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Dielectric Absorption in Polar Media and the Local Field

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The phenomena of dielectric dispersion and absorption in polar liquids subject to applied high frequency electrical fields are discussed on the basis of a modified Onsager theory for the local field. The results of this theory agree quite as well with experiment as do those from Debye's application of the hypothesis of hindered rotation with which the present work is compared. The application of the modified theory to the static case is also considered. A law of corresponding states is found to exist for the alcohols and an empirical equation proposed by Van Arkel and Snoek for "normal" polar liquids is shown to have an explanation in terms of the local field. The desirability of more complete measurements of dielectric constants and absorption as a function of temperature and frequency is stressed.

I. INTRODUCTION

THE familiar equations of Debye for the real and imaginary parts (ϵ' , ϵ'') of the dielectric constant of a polar liquid in an alternating electric field $E = E_0 \exp(i\omega t)$ of frequency ν ($\nu = \omega/2\pi$) are

$$\begin{aligned}\epsilon' &= \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1+x^2), \\ \epsilon'' &= (\epsilon_0 - \epsilon_\infty)x/(1+x^2).\end{aligned}\quad (1)$$

Here ϵ_0 is the dielectric constant at zero frequency, due to the permanent moment plus induced polarization, and ϵ_∞ is the dielectric constant at infinite frequency due to the induced polarization only. The frequency dependent variable x is given by

$$x = (\epsilon_0 + 2)\omega\tau/(\epsilon_\infty + 2), \quad (2)$$

where τ is the so-called relaxation time.

Equations (1) are derived on the assumption that the local field at a molecule can be represented by the Lorentz expression:

$$E_{\text{LOC}} = E + 4\pi P/3 = \frac{1}{3}(\epsilon + 2)E. \quad (3)$$

It is further supposed that the orienting effect of this field on the molecule of dipole moment μ is opposed by a viscous force proportional to the angular velocity of rotation of the molecule. For spherical molecules of volume V in a liquid of viscosity η the parameter τ is then given by¹

$$\tau = 3\eta V/kT,$$

T being the absolute temperature.

The Clausius-Mossotti expression for ϵ may be written

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} - \beta = 0, \quad (4)$$

where $\beta = 4\pi N\mu^2/9kT$ and N is the number of molecules per cc. It is well known that this expression, which is derived on assumption of the validity of (3), is not an adequate representation for polar media.² In particular, if induced polarization is neglected (4) predicts an infinite value of ϵ for $\beta = 1$. Such values of β are found at temperatures of the order of room temperature or higher for substances with a large dipole moment but such a behavior of ϵ is, needless to say, not found experimentally. For nonstatic fields, Eqs. (1), although of the proper form to account for many of the observed facts, require in many cases unreasonable values of V in the parameter τ to give the characteristic frequency region of dispersion and absorption correctly, especially for liquids of high dielectric constants.

Debye and his co-workers have achieved considerable success in explaining these discrepancies by assuming that the dipole axis of a given molecule in a liquid is bound to an axis defined by the configuration of its neighbors by a "hindering" potential $-\mu F \cos \vartheta'$ where F is a potential energy and ϑ' the angle between the axes.³

Van Vleck² has, however, shown on the basis of statistical-mechanical calculations of dipole-

² J. H. Van Vleck, J. Chem. Phys. **5**, 556 (1937).

³ P. Debye, Physik. Zeits. **36**, 193 (1935); P. Debye and W. Ramm, Ann. d. Physik **28**, 28 (1937).

¹ P. Debye, *Polar Molecules*, Chap. V.

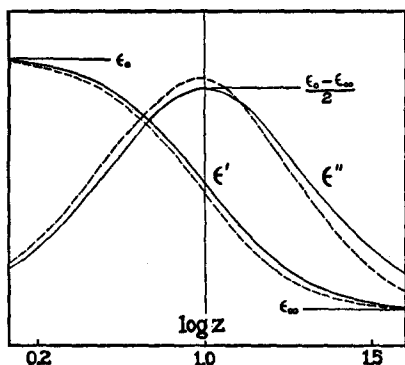


FIG. 1. Real and imaginary parts (ϵ' , ϵ'') of the dielectric constant plotted against the frequency dependent variable z . Solid curves are for the approximate equations, dashed curves for the Onsager theory as explained in the text. The scale for ϵ'' is twice that for ϵ' .

dipole coupling that the local field as given by (3) is not an adequate representation of the state of affairs. Onsager⁴ has obtained an expression for the local field on the view that the molecule in virtue of its electric moment has a modifying effect on the surrounding medium. This expression Van Vleck has shown to be in agreement with his results to a second approximation in the dipole-dipole coupling (the extent to which the calculations were carried). This agreement is, however, obtained only if one assumes in the dipole calculations that the molecules surrounding a given one may be represented as a continuous distribution. Van Vleck has also shown that the excessive saturation curvature of ϵ as a function of field strength found by using (3) is not predicted by the Onsager field. In view of all this it has seemed worthwhile to see what results are given by the Onsager theory as applied to the dielectric constant of polar liquids in radio-frequency fields.

II. DISPERSION AND ABSORPTION FOR THE ONSAGER LOCAL FIELD

A. *Derivation.*—Onsager's formula may be written

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} - \beta = (f - 1)\beta, \quad (5)$$

where $f = 3\epsilon(\epsilon_\infty + 2)/(2\epsilon + \epsilon_\infty)(\epsilon + 2)$. This formula

is derived on the assumption of a continuous medium in which a given molecule occupies a spherical cavity. For a more realistic picture of the environment as a discrete assemblage agreement with Van Vleck's results can be obtained in an empirical way by multiplying the right side of (5) by a factor q ($0 \leq q \leq 1$) as suggested by him in the paper referred to. Such a procedure can hardly be justified in any rigorous manner at the present time, but introduction of such a factor does not complicate matters unduly, and it is of interest to examine the behavior of the values of q required to obtain experimental agreement with (5) thus modified as will be done in Section III.

In Debye's analysis of the effect of a nonstatic field he shows that one obtains a complex factor multiplying the moment of the form $1/(1 + i\omega\tau)$. Exactly the same considerations apply in the Onsager case and the net result is simply that the terms involving β are multiplied by $1/(1 + i\omega\tau)$. The dielectric constant is then complex: $\epsilon = \epsilon' - i\epsilon''$. As it stands (5) is quadratic in ϵ and an exact solution is too unwieldy to be readily handled. However, if the quantity $3\epsilon/(2\epsilon + \epsilon_\infty)$ in f be replaced by $\frac{3}{2}$ the equation is linear in ϵ :

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} - \beta = q \left[\frac{3(\epsilon_\infty + 2)}{2(\epsilon + 2)} - 1 \right] \beta, \quad (6)$$

and the essential difference between the Onsager and Lorentz fields is retained. Making this approximation, inserting the complex modifying factor and solving for ϵ' , ϵ'' , one finds:

$$\begin{aligned} \epsilon' &= \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + z^2), \\ \epsilon'' &= (\epsilon_0 - \epsilon_\infty)z/(1 + z^2), \end{aligned} \quad (7)$$

where

$$\begin{aligned} z &= \omega\tau/(1 - \delta), \\ \delta &= \frac{1}{3}\beta(\epsilon_\infty + 2)(1 - q). \end{aligned} \quad (8)$$

The curves for ϵ' , ϵ'' are plotted against $\log z$ in Fig. 1 and for comparison the curves obtained by a rigorous solution of the Onsager equation with $\epsilon_0 = 10$, $\epsilon_\infty = 2$ are indicated by dashed lines. The error in the approximate analysis is obviously not serious even for this small a value of ϵ_0 .

B. *Comparison with experiment.*—It must be remembered that in applying the Debye Eqs. (1) the value of ϵ_0 is taken from the experimental data on the assumption that it satisfies the

⁴ L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

Clausius-Mossotti relation (4). This is, of course, not the case for polar substances, a fact which must be borne in mind when the results of the hypothesis of hindered rotation are compared with the present work. Since ϵ_0 does satisfy the modified Onsager Eqs. (6) derived on plausible assumptions, this latter relation is evidently preferable as a basis for consideration of dispersion and absorption.

Equations (7) are quite general expressions for ϵ' , ϵ'' in that they contain the results of the Debye theory and the unmodified Onsager theory as special cases for $q=0$ and 1, respectively. The various cases are seen from Eqs. (7) and (8) to differ only in the form of the variable z defined in (8). From Fig. 1 the center of the region of dispersion and absorption occurs for $z=1$. Writing $\omega=\omega_{\text{MAX}}$ for this case one has from (8):

- (a) $(\epsilon_0+2)\omega_{\text{MAX}}\tau/(\epsilon_\infty+2)=1$, $q=0$,
Debye,
(b) $\omega_{\text{MAX}}\tau/(1-\delta)=1$, Modified Onsager, (9)
(c) $\omega_{\text{MAX}}\tau=1$, $q=1$, Onsager.

Most liquids for which data on ϵ_0 over a wide temperature are available require values of q between 0.8 and 1.1 (see Section III) if Eq. (6) is to fit the facts. The corresponding values of δ do not depend markedly on the temperature and lie between 0.3 and -0.15 . For the alcohols δ has values between 0.7 and 0.9 but the values of q are strongly temperature dependent as discussed in Section III. It is seen from these values of δ and the fact that $(\epsilon_0+2)/(\epsilon_\infty+2)$ is a large number that the values of τ found for a given ω_{MAX} from the Debye case (a) of (9) are considerably smaller than those required by (b) or (c). Experimentally, the values of τ for polar liquids found assuming the Debye theory are much too small for liquids of large static dielectric constant ϵ_0 . That is, they require, on the assumption of viscous damping, values of the molecular volume V to which τ is then proportional, of a smaller order of magnitude than those inferred from independent data, e.g. the van der Waals volume for gases. The prediction of larger values of τ and hence V on the modified Onsager basis is thus in the right direction.

In general the experimental verification of (1) has consisted in seeing whether for a reasonable

value of the molecular volume V , assuming η known, the data for ϵ' , ϵ'' as a function of ω and T can be reproduced in their general behavior. It is unfortunate that almost the only nearly adequate data on dispersion and absorption of simple liquids are for the alcohols which are abnormal in their static dielectric properties and are otherwise known to be highly associated. Debye in his book finds very good agreement between the data of Mizushima on *n*-propyl alcohol for three different frequencies over a temperature range 20° to -60°C and calculated values of ϵ' , ϵ'' from Eq. (1) using a value $V=34\times 10^{-24}$ cm³ (radius 2.0×10^{-8} cm). As good agreement can be obtained from (7) and (8) using the value $V=60\times 10^{-24}$ cm³ and the values of q required to give ϵ_0 correctly in (6) for the static case.

Schmelzer⁵ has made absolute measurements of absorption for several alcohols at a single frequency and temperature and calculated the value of ω_{MAX} on the basis of an expression for ϵ'' as in (1) or (7). The values of V required on the basis of formulas (9) are given in Table I together with those deduced from the van der Waals equation of state.

A detailed agreement with other estimates of V is hardly to be expected when one considers the crudity of assuming viscous damping of spherical molecules but in view of how well such an hypothesis works for the problem of ionic mobilities one should expect a reasonable degree of correlation with values of V found in other ways. It is seen that the derivation with the modified local field does lead to quite reasonable estimates.

C. *Comparison with the hypothesis of hindered rotation.*—Debye and Ramm³ in their paper on the effect of hindered rotation consider three

TABLE I. Molecular volumes from the various assumptions about the local field and from the van der Waals coefficient (all $\times 10^{-24}$ cc).

SUBSTANCE	DEBYE	MODIFIED ONSAGER	ONSAGER	VAN DER WAALS
Water	$V=0.5$	4.1	12	13
Methyl Alcohol	16	38	132	28
Ethyl Alcohol	16	30	111	35
<i>n</i> -Propyl Alcohol	40	49	227	42
Butyl Alcohol	72	76	350	47

⁵ W. Schmelzer, Ann. d. Physik 28, 35 (1937).

cases:

- (a) The hindering energy $F \ll kT$,
- (b) The hindering energy F is comparable with kT ,
- (c) The hindering energy $F \gg kT$.

The effect in case (a) is to replace the quantity $1/(1+i\omega\tau)$ multiplying β by a series of terms of the form:

$$1/(1+i\omega\tau/\lambda_n), \quad (10)$$

where the λ_n are constants. These reduce for ω small to

$$[(1-y^2/9)-i\omega\tau(1-11y^2/54)],$$

where $y=F/kT$. The absorption is thus apparently reduced by the factor $(1-11y^2/54)$. However, y is to be so taken that the difference between ϵ_0 and ϵ_∞ is represented by $(1-y^2/9)\beta$ when one uses the correct value of the dipole moment μ in β rather than a spurious one. (The latter is implicitly done if one accepts the Clausius-Mossotti Eq. (4) as an expression for ϵ_0 .) The absorption equations are written in terms of $\epsilon_0 - \epsilon_\infty$ rather than β (Cf. Eqs. (1) and (7).) Hence the absorption written in this way is reduced by a factor $(1-11y^2/54)/(1-y^2/9)$ which has obviously much less effect than the factor one might at first expect to be correct.

From the series of terms in (10) one should expect a series of absorption regions and as a result a composite absorption curve somewhat broader, displaced to higher frequencies and with a slightly smaller maximum. This type of absorption is actually found for many *complex* substances but the curve is still much broader in most cases than such a series of terms seems capable of accounting for and in addition is in many cases symmetrical about the maximum on a logarithmic scale of frequency. It is difficult to see how this latter behavior can be given by terms of the form (10) with the constants λ_n varying in a reasonable way. There seems to be no evidence that the maximum of absorption is less or the frequency spread greater for *simple* liquids where we can have the greatest hope for the adequacy of either picture. If the region of dispersion and absorption is merely shifted on a frequency scale as compared to the prediction of the original Debye theory with a reasonable value of τ the explanation proposed here would seem to be superior.

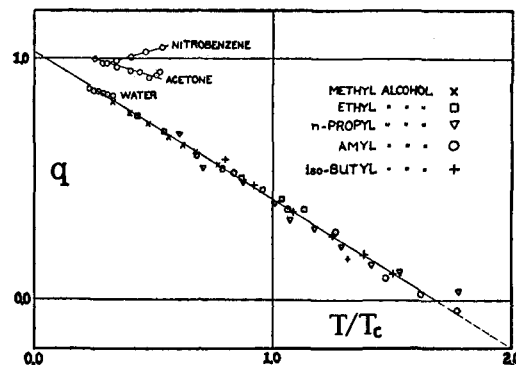


FIG. 2. The local field parameter q for the alcohols and water at different temperatures plotted against T/T_c ($=9kT/4\pi N\mu^2$).

The foregoing remarks apply only if the hindering energy F is small compared with kT . For many polar liquids much larger values of F are necessary to compensate for the inadequacy of the Clausius-Mossotti formula. Unfortunately, in the intermediate case that F is comparable with kT the series development of Debye and Ramm breaks down and no definite conclusions can be drawn.

If $F \gg kT$ the effect of temperature is small compared with that of F . Debye and Ramm show that in this case kT is replaced by $F/2$ where it appears in β and τ . F is again to be so taken that this modified β gives ϵ_0 correctly in Eq. (4) with the true value of the moment μ . The maximum value of the absorption is the same as that given by the original equation with the experimental value of ϵ_0 ; the only difference is that there is now a justification for using this value. However the absorption has a different frequency dependence because of the new significance of τ . In particular a given value of the frequency of maximum absorption and hence τ requires a larger value of the molecular volume V if τ is given by $3\eta V/(F/2)$ rather than $3\eta V/kT$. This is, as already discussed, in the right direction. If one computes V for strongly polar liquids with an appropriate F the values are found to be comparable with those obtained on the modified Onsager hypothesis but in general slightly smaller. The latter is thus quite as satisfactory in the way of quantitative agreement and in addition there is no need to account for a large hindering potential F .

The inadequacy of the experimental data for simple polar liquids makes a more detailed discus-

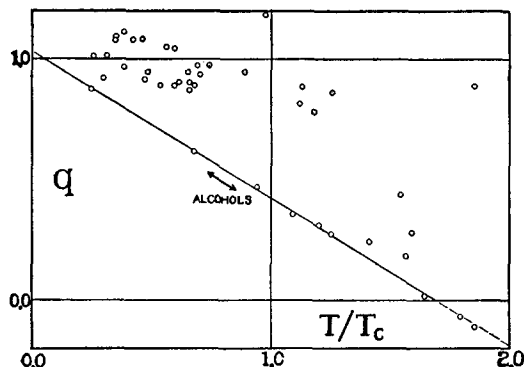


FIG. 3. The local field parameter q as computed from Wyman's data at room temperatures plotted against T/T_c .

sion hardly worthwhile at present. Enough has been said to show that the Onsager hypothesis leads to results which have the right trend from the original Debye theory and seems to work quite as well as Debye's hypothesis of hindered rotation. This lends additional confirmation to the view that a great deal of the difficulties with Eqs. (1) and (4) is due to the failure of Eq. (3) for the local field in polar media. A survey of the experimental data emphasizes the necessity for measurements over as wide a frequency and temperature range as possible, detailed consideration of isolated data being comparatively useless as the above discussion makes evident.

In the case of solids the interpretation of the relaxation time in terms of an ordinary viscosity is obviously impossible. One is then forced to introduce the relaxation virtually as an empirical parameter in the absence of a reasonable theory and there is therefore no such criterion for reasonableness of values found for τ as exists in the case of liquids.

III. THE LOCAL FIELD IN THE STATIC CASE

A. *The temperature dependence of q .*—It remains to consider briefly the values of the parameter q required to give agreement of (6) with experimental results. A value $q=0$ corresponds to the Lorentz local field and $q=1$ to the Onsager case. Intermediate values might be expected to simulate a local field of the Onsager type for discrete molecular configurations. In the case of cubic structures, agreement with the calculations of Van Vleck requires $q \approx \frac{1}{2}$.

One can hardly attach too much significance to

detailed behavior of the factor for specific cases but its general behavior should be of interest in indicating the extent to which dielectric constants of liquids can be explained in terms of dipole-dipole coupling. The significant parameter in such considerations is the temperature ($\beta = 4\pi N\mu^2/9kT$) and unfortunately there are comparatively little data for dielectric constants of polar liquids over a wide range of temperature. Perhaps the most complete data exist for various alcohols and water which are known to the chemist as highly associated and hence are not ideally suited for the present purpose. One might expect q to be more or less independent of T , its value to be between $\frac{1}{2}$ and 1. Actually q is for these substances strongly temperature-dependent. However, as pointed out to the writer by Professor Van Vleck, one should expect a law of corresponding states if dipole-dipole coupling is the important factor. That is, the values of q as a function of a reduced temperature T/T_c should all lie on the same curve. Here T_c is the "Curie" temperature, having the value $4\pi N\mu^2/9k$ if induced polarization is neglected.² How well such a condition holds for water and the alcohols is seen in Fig. 2. This rather striking behavior suggests the possibility of a gradual transition from coupling of the dipoles to the free rotation of Debye's original theory as the temperature increases. However, it is unwise to generalize too much on the basis of data for such a limited number of abnormal substances and in addition it should be remembered that the dipole moment μ is very nearly the same for all these liquids, being due primarily to the OH group. The behavior for acetone and nitrobenzene, also plotted in Fig. 2, serves further to emphasize this need for caution. These comprise the substances for which the *International Critical Tables* give fairly complete temperature data.

B. *The data of Wyman.*—Wyman⁶ has collected an extensive set of data on electric polarizabilities at room temperatures and dipole moments from which it is possible to compute q . Such values have been calculated for various related chemical series in his table for which the data seem reasonably reliable and they have been plotted against T/T_c in Fig. 3, which thus

⁶ J. Wyman, Jr., J. Am. Chem. Soc. **58**, 1482 (1936).

shows that the required values are in general not at all unreasonable on the Onsager picture. It would be highly desirable to have more complete data on the dielectric constants of polar liquids as a function of temperature to see whether such a behavior as indicated by Fig. 2 for the alcohols holds for other series of related substances. Such data should be very valuable in any attempt at understanding the electrical properties of polar liquids generally.

C. *The local field and the work of van Arkel and Snoek.*—Another line of evidence which lends confirmation to the modified Onsager hypothesis in regard to the local field is found in a study by van Arkel and Snoek⁷ of the experimental data for solutions of polar liquids in nonpolar solvents. They found that for a considerable number of "normal" polar liquids and over a wide range of concentrations the dielectric constant can be represented by a formula of the form:

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} = \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT + (4\pi C/3)N\mu^2},$$

C being a constant characteristic of the polar liquid (N =number of polar molecules per cc) having values between 1 and 2. In the notation of the present work this may be written:

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} = \frac{\beta}{1 + C\beta}. \quad (11)$$

Now if one rewrites the modified Onsager formula (6) in terms of β on the right side, it assumes the form (taking ϵ_{∞} to be the same for solute and solvent):

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} = \frac{2 + q}{2 + q(\epsilon_{\infty} + 2)\beta} \beta, \quad (12)$$

which is seen to be very similar to the expression (11). Namely, (12) differs from (11) only by having $2 + q$ instead of 2 in the numerator on the right. Furthermore, the values of C found to work in (11) over a considerable range of concentration are such as to make the factor on the right agree quite well with the right side of (12) for most of the cases considered by these authors. Most of

the data given are at one temperature or over only a limited range so the difference in functional dependence on β of the two expressions cannot be used to decide which of them is preferable. Here again it would be very desirable to have measurements at different concentrations made over as wide a temperature range as possible because of the dependence of β on T .

D. *Dielectric constants of solids.*—It should also be of interest to examine the values of q required to account for the dielectric properties of solids at various temperatures. There is, however, one thing to bear in mind: measurements of the dielectric constant as a function of T for solids have usually been made at a low frequency but one which is kept the same at all temperatures of measurement. Under such conditions many substances show a dielectric constant decreasing quite rapidly with T ,⁸ a behavior totally inexplicable in terms of the local field. However, it should be remembered that the relaxation times found experimentally for solids are very long as compared to those for liquids and may be expected to become increasingly so at lower temperatures. Thus the characteristic region of dispersion of the dielectric constant and absorption occurs at lower and lower frequencies and the dielectric constants found experimentally as above may be very far from the static dielectric constants at low temperatures, particularly if this region of dispersion is much broader than that predicted by the simple theories. Because of this difficulty and the incompleteness of dispersion and absorption measurements as a function of frequency no attempt has been made in the present work to carry out an analysis of the data for solids. It would be highly interesting to see how much of the apparent decrease is real and how much is due to the relaxation time by means of dispersion and absorption measurements over a wide frequency range.

IV. CONCLUSION

From the considerations above it appears reasonable to conclude that the difficulties found in attempts to apply the Clausius-Mossotti equation and the Debye equations for dispersion and absorption to measurements on dielectric media

⁷ A. E. v. Arkel and J. L. Snoek, *Trans. Faraday Soc.* **30**, 707 (1934).

⁸ See, for instance: R. H. Fowler, *Statistical Mechanics*, 2nd Ed., p. 824.

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.

The writer is indebted to Professor J. H. Van Vleck, who suggested the problem, for his interest and helpful advice.

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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,

ΔF^\ddagger = free energy of activation for viscous flow per molecule.

Recently, Harkins and Meyers,² and Langmuir and Schafer³ 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.

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

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

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