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can be traced in large part to inadequacy of the Lorentz expression (3) for the local field. The hypothesis of hindered rotation then seems much less convincing as an explanation of the general behavior of such substances unless one considers it as an expression of the dipole-dipole coupling in the fashion that the Onsager local field appears to be. This latter with the modifying factor q is seen from several points of view to be a very satisfactory representation of the general behavior of dielectrics when one considers the crudeness of some of its basic assumptions. Because of the importance of temperature and frequency as parameters affecting the electrical properties of polar substances it would seem best to make a more detailed, critical study only when measurements are available over a wide range of these quantities for a reasonable number of different substances.

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Theory of the Viscosity of Unimolecular Films

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The equation for the fluidity of a liquid based on the reaction rate theory of viscous flow is modified to interpret the viscosity data for liquid films. The free energy of activation for viscous flow in the surface films, as calculated from the viscosity data of Harkins and Meyers, and Langmuir and Schafer, is found to be about twice that for flow in the liquid in bulk. This may be explained by the occurrence of various types of association in the liquid films, e.g. lateral association of the surface molecules with one another and vertical association with the solvent (solvation of the polar groups). Equations are given for the pressure and temperature effect on surface viscosity. It is shown how the knowledge of these effects may be used to interpret the structure of the films, and to separate and evaluate the contributions to the free energy of activation due to lateral association, solvation and hydrogen bonds.

THE general equation for the fluidity of a liquid has been formulated as follows:[1]

$$\phi=\frac{\Delta V}{f\lambda_1}=\frac{kT}{h}\cdot\frac{\lambda}{f\lambda_1}\left\{\exp\left(\frac{-\Delta F\ddagger+(\lambda_2\lambda_3\lambda/2)f}{kT}\right)-\exp\left(\frac{-\Delta F\ddagger-(\lambda_2\lambda_3\lambda/2)f}{kT}\right)\right\} \quad (1)$$

λ = distance between equilibrium positions in direction of flow,
λ_1 = perpendicular distance between adjacent molecules in direction of flow,
λ_2 = distance between adjacent molecules in direction of flow,
λ_3 = distance between molecules in plane of flow and normal to direction of flow,
f = applied external force per square centimeter,
ΔV = relative velocity of adjacent layers a distance λ_1 apart,
$\Delta F\ddagger$ = free energy of activation for viscous flow per molecule.

Recently, Harkins and Meyers,[2] and Langmuir and Schafer[3] have determined the absolute viscosities of films of the liquid type. Whatever the mechanism for viscous flow in the surface layer, it can be treated by the same general reaction rate theory, since it is a process involving an activation energy. The three-dimensional equation may thus be easily modified to interpret these new data.

[1] Eyring, J. Chem. Phys. **4**, 283 (1936). Eyring and Ewell, ibid. **5**, 726 (1937).

[2] Harkins and Meyers, J. Chem. Phys. **5**, 601 (1937); **6**, 53 (1938).

[3] Langmuir and Schafer, J. Am. Chem. Soc. **59**, 2400 (1937).

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TABLE I.

COMPOUND	$\Delta F\ddagger$ FOR LIQUID FILMS	$\Delta F\ddagger$ FOR PURE LIQUIDS	$\Delta F\ddagger$ (FILM)/ $\Delta F\ddagger$ (LIQ.)
Myristic acid	10360 cal.[2]	5770@70°C	1.80
Palmitic acid	10900[2]	5920 " "	1.84
Stearic acid	11030[2]	6300 " "	1.75
Oleic acid	10360[2]	6220@20°C	1.67
Cetyl alcohol	15300[3]	5800@60°C	2.62

The shear force acting on a single molecule at the interface is $f\lambda_2$ and it acts through a distance $\lambda/2$. Thus in the two-dimensional case

$$\Delta V=\lambda\frac{kT}{h}\left\{\exp\left(\frac{-\Delta F\ddagger+(\lambda/2)\lambda_2 f}{kT}\right)-\exp\left(\frac{-\Delta F\ddagger-(\lambda/2)\lambda_2 f}{kT}\right)\right\}. \quad (2)$$

Therefore the fluidity

$$\phi=\frac{\lambda kT}{\lambda_1 fh}e^{-\Delta F\ddagger/kT}\left\{\exp\left(\frac{\lambda f\lambda_2}{2kT}\right)-\exp\left(\frac{-\lambda f\lambda_2}{2kT}\right)\right\}.$$

This, on expansion, when $\lambda f\lambda_2 \ll kT$, becomes

$$\phi=\frac{\lambda\lambda\lambda_2}{\lambda_1 h}e^{-\Delta F\ddagger/kT}$$

To a first approximation $\lambda_1=\lambda$, and

$$\phi=(a/h)e^{-\Delta F\ddagger/kT} \quad (3)$$

where a is the cross-sectional area of the units which flow. Although the correctness of our general equations (2) and (3) does not depend on the exact mechanism of flow, we may most easily interpret the viscosity of liquid films by assuming the same model as was used in the case of the three-dimensional liquid. Therefore we picture the molecules oriented at the surface as rolling around one another whenever there is a neighboring hole in the surface which permits this rotation.

Using the available viscosity data we have calculated $\Delta F\ddagger$ for the viscous flow of the liquid films, and compared the values with those for the pure liquids obtained from the three-dimensional equation and viscosity data available in the literature. We have assumed in the calculation that a is the cross section of a single molecule; doubling the value of a increases $\Delta F\ddagger$ by only about 300 cals. The results are given in Table I.

Langmuir and Schafer found that the surface viscosities showed large variations with the age of the water on which the films were spread, the age of the film, the pH of the water, etc. With new water and newly spread monolayers, the surface viscosity of stearic acid was found to vary from 0.002 surface poises at pH 5.8 to 2.6, at pH 9.0. This corresponds to a variation in $\Delta F\ddagger$ from 12,100 cal. to 16,500 cal.

It is evident from these considerations that the free energy of activation for viscous flow in the surface layer is about two to three times that for flow in the liquid in bulk. In viscous flow, as in a chemical reaction, the process will go principally by the path requiring the least expenditure of free energy. Since the units of flow in the liquid are probably single molecules, there is evidently some degree of association in the liquid films. This may be due to lateral association of the surface molecules to give dimers, trimers, etc., or to vertical association or solvation of the polar groups. In either case the free energy of activation required for the flow process will be greater than it would be if the flow units were single molecules.

The widely varying viscosities found by Langmuir and Schafer suggest that no single explanation will cover all the observed data. Thus the high values of $\Delta F\ddagger$ may be due to a combination of such factors as vertical association, lateral association, and salt formation. The picture is akin to the situation in reaction kinetics in a system where there are a great many possible simultaneous reactions, with widely different reaction rates. The viscous flow process may be considered as a bimolecular reaction, consisting of the collision of a pair of molecules, rotation of the activated complex formed, and then dissociation of the complex.

If there are two different molecular species present, e.g. double molecules and single molecules, we may formulate the fluidity for the binary system as follows

$$\phi=\phi_1\frac{n_1^2}{n_{01}^2}+2\phi_{12}\frac{n_1 n_2}{n_{01}n_{02}}+\phi_2\frac{n_2^2}{n_{02}^2}. \quad (4)$$

Here ϕ_1 is the specific fluidity for the rotation of

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two single molecules, ϕ_{12}, for the rotation of a single around a double molecule, and ϕ_2, for the rotation of two double molecules; n_1 and n_2 are the number of molecules of each species per cc in the mixture, and n_{01} and n_{02} are the numbers per cc in a system containing only the one type of molecule. We see that the presence of large molecules will decrease the fluidity by cutting down the number of pairs of small molecules which are able to rotate. It is to be noted, however, that even if a large proportion of the surface molecules have such a large $\Delta F\ddagger$ as to be practically immobilized, the over-all fluidity, ϕ, may still be appreciable since it is the processes of low $\Delta F\ddagger$ that mainly determine the reaction rate. In other words ϕ_1 is much larger than ϕ_{12} or ϕ_2.

We may predict the pressure effect on viscosity as in the three-dimensional case. If δs is the area of the surface hole necessary for viscous flow, the free energy required to make a hole this size in the surface is $(p+p_i)\delta s$, per molecule. Here p is the applied external pressure; p_i is the internal pressure, defined as $(\partial E/\partial s)_T$ where s is the surface area; p and p_i are actually pressures per unit length per film thickness. Because film thickness cannot usually be varied arbitrarily, this dimension is customarily ignored in specifying surface forces and energies. If we put $N\delta s=\Sigma$, the free energy of making one mole of holes becomes $(p+p_i)\Sigma$.

We may now write

$$\Delta F\ddagger = RT\ln f+(p+p_i)\Sigma+\Delta F_s\ddagger. \qquad (5)$$

Here f is the partition function for the translational degree of freedom of the normal liquid which, in the activated state, is included in the factor kT/h. $RT\ln f$ amounts to about 1 kcal. for most substances. $\Delta F_s\ddagger$ is the structural free energy of activation. For nonpolar molecules it is negligible, but for systems having directional bonds, e.g. hydrogen bonds, the satisfactory saturation of these bonds in the activated state may be prevented because of their short range, directional nature.

It was shown in earlier treatments for liquids that p_iV ($V=Nv$, where v is volume of the hole required for flow process) was approximately one-third the energy required to vaporize the unit which flowed. Since the energy required to make a hole the size of a molecule equals the energy of vaporization, this was interpreted to mean that a hole one-third the size of the molecule is required for viscous flow. This picture then led automatically to an explanation of the pressure effect on viscosity. If we assume that $p_i\Sigma$ is one-third the energy required to vaporize the flow unit from the surface, we may apply this same treatment to the liquid films. Eq. (5) thus becomes

$$\Delta F\ddagger = RT\ln f+\Delta E_v/3+\Delta F_s\ddagger+p\Sigma. \qquad (6)$$

We might also use the well-known thermodynamic relationship $p+p_i=(\alpha/\beta)T$, where α and β are the coefficients of thermal expansion and compressibility of the liquid films, respectively. We then obtain from Eq. (5)

$$\Delta F\ddagger = RT\ln f+(\alpha/\beta)T\Sigma+\Delta F_s\ddagger. \qquad (7)$$

Eq. (7) suggests that if we knew the variation of α and β with temperature and pressure, we should have a method of predicting the temperature and pressure variation of the viscosity, provided that changes in $\Delta F_s\ddagger$ were negligible.

The only experimental measurement of the variation of surface viscosity with pressure is that of Talmud, Lubman, and Suchowolskata.[4] They found well defined maxima in the pressure *vs.* viscosity curves, which they attributed to a variation in the degree of hydration with pressure. Such a variation is likewise indicated by Langmuir's theory of the structure of liquid films. Since these authors gave no absolute viscosities, we were unable to calculate $\Delta F\ddagger$ from their data. We shall see below however that we can estimate the effect of hydration on $\Delta F\ddagger$, so that a further determination of the variation of viscosity with pressure might enable us to determine whether or not hydration varies with pressure.

A knowledge of the temperature coefficient of the surface viscosity would enable us to separate the entropy and energy terms in $\Delta F\ddagger$. This would furnish a method of investigating further the mechanism of the flow process. Any mechanism tending to decrease the number of molecules which flow readily would result in a decrease in the entropy of activation. A change in the type of molecule or of its interaction with the solvent would be evidenced by a change in the energy term.

[4] Talmud *et al.*, Zeits. f. physik. Chemie **A151**, 401 (1930).

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Although we do not know the temperature variation of the surface viscosities we may roughly separate the entropy and energy terms by the following approximations. From the temperature coefficient of the viscosity of liquid stearic acid,[5] we find that at 70°C, $\Delta F\ddagger = 6300$ cal., $\Delta H\ddagger = 3580$ cal.; and $\Delta S\ddagger = 8$ e.u. It is probably safe to assume that the principal difference in the $\Delta F\ddagger$ terms in liquid in bulk and liquid film is in the terms for $\Delta H\ddagger$. Making this assumption we find that $\Delta H\ddagger$ for the film is 4830 cal. greater than for the fluid in bulk. This difference would be explained if each stearic acid molecule flowing in the surface had to drag with it one water molecule, since $\Delta H\ddagger$ for the viscous flow of water is about 4800 calories.[6]

Since the chief factor determining the viscosity of unimolecular films is $\Delta H\ddagger$, it is of interest to consider another method of estimating the contributions which make up this quantity. If the unit which flows is a single acid molecule with one or more solvent molecules attached, the energy required to make a hole can be written as the sum of two terms.

$$\Delta H\ddagger = \Delta H_1\ddagger + \Delta H_2\ddagger.$$

The term $\Delta H_1\ddagger$ is the energy required to make a hole in the fatty acid surface, while $\Delta H_2\ddagger$ is the energy required to extend the hole into the solvent. We expect $\Delta H_1\ddagger$ to be approximately one-third the heat of vaporization of a liquid film to a gaseous film. We have already seen that $\Delta H_2\ddagger$ can be estimated from either the viscosity or heat of vaporization of the solvent.

On the basis of his duplex film theory Langmuir found that the two-dimensional vapor pressure of films of myristic acid on dilute HCl obeyed the Clapeyron equation.[7] He gives the following equation, calculated from Adam's data:

$$\log_{10} p' = 8.058 - 1950/T.$$

From this we find that ΔE_{vap} of liquid to gaseous film $= 8750$ cal. Therefore $\Delta H_1\ddagger$ for myristic acid $= 8750/3$ or 2920 cal. Considering the approximations involved, this agrees reasonably with the 3580 cal. found for the energy of activation for viscous flow of stearic acid.

It should be emphasized that the gaseous film in equilibrium with a liquid film cannot be considered as analogous in all respects to a three-dimensional gas-liquid system. Since even for gaseous films there probably is some activation energy for viscous flow due to the solvated polar groups, we shall not, in general, have the situation in the real gas, where viscosity increases with temperature.

We have distinguished in the case of the liquid films two types of association: lateral association of the fatty acid molecules with themselves, and vertical association between the polar groups and the underlying water molecules. Thermodynamic consideration of the equation of state for the unimolecular films measures the lateral association. Kinetics provides a method of measuring both types of association. Thus a gaseous film will exhibit thermodynamic properties similar to those of a real gas. In regard to rate processes, such as viscosity and diffusion, the gaseous films will probably have the properties of a liquid.

We have outlined briefly the possible approaches to the viscosity data for liquid films on the basis of the reaction rate theory of viscous flow. As further data become available, the application of such methods should tell us more of the actual mechanisms involved, and of the actual structure of the surface layers.

We wish to acknowledge our indebtedness to Dr. Irving Langmuir and to Professor Hugh S. Taylor for helpful discussions on this subject.

[5] Bingham and Fornwalt, J. Rheology **1**, 372 (1930).
[6] Eyring and Ewell, reference 1, p. 733, Table 6.
[7] Langmuir, J. Chem. Phys. **1**, 770 (1933).

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