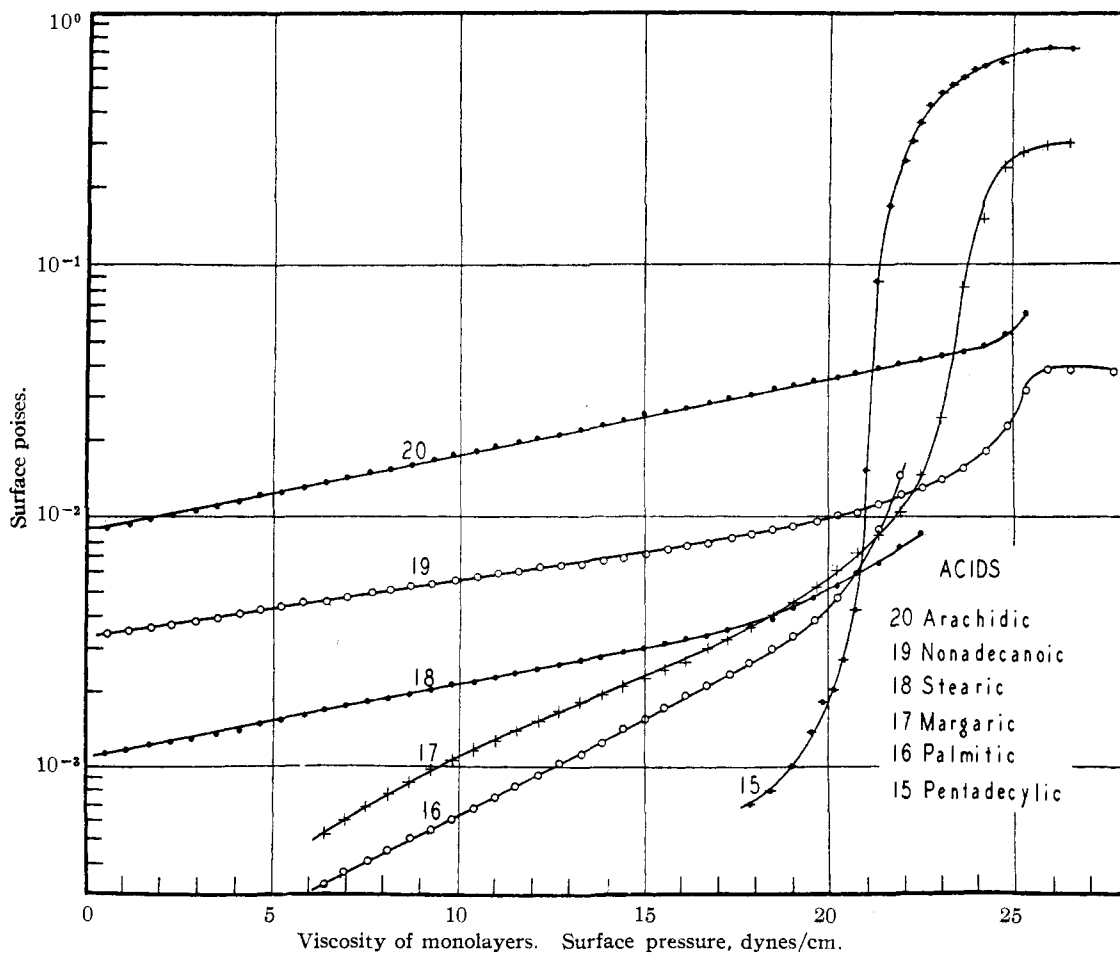(5) Films designated as "plastic" exhibit a non-

Fig. 1.—Viscosity of monolayers of the long chain fatty acids with from 15 to 20 carbon atoms per molecule.

Newtonian viscosity, that is, the viscosity varies with the rate of shear.

(6) The film viscosity begins to increase more rapidly than corresponds to eq. 1 at a pressure considerably below that of the sharp kink in the film-pressure–area curve. Also, the rise in viscosity between the low pressure condensed film and the high pressure condensed film is larger the shorter the hydrocarbon chain of the fatty acid.

(7) Above the transition pressure the surface viscosity increases less rapidly until it approaches some degree of constancy.

(8) The viscosities of the monolayers of the acids are very much less than those of the corresponding alcohols (Table II). Thus, at four dynes per cm. pressure with 16 carbon atoms in the molecule the alcohol film is of the order of 33 times more viscous than that of the acid; with 17 carbon atoms the factor is the same, while with 18 carbon atoms it has fallen to 17 times that of the acid.

TABLE II

SURFACE VISCOSITY AT A PRESSURE OF 4 DYNES PER CM.

| | Surface poises | |
	Acid	Alcohol
C_{14}	....	0.0005
C_{15}	....	.0031
C_{16}	0.0002	.0066
C_{17}	.0003	.0100
C_{18}	.0014	.0230
C_{19}	.0040	....
C_{20}	.0115	....

Relations (2), (3), (4), (5), (6), and (7) are the same as were found in earlier work with the alcohols.

Since the investigations were not continued beyond the kink-point into the plastic region except with the 15, 17, and 19, or odd acids it may seem that the general statement (4) has not been shown to hold for the even acids. That the non-Newtonian viscosity of the "plastic" film decreases with the length of the hydrocarbon chain has been found to be general for the alcohols, and the appearance of the high pressure ends of the surface viscosity curves seems to indicate that the even acids may be included in the relationship.

The inclusion of the surface viscosity measurements in the "plastic" region of the odd-numbered carbon atom acids is due to the fact that the transition from liquid to "plastic" film is accomplished much more easily if the number of carbon atoms is odd. In carrying out a series of viscosity measurements the film is compressed very slowly,

since a long pause is made after a pressure increment of one-quarter to one-half a dyne per cm. in order to complete a measurement of the surface viscosity. However, the transition from liquid to "plastic" film may be brought about with acids which contain an even number of carbon atoms provided the compression is sufficiently rapid.

4. The Use of Viscosity Measurements in the Detection of New Types of Phase Transitions

A paper to be published later by Nutting and Harkins indicates that at 25° with increasing pressure the transition Expanded → Intermediate film occurs at 8.3 dynes per cm. and 33.4 sq. Å. The intermediate film exhibits a very high, but not infinite, compressibility, and this decreases rapidly as the pressure rises.

Now it is sometimes assumed that this intermediate film, provided it does not collapse at too low pressures, finally changes to some form or other which has some of the characteristics of a condensed film. Whether this film is liquid or solid, or whether the transition to the condensed state is gradual or sudden, has not been known.

However, the pressure–area relations of the pentadecylic acid monolayer at high pressures as shown in enlarged form in Fig. 2 give some interesting relations which prove that there are sudden changes of state, as

(1) Liquid condensed ——→ "Plastic" solid film at 21.1 dynes per cm. and 20.6 sq. Å.

Thus the pressure–area relations exhibit intersections of straight lines at this point. However, since these straight lines are short, the straightness might be the result of accident.

That the above transformation from the liquid condensed to "plastic" solid actually takes place is proved definitely by the following viscosity relations shown by Fig. 1.

(a) Between 19.8 and 21.4 dynes per cm. the viscosity of the pentadecylic acid film increases from 0.005 to 0.107 surface poises, or an increase of 21 times, with the most rapid increase at 21.1 dynes per cm., which is the kink-point in the f, a diagram.

(b) Below 19.8 dynes per cm. the film is liquid since the viscosity is Newtonian. Above 21.4 dynes the film is "plastic" in the sense that the viscosity is non-Newtonian.

(2) There also appears in Fig. 2 an intersection at 25° between two straight lines at 17.7 dynes per cm., and 21.8 sq. Å. Whether this rep-

resents an actual transition can be proved by viscosity measurements in this region.

As may be seen from Fig. 2, the work of Nutting and Harkins exhibits also other kinks between what appear to be two straight lines, at $t = 21.7°$, $f = 15.50$, and $a = 22.15$; and also at $t = 17.9°$, $f = 12.15$, and $a = 22.42$. These may indicate transitions from liquid condensed to "solid" films, but this is not certain until viscosity measurements are made at these temperatures and pressures.

5. Preliminary Experiments on the Effect of Temperature upon the Viscosity of a Monolayer

Since nothing has been known earlier as to the influence of temperature upon the viscosity of a monolayer, the general magnitude and sign of the effect have been determined. While apparatus for the precise determination of superficial viscosity, and for the accurate regulation of the temperature, were both available, it was not convenient to bring them together at this time, so the determination of the exact temperature coefficient has been deferred until this can be done.

The viscosity of a liquid layer of arachidic acid is found to be multiplied by about five by a decrease of temperature from 25 to 10° (Fig. 3). This is an extremely great increase for such a small temperature interval.

The values obtained at 31.5° indicate that the viscosity changes much less rapidly at the higher than at the lower temperatures. The explanation of the high values at 10° may be related to a phenomenon noted at this temperature. At 25° the portion of the curve in which the logarithm of the viscosity is linear with respect to the pressure (f) is a true liquid. At 10°, however, the monolayer exhibits a non-Newtonian viscosity above a pressure of about 11 dynes per cm., although the transi-
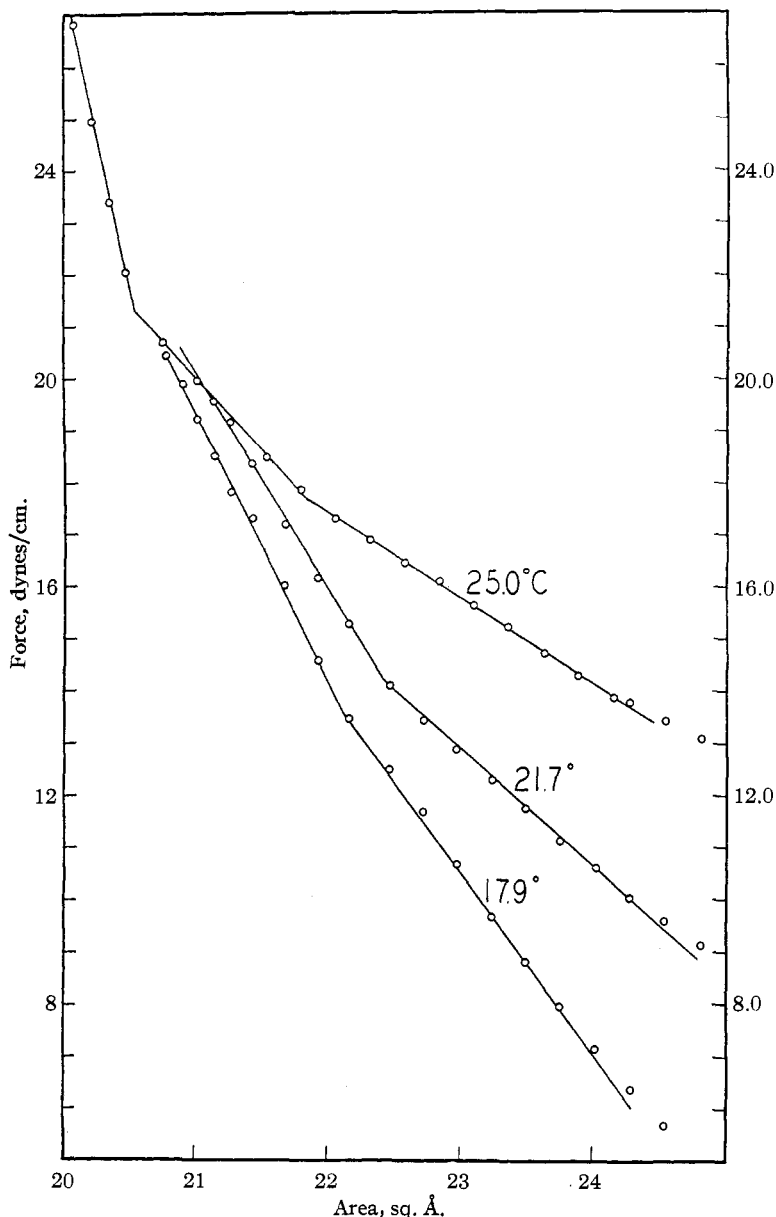

Fig. 2.—Pressure–area relations of pentadecylic acid. In passing from below to above the kink at 25°, 21.1 dynes per cm., and 20.6 sq. Å., there is an enormous increase in viscosity, which indicates that the transition Liquid-Condensed → "Plastic-Solid" occurs at this point. The other kinks have not as yet been proved to represent phase transformations, since the viscosities in these regions have not been measured.

tion to the "solid" state does not occur until a higher pressure is reached. This type of behavior was noted by Fourt and Harkins[2] in films of octadecyl alcohol. It is possible that with this alcohol at 23°, and arachidic acid at 10°, the molecules have become so tightly packed that they are in a state such that the intermolecular energy decreases, instead of increasing, with increasing pressure.
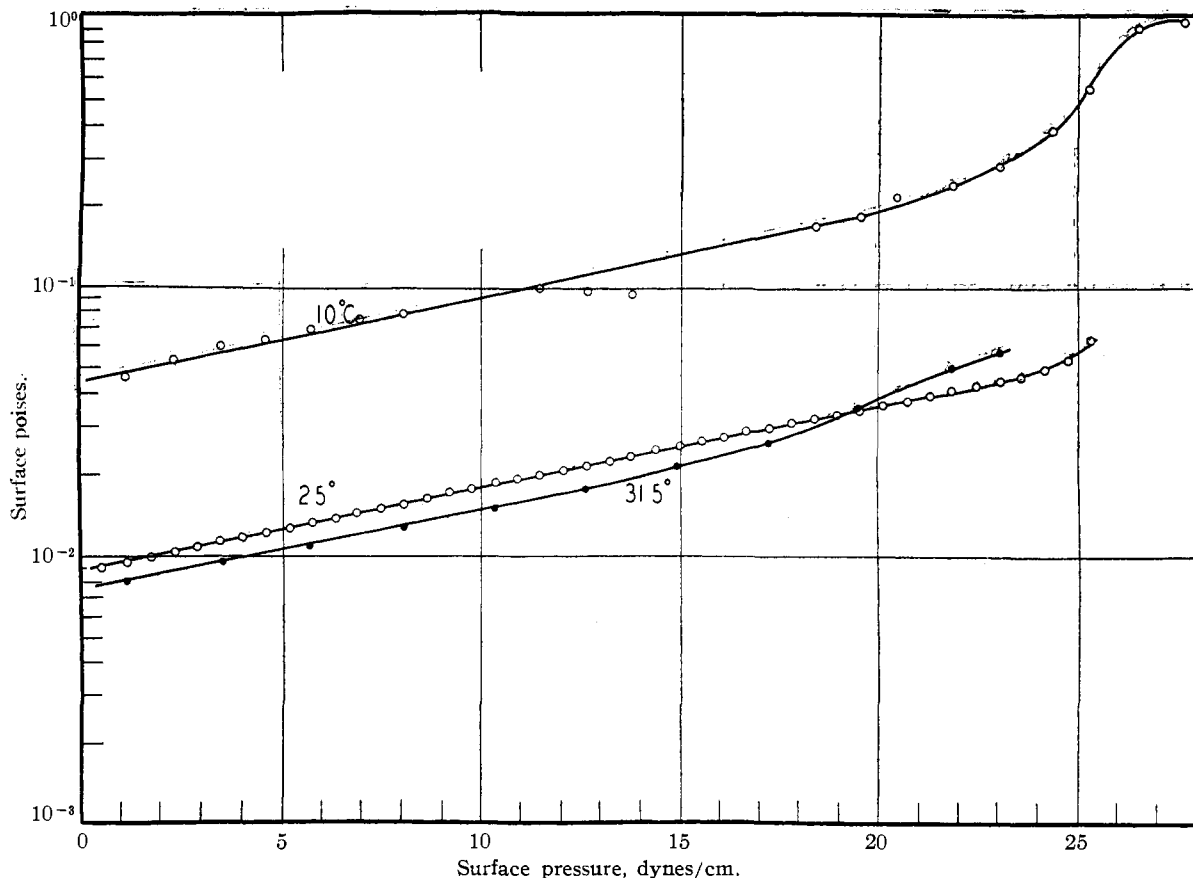
Fig. 3.—Effect of change of temperature upon the viscosity of arachidic acid (20 C atoms).

6. Relation to Theory

The heat motion in a liquid, as in a solid, may be considered as an oscillation about an equilibrium position but in the liquid this position is itself subject to a jerky translating motion of mean distance δ. The average longevity of this equilibrium position decreases rapidly with the temperature, and is given by Frenkel[5] as

$$\tau = \tau_0 e^{U/kT} \qquad (2)$$

where τ_0 is the period of the oscillations ($\sim 10^{-13}$ sec.) and U is an activation energy corresponding to a transition from one equilibrium position to another, and $U \sim$ a few thousand calories per mole.

From this he obtains the self-diffusion coefficient (D) of a non-crystalline body as

$$D = \frac{\delta^2}{6\tau} = \frac{\delta^2}{6\tau_0} e^{-U/kT} \qquad (3)$$

and by the use of Einstein's relation $Dc = kT$, in which c is the coefficient of friction, and of Stokes' law $\varphi = 6\pi \eta r$, and the assumption that

the radius $r \cong \delta$, he obtains for the viscosity η the relation

$$\eta = \frac{kT\tau_0}{\pi\delta^2 r} e^{U/kT} \qquad (4)$$

This may be written

$$\eta = nkT\tau_0 e^{\frac{U}{kT}} = M_R\tau_0 e^{\frac{U}{kT}} \qquad (5)$$

where M_R is the coefficient of rigidity.

Andrade's equation is similar, and that of Prandl has the same general form.[6] All of these equations, and that of Eyring, as discussed later, lead to expressions of the following form for the two-dimensional viscosity σ.

$$\varphi = \frac{1}{\sigma} = A e^{-\Delta F/kT} \qquad (6)$$

where A and ΔF are either independent of or vary slowly with temperature. ΔF may be considered as the free energy of activation for diffusion.

Theory of Moore and Eyring.—A theory of the viscosity of liquid monolayers has been de-

(5) J. Frenkel, Trans. Faraday Soc., 33, 58 (1937).

(6) Andrade, Phil. Mag., [7] 17, 705 (1934); Prandl, Z. angew. Math. Mech., 8, 85 (1928).

veloped by Moore and Eyring.[7] Before this is discussed it may be well to consider some of the fundamental ideas of Eyring's theory of three-dimensional viscosity. He takes over from Frenkel's theory of electrical conduction and diffusion[8] in crystals the idea of ionic or molecular "holes," though Frenkel does not utilize this conception in his own theory of viscosity.

Eyring considers that each of the N molecules of a liquid is bound to the others by n_i bonds of each particular kind, of strength E_i, so that the total energy $E = N \Sigma_i n_i E_i$. To vaporize the N molecules the energy required is $NE/2$, since each bond belongs to two molecules. This is true if no hole is left, but if it is left the energy per molecule is E. However, if this molecule is returned to the liquid the energy $E/2$ is gained, so $E/2$ is the energy required either to make a hole of molecular size in the liquid, or to vaporize a single molecule. That is, the energy is the same for a hole of molecular size to detach itself from empty space and pass into the liquid as for a molecule to detach itself from the liquid and pass into empty space. Eyring considers that the number of molecules in unit volume of vapor in equilibrium with the liquid, is a rough measure of the number of holes in unit volume of liquid. Moore and Eyring apply this idea to the viscosity of a monolayer on an aqueous subsolution.

Let us consider the vaporization process for a monolayer of a long chain acid, such as one of those considered in this paper. Eq. (1) which exhibits the experimental data is related closely to eq. (3) of Moore and Eyring. This may be put in the following form

$$\log \sigma = \log (h/a) + \Delta F/kT \qquad (7)$$

in which their equation (5) gives

$$\Delta F = RT \ln f' + (p + p_i)Na + \Delta F_s \qquad (8)$$

in which $f' = (2\pi m k T)h^{-1} V_f^{1/3}$ is the partition function for one translational degree of freedom in the normal liquid film, and will not vary appreciably with pressure, and only to a small extent with the compound in the case we consider. Thus we may write

$$\Delta F = \Delta F_s + NW + RT \ln f' \qquad (9)$$

where ΔF_s is approximately constant and W is the work of producing a hole in the film of the size of

(7) W. J. Moore and H. Eyring, *J. Chem. Phys.*, **6**, 391 (1938).

(8) J. Frenkel, *Z. Physik*, **35**, 652 (1926); C. Wagner and W. Schottky, *Z. physik. Chem.*, **B11**, 163 (1930); W. Schottky, *ibid.*, **B29**, 335 (1935); C. Wagner, *ibid.*, **B22**, 181 (1933); W. Jost, *J. Chem. Phys.*, **1**, 466 (1933); *Z. physik. Chem.*, **A169**, 129 (1934); W. Jost and G. Nekleo, *ibid.*, **B32**, 1 (1936).

the molecule. The principal assumption now enters, and this in three dimensions is expressed by

$$W = (p + p_i)v_0 \qquad (10)$$

in which p_i is the internal pressure $(\partial E/\partial V)_T$, and v_0 is the volume of a molecule. When converted into two dimensions these relations may be expressed, due to the cancellation of constant terms, as

$$\log \frac{\sigma}{\sigma_0} = (W - W_0)/kT \qquad (11)$$

where σ_0 is the viscosity coefficient of the film in the arbitrary reference state in which the work of forming a hole is W_0. If the theory can be regarded as correct, we have found empirically that

$$(W - W_0)/kT = Kf \qquad (12)$$

in which f is the pressure per unit length of the film.

If the equation of state

$$(f - f_0)(a - a_0) = kT \qquad (13)$$

is applied, then thermodynamics gives $f + f_i = T \left(\frac{\partial f}{\partial T}\right)_a$, as simply $f - f_0$. Thus if Eyring's formula for W is used, the work $W = (f - f_i)a_0$ becomes

$$W = (f - f_0)a_0 \qquad (14)$$

If now the hypothetical reference state is taken as that in which W_0/kT is given by $-f_0a_0/kT$, our formula is obtained with $K = a_0/kT$. Thus, to the extent to which the above equation of state is valid, our results are in agreement with the theory of Moore and Eyring.

The extent of the numerical agreement may be seen by assuming a to be 22 sq. Å., which is moderately close to its mean value. Then the term

$$a/kT = \frac{22 \times 10^{-16}}{1.37 \times 10^{-16} \times 298} = 0.054$$

in absolute units, while our values of K vary for the acids from 0.022 to 0.076.

The theoretical relations, which might indicate that in the "plastic" solid phase the viscosity should decrease with the length of the chain, are not obvious. It is somewhat simpler to explain the fact that in this phase the viscosity is nearly independent of pressure. In a private communication Moore and Eyring suggest a connection with the well-known diagram which exhibts the relation between inter-molecular distance, or area (Fig. 4), and energy. They assume that in the liquid the molecular area corresponds to a, where increasing the pressure decreases the area but increases the energy E_a, of transfer of a molecule

from liquid to gaseous film (or to make a hole of molecular size in the liquid film). Some fraction of this, plus the work done against the internal pressure, is taken as the activation for viscous flow. Since the entropy of activation will be only slightly changed by the added pressure, these changes constitute very nearly the total change in free energy due to the change in pressure.
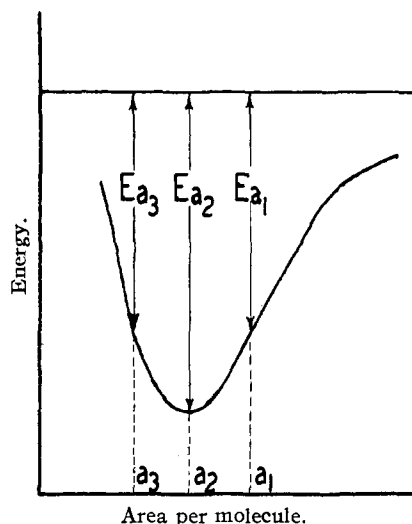

Area per molecule.

Fig. 4.

In the "plastic" solid state they assume the area to be close to the energy minimum, as at a_2. The application of pressure now decreases the internal energy E_{a_2} toward E_{a_1}, and this largely compensates for the work fa against the external pressure, so ΔF and hence the viscosity of the film become much less dependent upon the pressure.

In the "solid plastic" state the energy of activation includes not only the energy required to make holes of molecular size, but also an activation for the migration of the hole. This latter energy is one of the principal contributors to the structural term ΔF_s.

The increase of viscosity with the length of the molecule is explained in this type of theory by the increase in the energy of vaporization, i. e., the process: liquid film → gaseous film.

Moore and Eyring consider that the decrease in viscosity with the length of the molecule is due to a better locking together of the structure with the shorter hydrocarbon chains. According to Eyring's theory the viscosity is independent of the rate of shear only when the work done by the force applied in carrying a molecule over the barrier is small compared with kT.

If $p_i Na$ is taken as $E_v/3$ the internal heat of vaporization, then eqs. (7) and (8) may be expressed in two dimensions as

$$\Delta F = RT \ln f' + E_v/3 + F_s + fa \qquad (15)$$

or more generally $E_v/3$ may be replaced by E_v/n, where n is of the order of 3 or 4 in three dimensions and is not known for two. A paper by Eirich and Simha[9] which has just appeared endeavors to identify the value of n for three dimensions with a function φ or λ_i/h_s, in which λ_i is the internal latent heat of vaporization per molecule, and h_s is the Gibbs heat function for the surface per molecule. The reciprocals of these values were given by Harkins and Roberts.[10] The values vary from 2 to 7 at ordinary temperatures, to extremely high values at higher temperatures, for ordinary liquids.

Summary

1. The viscosity (σ) of monolayers of long chain acids on aqueous subsolution has been measured. With condensed liquid films the increase in logarithm of the viscosity is proportional to the film pressure.

2. In section 3 of the paper eight important relations are listed beneath Table I, and these should be considered as the most important part of this summary.

3. The compression of a monolayer of pentadecylic acid at 25° and pH 2 gives the following types of film in succession: (I) Gas, (II) Expanded, (III) Intermediate, (IV) Liquid-Condensed, and (V) Plastic-Solid. The transformation IV → V has never before been detected in a case in which the liquid condensed is formed from the intermediate type of film. In this work the great increase in viscosity between the two states makes it certain that the transformation occurs.

4. The viscosity of a monolayer of arachidic acid is found to decrease as the temperature rises. This is the first determination of the temperature effect.

5. The experimental results are compared with theories of viscosity in three dimensions,

(9) F. Eirich and R. Simha, J. Chem. Phys., 7, 116 (1939).
(10) W. D. Harkins and L. E. Roberts, THIS JOURNAL 44, 656, column 15 (1922).

and particularly with the two dimensional theory of Moore and Eyring. The theory indicates a general correspondence between our value of k', in the equation

$$\log \sigma = \log \sigma_0 + k'f$$

and their value a/kT, where k' is a constant. If k is the Boltzmann constant then in absolute units $a/kT = 0.054$, while k' varies in our work from 0.022 to 0.076.

Pyrrolidinium Analogs of Choline and Betaine. Onium Compounds. XXI
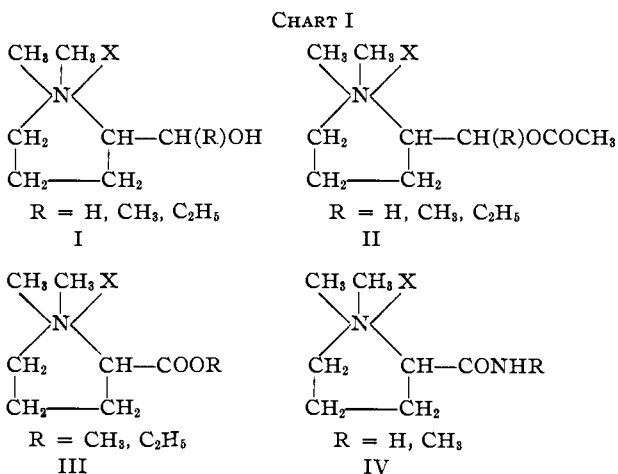
BY R. R. RENSHAW[1] AND W. E. CASS[2]

The work described in this paper represents a continuation of previous investigations on the synthesis[3] and pharmacology[4] of nitrogen heterocyclic onium compounds having a substituent on the cyclic carbon atom. The preparation of certain pyrrolidinium derivatives is described here.[5] In these compounds the carbon chain of choline or betaine is contained partly in the heterocyclic ring. On this basis compounds, which may be considered analogous to choline, β-methyl choline and β-ethyl choline, I, the acetylated derivatives of these cholines, II, the methyl and ethyl esters of betaine, III, and the amide and methyl amide of betaine, IV, have been obtained. Certain tertiary pyrrolidine salts, closely related to these compounds, also have been prepared.

CHART I

$$
\begin{array}{cc}
\text{I} & \text{II} \\
R = H, CH_3, C_2H_5 & R = H, CH_3, C_2H_5 \\
\text{III} & \text{IV} \\
R = CH_3, C_2H_5 & R = H, CH_3
\end{array}
$$

(1) This paper is being published, following the death of Professor Renshaw, by his collaborator.

(2) This paper has been constructed from a thesis presented by W. E. Cass, June, 1938, for the degree of Doctor of Philosophy at New York University.

(3) Renshaw and Conn, THIS JOURNAL, **59**, 297 (1937); Renshaw, Ziff, Brodie and Kornblum, *ibid.*, **61**, 638 (1939).

(4) Hunt and Renshaw, *J. Pharmacol.*, **35**, 75 (1929); **37**, 177 (1929).

(5) The physiological activity of these compounds is being determined in coöperation with Drs. Green and Brodie at the Department of Pharmacology, College of Medicine, New York University, and will be reported elsewhere.

Choline and Acetylcholine Analogs.—(1-Methylpyrrolidyl-2)-methanol was obtained by the reduction of the ethyl ester of hygric acid (1-methyl pyrrolidine-2-carboxylic acid) with sodium and alcohol. (A new synthesis for hygric acid will be described below.) Methyl iodide added readily to this substance in dry ether with the production of the choline analog (I, R = H). Treatment of (1-methylpyrrolidyl-2)-methanol in dry ether with acyl halides yielded hydrohalide salts of esters of this tertiary amino alcohol.

In the preparation of the remaining members of this series (I, R = CH_3, C_2H_5), 2-pyrrolidyl methyl and ethyl methanols were obtained by the reduction of 2-acetyl- and 2-propionylpyrroles with sodium and alcohol, according to the method of Hess.[6] It was found advisable to modify the procedure of Hess by using larger amounts of carefully dried alcohol and a stirring technique which favored more rapid reaction. The yields of pyrrolidine alcohols were 25–30%. The onium derivatives of these pyrrolidine alcohols were obtained by treating the secondary bases in alcohol solution with an excess of methyl iodide in the presence of an excess of barium hydroxide.

The acetylcholine analogs (II) were obtained in all cases by heating the quaternary alcohols (I) at 100° in a sealed tube with a large excess of acetic anhydride for five to ten hours. The crude onium derivatives were precipitated from the acetic anhydride by the addition of dry ether.

Betaine Ester and Amide Analogs.—Compounds in this group are all derivatives of hygric acid. This substance has been synthesized by Willstätter and Ettlinger[7] in several steps from malonic ester. Hygric acid was here prepared by a method involving the catalytic hydrogenation of 1-methylpyrrole-2-methylcarbonamide, a

(6) Hess, *Ber.*, **46**, 3123 (1913).

(7) Willstätter and Ettlinger, *Ann.*, **326**, 91 (1903).