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A New Method of Determining the Relaxation Time and the Dipole Moment of Polar Substances; Its Application to Fatty Acids

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A new method of determining the relaxation time and the electric dipole moment of polar substances has been worked out. This method uses dilute solutions of polar substances in non-polar solvents, and is based on measuring the dielectric constant and the coefficient of anomalous absorption of these solutions as a function of concentration The measurements must be made at a constant frequency, in the vicinity of the maximum of anomalous absorption.

The method has been applied to formic, acetic, propionic, and *n*-butyric acids in the dioxane. The measurements have been made at 25.6-cm wave-length, using the Drude-Coolidge method, with Slatis' correction for induction effect in the condenser leads. The relaxation time data obtained were used to calculate the volume of the particle which becomes oriented by the impressed electric field. The volumes computed were proportional to the molecular volumes. This indicated that the anomalous absorption of ultra-high frequencies in fatty acids is due to the orientation of the entire molecule as a unit. This means that the dipole-bearing group of the fatty acid molecules (i.e., carboxyl) is not free to be oriented independently of the rest of the molecule. The experimental data used to calculate the relaxation time, were used to determine the dipole moments of fatty acids. The results obtained were in agreement with earlier determinations, thus furnishing a good support in favor of the validity of the relaxation time data obtained.

POLAR substances possess two specific characteristics. One is the electric dipole moment μ which characterizes the electrical asymmetry of their molecules. Another is the relaxation time τ which characterizes the time lag in their response to changes in the impressed field. The relaxation time determines the frequency at which the maximum of the so-called anomalous absorption is observed in the range of ultra-high frequencies.[1] Knowing the relaxation time one can evaluate the size of the particle which becomes oriented by the impressed field, and which, therefore, is responsible for the anomalous absorption.

The methods of determining the dipole moment are numerous.[2] Many of them are based on measurements of dielectric constant in the region of frequencies where the absorption is low, and where the accuracy of measurements is high. As a result, the dipole moments of a very large number of polar substances were measured accurately in the past.

The methods of determining the relaxation time are few. Three of them are used most frequently. The first is based on measuring the dielectric constant and the coefficient of absorption as a function of frequency. The second is based on measuring the temperature dependence of absorption (i.e., of losses) at some constant frequency. The third requires measuring the rate of increase in temperature of a polar substance placed in a high frequency field. The measurements required by these methods must be made in the region where the absorption is high, and where the accuracy, in general, is rather low. For this reason our knowledge of the relaxation times lags far behind our knowledge of the dipole moments. As a result, little is known about the identity of the particle whose orientation causes the absorption. In the case of water and of some other substances this particle may be identified with the whole molecule, indicating that the molecule as a unit becomes oriented in an impressed field. In the case of alcohols, as has been

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[1] See P. Debye, *Polar Molecules* (The Chemical Catalog Company, Inc., New York, 1929), Chapter 5.

[2] See C. H. Douglas Clark, *The Fine Structure of Matter* (John Wiley and Sons, Inc., New York, 1938) Part 2, pp. 330–334.

shown by Keutner and Potapenko,[3] the oscillating particle is likely to be the OH-group, indicating that the latter is free to become oriented independently of the rest of the molecule.

The difficulty of studying the polar properties of substances like water, alcohols, acids, etc., may be easily attributed to their molecular association. So far this association has not been adequately taken into account in the theory of anomalous dispersion and absorption. By using dilute solutions of polar substances in non-polar solvents one can reduce the dipole-dipole coupling and minimize the association. The desirability of working with dilute solutions for determining the relaxation time was pointed out long ago by Debye.[4]

The new method of determining the relaxation time and the dipole moment described here makes use of dilute solutions of polar substances in non-polar solvents. This method is based on measuring the dielectric constant and the coefficient of anomalous absorption as a function of concentration at one frequency in the vicinity of the maximum of anomalous absorption. The method is simple, and the solutions required must be of high dilution. This reduces the losses caused by the studied substance, and it increases considerably the accuracy of measurements.

I

For a mixture of two liquids, the molar polarization is given by

$$P = P_1 f_1 + P_2 f_2 = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_1 f_1 + M_2 f_2}{\rho}, \tag{1}$$

where M is the molecular weight, f is the molar fraction, and the subscripts 1 and 2 refer, respectively, to the solvent and the solute; ϵ and ρ are the dielectric constant and the density of the solution. If the solvent is a non-polar substance, P_1 is a constant, and at very high dilution, when there is no dipole interaction, P_2 should be constant. Therefore $P_1 f_1 + P_2 f_2 = P_1 + (P_2 - P_1) f_2$ is a linear function of f_2 at high dilution. We can thus obtain P_1 and P_2 from the intercept and slope of a linear extrapolation of the $P - f_2$ curve to the point $f_2 = 0$. In the region of absorption the dielectric constant ϵ and the polarization P are complex and, because of this, the process of extrapolation must be carried out separately for the real and imaginary parts. Expressions for these can be obtained by substituting $\epsilon = \epsilon' - i\epsilon''$ and $P = P_r - iP_i$ into Eq. (1), giving

$$P_r = \frac{\epsilon'^2 + \epsilon' - 2 + \epsilon''^2}{\epsilon'^2 + 4\epsilon' + 4 + \epsilon''^2} \frac{M_1 f_1 + M_2 f_2}{\rho}, \tag{2}$$

$$P_i = \frac{3\epsilon''}{\epsilon'^2 + 4\epsilon' + 4 + \epsilon''^2} \frac{M_1 f_1 + M_2 f_2}{\rho}.$$

Equations (2) allow one to compute P_r and P_i when ϵ' and ϵ'' are determined. By plotting P_r and P_i as functions of f_2 one can determine their values for $f_2 = 0$ by extrapolation.

The frequency dependence of P of a polar substance may be represented according to Debye[1]

$$P = \frac{4\pi N}{3} \left[\alpha_0 + \frac{\mu^2}{3kT} \frac{1}{1 + i\omega\tau} \right], \tag{3}$$

where N is the Avogadro number, α_0 is the distortion polarizability of the molecules, μ is their dipole moment, k is the Boltzmann constant, T is the absolute temperature, ω is the angular frequency, and τ is the relaxation time. Equation (3) has been derived on the assumption that the force acting upon a molecule in a polarizable medium is equal to $E + 4\pi P/3$. Several attempts have been made to improve the theory by considering the interaction of dipoles. A semi-empirical correction proposed by van Arkel and Snoek,[5] and well supported by experiments, consists in substituting $(3kT + Cn\mu^2)$ in place of $3kT$ in the denominator of Eq. (3) when it is applied to the static case, i.e., when $\omega = 0$. Here n represents the number of dipoles per unit volume, and C is a constant the physical meaning of which has been elucidated on the basis of

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[3] E. Keutner and G. Potapenko, Physik. Zeits. **38**, 635 (1937); **40**, 100 (1939). About alcohols see also G. Martin, Physik. Zeits. **37**, 665 (1936); L. D'Or and J. Henrion, Physik. Zeits. **38**, 426 (1937); J. Haefelin, Arch. Sc. Phys. Nat. **28**, 19 (1946). About other substances see W. Jackson, Proc. Roy. Soc. **150**, 197 (1935); R. W. Sillars, Proc. Roy. Soc. **169**, 66 (1938); E. Fischer, Zeits. f. tech. Physik **19**, 531 (1938); K. Schmale, Ann. d. Physik **35**, 671 (1939); W. Kauzmann, Rev. Mod. Phys. **14**, 12 (1942); G. Klages, Physik. Zeits. **43**, 151 (1942); H. Froelich, J. Inst. Elec. Eng. **91**, 456 (1944).

[4] P. Debye, Trans. Faraday Soc. **30**, 679 (1934).

[5] A. van Arkel and J. Snoek, Physik. Zeits. **33**, 662 (1932).

Onsager's theory by Boettcher.[6] In the case of dilute solutions n is small. Therefore, in our case $Cn\mu^2$ is negligible compared to $3kT$, and the Debye Eq. (3) may be used in its original form, i.e., as written.

The relaxation time is related to the size of the particle which the impressed field orients. For the spherical particle of radius a one may take[1]

$$\tau = 4\pi\eta a^3/kT, \tag{4}$$

where η is the viscosity of the liquid surrounding the particle (see later). This relation has been modified by Perrin[7] to take into account ellipsoidal particles. When the excentricity is small and when the dipole moment is approximately parallel to one of the axes of the ellipsoid, one may take

$$\tau = 4\pi\eta a_1 a_2 a_3/kT, \tag{4'}$$

where a_1, a_2, a_3 are the semi-axes of the ellipsoid representing the oscillating particle.[8]

If we make the abbreviations

$$P_a = 4\pi N\alpha_0/3, \tag{5}$$

$$P_d = 4\pi N\mu^2/9kT, \tag{5'}$$

Eq. (3) assumes the form

$$P = P_a + P_d(1/1 + i\omega\tau). \tag{6}$$

Letting P_0 be the value of the molar polarization for very low frequencies ($\omega\tau \ll 1$), we obtain

$$P_0 = P_a + P_d. \tag{7}$$

Substituting this into Eq. (6) to eliminate P_a, and again setting $P = P_r - iP_i$, we obtain

$$P_r = P_0 - P_d(\omega^2\tau^2/1 + \omega^2\tau^2), \tag{8}$$

$$P_i = P_d(\omega\tau/1 + \omega^2\tau^2). \tag{9}$$

Solving these simultaneously for P_d and τ gives

$$P_d = \frac{P_i^2 + (P_0 - P_r)^2}{P_0 - P_r}, \tag{10}$$

$$\tau = \frac{1}{\omega}\frac{P_0 - P_r}{P_i}. \tag{11}$$

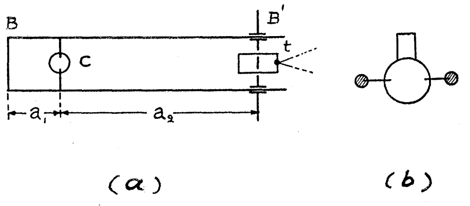

FIG. 1. a. Schematic diagram of the apparatus. b. Condenser.

Alternatively, if we substitute Eq. (7) into Eqs. (10) and (11) to eliminate P_0,

$$P_d = \frac{P_i^2 + (P_r - P_a)^2}{P_r - P_a}, \tag{12}$$

$$\tau = \frac{1}{\omega}\frac{P_i}{P_r - P_a}. \tag{13}$$

We thus have two alternative sets of Eqs. (10), (11) and (12), (13) for the determination of P_d and τ from the values of P_r and P_i of the solute, obtained by the extrapolation of the $P_r - f_2$ and $P_i - f_2$ curves. From an examination of Eq. (8) we see that, for $\omega\tau \ll 1$, we have $P_r \approx P_0$ and, for $\omega\tau \gg 1$, we have $P_r \approx P_0 - P_d = P_a$. Therefore, Eqs. (10) and (11), containing $P_r - P_0$, will give unreliable results for small $\omega\tau$, and Eqs. (12) and (13) containing $P_r - P_a$ will give unreliable results for large $\omega\tau$. When $\omega\tau$ is sufficiently close to 1 so that either set of equations should give good results, then Eqs. (10) and (11) should be used if P_0 is known better than P_a. If the opposite is true, Eqs. (12) and (13) should be preferred. Usually P_0 can be measured accurately by conventional methods at lower frequencies, while P_a is not easily obtainable by direct measurements. For P_a one can use either the polarization in the solid state, or the extrapolated value of the molar refraction measured either in the visible spectrum or, better, in the infra-red.

From the values of P_d and τ thus obtained one can calculate the dipole moment μ using Eq. (5'), and the volume of the rotating particle,

$$V = (4\pi/3)a_1 a_2 a_3 = \tau kT/3\eta, \tag{14}$$

[see Eq. (4')].

II

The method described has been applied to fatty acids. The choice has been based on the

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[6] C. J. F. Boettcher, Physica 5, 635 (1938); L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).

[7] F. Perrin, J. de phys. et rad. 5, 497 (1934).

[8] When the eccentricity is appreciable, the right-hand side of Eq. (4') must be multiplied by a factor b depending upon the shape of ellipsoid. This factor can be taken from a table computed by A. Budo, E. Fischer, and S. Miyamoto, Physik. Zeits. 40, 337 (1939).

fact that the molecular structure of these acids is well known, including the magnitude and the direction of the dipole moment relative to the rest of the molecule.

The dielectric constant ϵ' and the coefficient of anomalous absorption κ of dilute solutions of formic, acetic, propionic, and *n*-butyric acid in dioxane were measured at a wave-length of 25.6 cm ($\nu=1172$ mc), by use of the well-known Drude-Coolidge[9] method. This method uses a "Lecher System," i.e., two parallel wires bounded by two bridges B and B' (see Fig. 1a), and a small condenser C (see Fig. 1b) put across the wires and filled with the liquid chosen.

Dioxane has been chosen as solvent because the fatty acids do not show noticeable association in dilute dioxane solutions.[10] Benzene has been tried and rejected as solvent because of the low solubility of the formic acid in it, which did not permit accurate measurements in the set-up used.

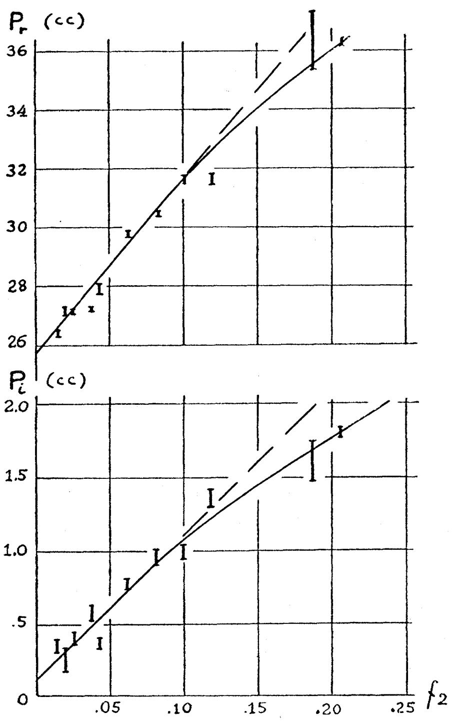

FIG. 2. Polarization curves: formic acid in dioxane.

The Drude-Coolidge method has been chosen in preference to other methods which use coaxial or hollow transmission lines. In cases when liquid dielectrics of considerable anomalous absorption are studied in the range of approximately 20- to 200-cm wave-length ($\nu=1500$ to 150 mc), the Drude-Coolidge method seems to be the best, provided the long neglected effects of condenser leads and, when needed, of the conductivity of the liquid are taken into account. In the case when the absorption is appreciable, the losses in the system depend primarily upon the losses in the dielectric, and an improvement in Q of the empty system, which may be achieved by the use of a coaxial or a hollow transmission line, does not offer much advantage. At the same time the Drude-Coolidge method, besides being very convenient, possesses a number of advantages. One of them is the very small amount of liquid required. The latter is kept in a closed condenser so that the only metal parts in contact with the liquid are the two small pieces of platinum projecting into the glass flask (see Fig. 1b). In this way the possibility of

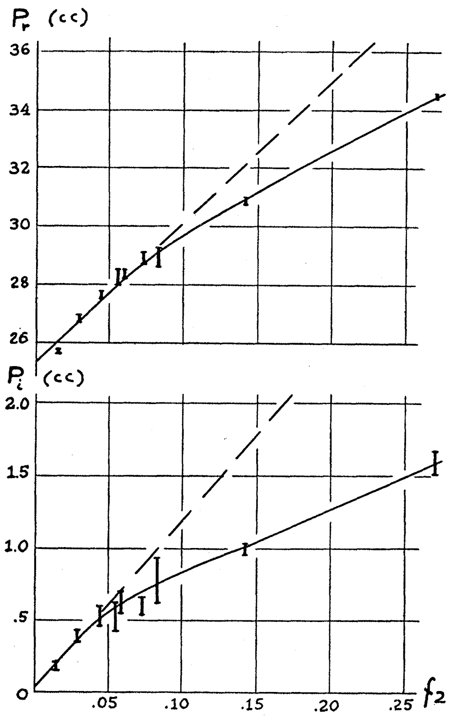

FIG. 3. Polarization curves: acetic acid in dioxane.

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[9] W. D. Coolidge, Wied. Ann. **69**, 125 (1899). See an extension of it to absorbing liquids by G. Potapenko, Zeits. f. Physik **20**, 21 (1923).

[10] Cf. C. J. Wilson and H. H. Wenzke, J. Chem. Phys. **2**, 546 (1934).

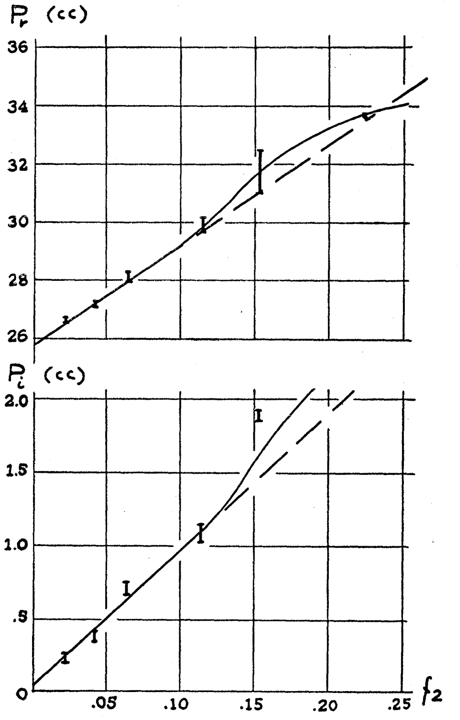

FIG. 4. Polarization curves: propionic acid in dioxane.

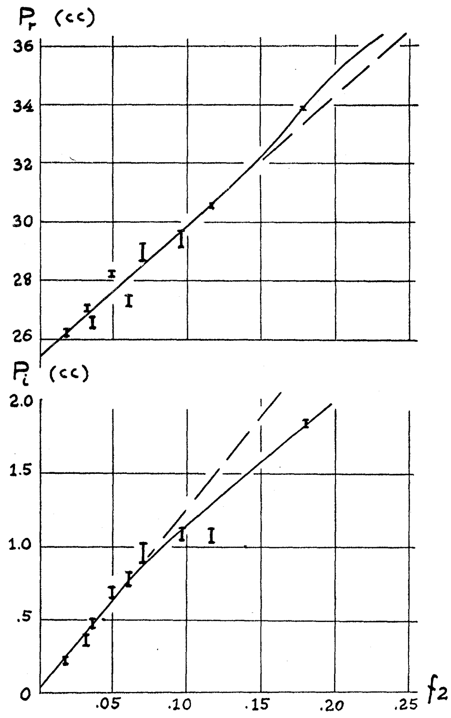

FIG. 5. Polarization curves: butyric acid in dioxane.

contamination and of leakage or evaporation of the liquid are minimized.

The bridge B' was movable, allowing the system to be tuned in resonance with a generator[11] loosely coupled with it. Two resonance curves must be measured to determine ϵ' and κ: one measured having the condenser filled with the solution chosen, another one measured when the system is empty (i.e., the condenser either empty or absent). The thermocouple t shown (see Fig. 1a) was used to measure the resonance curves.

The old theory of the Drude-Coolidge method disregarded the effect of leads which connect the condenser C ("lumped capacity") with the parallel wires. The effect of leads may be resolved into the potential drop along them and into the inductance between the eddy currents in them and in the parallel wires. This inductance is equivalent to a change in the propagation constant of the parallel wires in the vicinity of the leads. The potential drop along the leads may be disregarded when the leads are short compared to λ/4, and when the current through the condenser is small. The inductance was taken into account by Slatis.[12] His extension of the

TABLE I. Polarization components and relaxation times.

Substance	P_r(cc)	P_i(cc)	P_a(cc)	$\tau\times10^{10}$(sec.)
Formic acid $HCOOH$	88.42	10.04	8.56	0.171
Acetic acid CH_3COOH	73.95	11.77	13.00	0.260
Propionic acid C_2H_5COOH	62.02	9.45	17.50	0.285
n-Butyric acid C_3H_7COOH	70.50	12.58	22.25	0.350

TABLE II. Volume of particle.

Substance	V_{exp}(A)	V_{str}(A)	V_{exp}^*(A)
$HCOOH$	17.3	44.4	48.1
CH_3COOH	26.2	67.5	72.8
C_2H_5COOH	28.8	80.5	80.0
n-C_3H_5COOH	35.3	98.5	98.1

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[11] The generator was of the positive grid type, employing an FP-126 tube. No external circuit was used, the frequency being determined solely by the shorted grid helix and the electrode potentials. The oscillating circuit being entirely within the tube, and the potentials ($Eg=385V$; $Ep=-8V$) kept reasonably constant, the drift in the wave-length of the oscillations generated did not exceed 0.01 cm during a run of several hours.

[12] H. Slatis, Ann. d. Physik **32**, 734 (1938); **36**, 397 (1939).

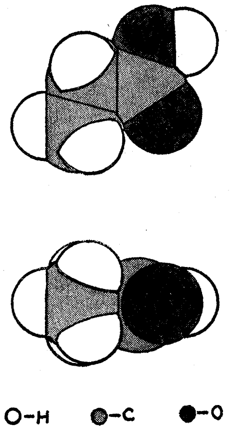

FIG. 6. Model of the propionic acid molecule. The models of molecules of other acids may be obtained from this one by either subtracting or adding one or more CH_2-groups.

old theory leads to the following formula:

$$\delta_0+\epsilon'\delta+2\pi\vartheta=\frac{\lambda}{2}[\cot\alpha(a_1-\vartheta)+\cot\alpha(a_2-\vartheta)], \tag{15}$$

where

$$\delta_0=4\pi k_0 \ln\frac{s}{r}, \quad \delta=4\pi k \ln\frac{s}{r}, \tag{16}$$

$$\vartheta=\frac{L_{12}{}^2}{4L_{22}+\ln(s/r)}. \tag{17}$$

Here k_0 and k are, respectively, the ballast capacity and the working capacity of the condenser C, both in cm;[13] s is the distance between the centers of parallel wires; r is their radius; $\alpha=2\pi/\lambda$; λ is the wave-length, in cm; a_1, a_2 are shown on Fig. 1a, measured at resonance, in cm; L_{12} is the mutual inductance between each condenser lead and the neighboring parallel wire; L_{22} is the self-inductance of the leads. Equation (15) allows one to calculate ϵ' when δ_0, δ, λ, ϑ are known, and a_1, a_2 are measured. To calculate κ Slatis derived another equation, assuming the losses are determined by measuring the heights of resonance curves. The accuracy of determining ϵ' and κ can be considerably increased, especially in the case of appreciable absorption, by measuring full resonance curves instead of their maxima only. Full resonance curves allow one to determine the damping decrement from the lengths of several chords, and to determine the position of maximum from the average of the midpoints of same chords. Slatis' theory can be extended to the case when full resonance curves are measured. The extension yields[14]

$$\frac{\kappa}{1-\kappa^2}=\frac{d\gamma}{4\pi}\,\frac{\delta_0+\epsilon'\delta+2\pi\vartheta}{\epsilon'\delta}\left[1+\alpha\frac{(a_1-\vartheta)\dfrac{\sin\alpha(a_2-\vartheta)}{\sin\alpha(a_1-\vartheta)}+(a_2-\vartheta)\dfrac{\sin\alpha(a_1-\vartheta)}{\sin\alpha(a_2-\vartheta)}}{\sin\alpha(a_1+a_2-2\vartheta)}\right]. \tag{18}$$

Here $d\gamma=\gamma-\gamma_0$, where γ and γ_0 are the logarithmic damping decrements of the loaded and of the empty system, respectively. When ϵ' and κ are determined, ϵ'' can be computed

$$\epsilon''=2\epsilon'\kappa/1-\kappa^2. \tag{19}$$

The constant ϑ in Eqs. (15) and (18) may be considered as the correction for the effect of short leads. At $\vartheta=0$ Eq. (15) goes over into the old Morton-Coolidge equation,[9] and Eq. (18) goes over into the one derived by Potapenko.[9] In practice, because of the difficulty of computing L_{12} and L_{22}, ϑ is just an experimental constant, as δ_0 and δ are. In our case we had $\delta_0=0.562$ cm, $\delta=0.462$ cm, $\vartheta=0.011$; the correction for the so-called "displacement" of each bridge[15] was $\beta=0.055$ cm; $s=2.0$ cm; $r=0.1$ cm. The length of leads was below 0.5 cm, and κ did not exceed 0.07.

P_r and P_i, calculated by substituting ϵ' and ϵ'' obtained into Eqs. (2), are plotted in Figs. 2–5. The vertical range of the plotted points represents the probable error of the mean of a number of observations. The broken straight lines are those used for the extrapolation to

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[13] In terms of k_0 and k, the capacity of the condenser filled with a dielectric equals $C=k_0+\epsilon' k$.

[14] The derivation will be published elsewhere.

[15] P. Drude, *Physik des Aethers* (F. Enke, Stuttgart, 1912), p. 602; β was determined from $\lambda/2=(a_1+a_2)+2\beta$, where $(a+a_2)$ was measured at resonance while the condenser was removed from the system.

infinite dilition. They give the best fit for the low concentration range as computed by the least squares method. Table I contains the resulting extrapolated values of P_r and P_i of the solute, together with P_a and τ. Equation (13) was used to calculate τ in preference to Eq. (11), because of the smallness of $\omega\tau$ obtained. The values of P for the solid state found in the literature were too inconsistent to calculate P_a. Because of this, P_a shown in Table I were computed by extrapolation by means of Hartmann's formula from molar refractions measured in the optical spectrum. Such computation is conventional, but it neglects the dispersion in the infra-red, and it introduces an error in P_a. In our case the effect of this error may be disregarded, because our P_r values are much larger than P_a values, as Table I shows.

Substituting the values of τ found into Eq. (14), and using for $\eta = 1.34\ cP$ for dioxane,[16] we obtain the values V_{exp} listed in the second column of Table II. These values increase from formic to butyric acid, i.e., they increase with the size of molecule. In the third column of Table II are listed for comparison the values of V computed from the known structure of the molecule. This computation was done by constructing a model of each molecule, the envelope of the model being determined by the van der Waals radii of the atoms. Values for these radii, as well as for interatomic distances and bond angles, were taken from Pauling.[17] An example of these models is shown in Fig. 6. V_{str} was then computed as the volume of the ellipsoid whose principal axes were equal to the maximum dimensions of the model in three mutually perpendicular directions.

The experimental values V_{exp} are consistently smaller than the computed V_{str} values. However, these experimental values were calculated by use of the macroscopic value for η. It has been suggested by Fischer,[18] on the basis of his experiments with solutions of ketons and some other substances in benzene, that in dealing with molecular phenomena it is better to replace the macroscopic viscosity η by the effective molecular viscosity $\eta^* = 0.36\eta$. Substituting $\eta^* = 0.496\ cP$ in place of η in Eq. (14), we obtain the V_{exp}^* values listed in the last column of Table II. As one can see, V_{exp}^* values are in agreement with the V_{str} values. The agreement, in fact, is as good as could be expected in view of the rather approximate method of computing V_{str}. This agreement over a series of volumes which change by a factor of 2 allows one to conclude that in the case of fatty acids the entire molecule oscillates in a high frequency field. In other words, the anomalous absorption of ultra-high frequencies in fatty acids is due to the orientation of the entire molecule as a unit.

TABLE III. Dipole moments.

Substance	P_d(cc)	$_s u \times 10^{18}$(e.s.u.)	$_s u \times 10^{18}$(e.s.u.) Z.	W.W.	P.H.G.
HCOOH	81.2	1.98	1.51	2.07	1.82
CH_3COOH	63.2	1.75	1.73	1.74	1.68
C_2H_5COOH	46.5	1.50	1.74	1.75	1.68
n-C_3H_7COOH	51.5	1.58			1.65

Our conclusion, strictly speaking, refers to lighter acids investigated. In heavier fatty acids, when the length of chain becomes considerable, some internal rotations in the chain may take place. In such case the anomalous absorption will be due to the orientation of a part of the molecule only.

It should be mentioned that Fischer suggested[18] that the ratio $\eta^*/\eta = 0.36$ must hold for any liquid. The agreement between our V_{str} and V_{exp}^* values supports this suggestion, or at least extends it to the solutions in dioxane.

The orientation of the fatty acid molecules as a unit means that their dipole-bearing group, i.e., the carboxyl group $-COOH$, is firmly bound to the rest of the molecule. This may be contrasted with the results found earlier for alcohols.[3] There the V_{exp} values were independent of the size of the molecule, and close to the volume of their dipole-bearing OH-group, thus indicating that the anomalous absorption in alcohols is due to the orientation of the OH-group alone, as it has been mentioned earlier. The direction of dipole moment in fatty acid molecules is approximately perpendicular to the $C-C$ band which binds the carboxyl with the rest of the molecule. Under these circumstances, the impossibility of independent orientation of carboxyl must be

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[16] H. Hartmann, Zeits. Phys. Chem. **A191**, 197 (1942).

[17] L. Pauling, *The Nature of Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition, pp. 164–203.

[18] E. Fischer, Physik. Zeits. **40**, 645 (1939).

ascribed to intramolecular forces which tend to hinder such orientation. It is easy to see that the two oxygen atoms of the carboxyl are likely to have a much greater interaction with the neighboring hydrogen atoms of the rest of the chain than does the hydrogen atom of the hydroxyl with its neighbors. This difference in the interaction forces is evidently sufficient to allow the OH-group in alcohols to be oriented independently of the rest of the molecule, while precluding the independent orientation of the COOH-group in acids.

The hindering of independent orientation of a group in an impressed field must not be confused with the hindering of rotation of the same group around its bond. The hindering of rotation around a bond, which is of interest to structural chemistry, determines the most probable position which the group occupies relative to the rest of the molecule. The hindering of orientation in a high frequency field, with which we are concerned, restricts the freedom of a group to oscillate about this most probable position.

It should be pointed out that our results give no indication on any independent oscillation of the OH-group within the carboxyl. This is in agreement with Zahn,[19] who found on the basis of his dipole moment measurements, that the H-atom of the OH-group in the carboxyl is firmly bound to the O-atom of its C=O group.

From the P_r, P_i, P_a values which we have used to calculate τ and V, we can calculate the dipole moments using Eqs. (5′) and (12). The results of these calculations are shown in the third column of Table III. This table also shows the dipole moment values obtained by Zahn[19] (fourth column), by Wilson and Wenzke[10] (fifth column), and by Pohl, Hobbs, and Gross[20] (sixth column). We see that our values are in agreement with these earlier determinations, with the possible exception of propionic acid, which is low, but still of correct order of magnitude. This check renders a good support in favor of the validity of our results for τ and V computed from the same data.

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[19] C. T. Zahn, Phys. Rev. **37**, 1516 (1931).

[20] H. Pohl, M. Hobbs, and P. Gross, J. Chem. Phys. 9, 408 (1941).

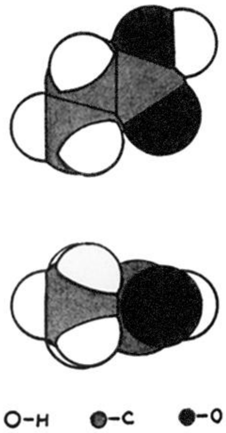

FIG. 6. Model of the propionic acid molecule. The models of molecules of other acids may be obtained from this one by either subtracting or adding one or more CH_2-groups.