# Dispersion and Absorption of Ultra-High Frequency Electromagnetic Waves in some Fatty Acids

Thesis by

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In Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
California Institute of Technology
Pasadena, California
1947

# Abstract

The problem of this work is to determine whether the carboxyl group of the fatty acids rotates independently of the remainder of the molecule when subjected to an alternating electromagnetic field. The dielectric constant and absorption coefficient of dilute solutions of formic, acetic, propionic, and butyric acids in dioxane are measured at a wavelength of 25 centimeters, using Drude's second method. A method is developed for computing the effective volume of the rotating portion of the molecule from this data. The computed volumes are found to be proportional to the molecular volumes, proving that for the acids investigated, the entire molecule rotates as a unit.

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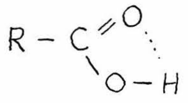
## Introduction

Measurements made by Keutner and Potapenko(1,2)* on the series: methyl, ethyl, n-propyl and n-butyl alcohol in an alternating electric field showed that the volume of the portion of the molecule which oriented itself in the field was independent of the length of the hydrocarbon chain. They concluded that, since the permanent electric dipole moment of these molecules resided chiefly in the O-H group and was oriented perpendicular to the C-O bond, the O-H group was rotating about the C-O bond independently of the remainder of the molecule.

Keutner and Potapenko also found that for di-ethyl ether no such independent rotation of the dipolar group took place, even though the moment of the group was directed perpendicular to the long axis of the molecule. This is because the dipolar group is bound to the two adjacent hydrocarbon chains by bonds making an angle with each other, so that independent rotation of this group would require accompanying deformations of the whole molecule.

A necessary condition for the independent rotation of a polar group within a molecule is thus that the dipole moment of the group should be directed approximately perpendicular to a single bond which joins the group to the remainder of the molecule. This condition is satisfied by the carboxyl group 

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* Superscript numerals refer to the bibliography at the end of this work. An asterisk will continue to designate a footnote.

for which the dipole moment is approximately perpendicular to the R-C bond. Therefore it was of interest to discover whether this phenomenon of independent rotation would actually be exhibited by the carboxyl group. To investigate this, the fatty acid series was chosen as one providing a simple sequence of molecules of varying size, containing single carboxyl groups. The following work was thus undertaken with the purpose of determining whether the volume of the portion of the lighter fatty acid molecules which oriented itself in an alternating electric field was independent of the size of the whole molecule.

The method of attack was that of studying the dispersion and absorption of dilute solutions of the liquid acids in non-polar solvents within the region of anomolous dispersion characterized by the orientation of the permanent dipoles of the acid molecules.

## Method of Measurement

The method adopted was that known as Drude's second method(3), as modified by Coolidge(4) and Potapenko(5), which consists in measuring the changes in the resonance curve of a Lecher wire system on introducing a small condenser containing the dielectric to be investigated. The measurements had to be made at ultra-high frequencies for reasons to be explained later. On account of this, resonance methods and bridge methods were discarded as inadequate. Drude's second method was chosen in preference to other transmission line methods because it requires a very small amount of the substance to be tested. This is important because the work had to be carried out at a frequency where the absorption of the dielectric is fairly high, so that large amounts of the substance tested would flatten the resonance curves to the point where they were no longer measurable.

## Apparatus

The apparatus consisted of an ultra-high frequency generator and a measuring system.

The generator used for most of the measurements was a positive grid oscillator, employing an FP126 tube (Fig. 1). No external tuned circuit was used, RF chokes being inserted in all the tube leads. Thus the frequency was determined solely by the tube constants and electrode potentials. The filament was supplied from three low resistance storage cells, which were trickle charged during operation in order to maintain constant voltage. The resistor $R_1$ was a mercury column rheostat used to adjust the filament current to 5.70 amperes. $R_2$ was a 5000 ohm wire-wound resistor in

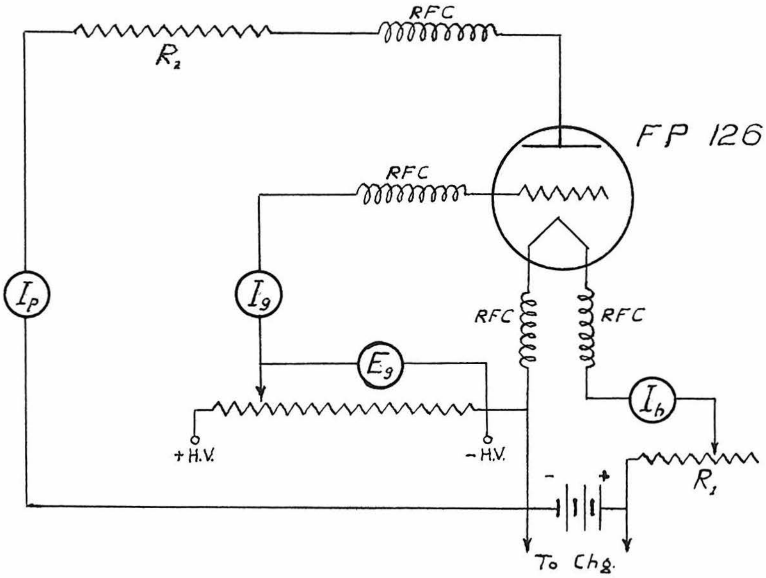


Fig. 1. The Generator Circuit

the plate circuit which served to keep the plate slightly negative with a consequent increase in the output of the tube. The high voltage for the grid was supplied by a well filtered rectifier whose output was fed through a degenerative voltage regulator (Fig 2). Normal operating conditions were:

$I_h$ = 5.70 a.
$E_g$ = 385 v.
$I_g$ = 20.0 ma.
$E_p$ = -8.0 v.
$I_p$ = 1.60 ma.

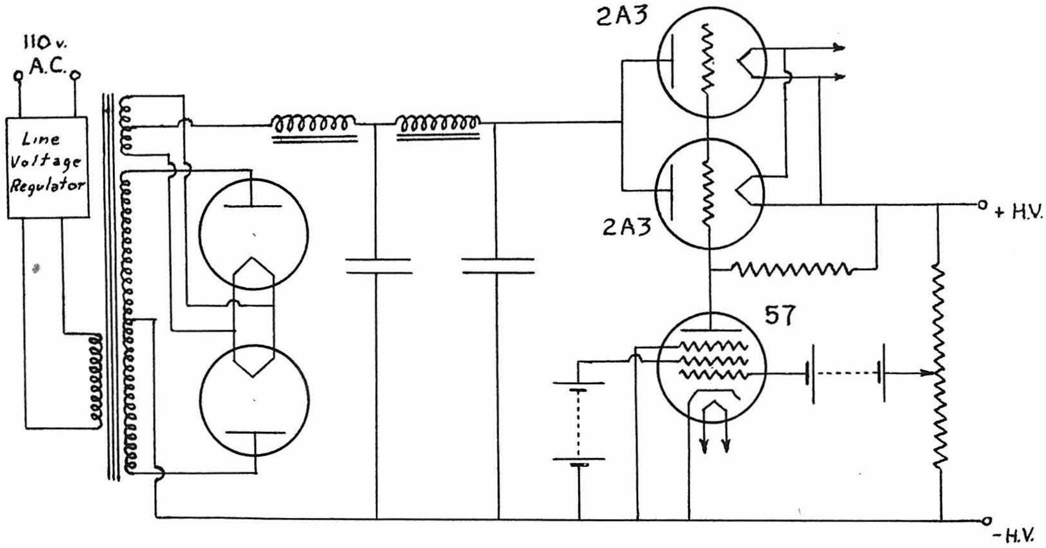


Fig. 2. The High Voltage Supply

Operating under these conditions the tube oscillated at a frequency corresponding to "higher order" oscillations (second order "dwarfs") having a wavelength of about 25.6 cm.(6) We also occasionally used a region of oscillation at $E_g$ = 210 volts which produced third order "dwarfs" of the same wavelength.

Since the high-frequency circuit was contained almost entirely within the tube envelope, it was comparatively free from external disturbances. The electrode potentials were closely controlled, so that once thermal equilibrium was established in the tube, the wavelengths of the oscillations generated did not vary by more than 0.01 cm during the course of a three hour run.

The power output of this generator was very small, but was sufficient to give large deflections in the measuring system with low coupling between the two.

An additional generator, consisting of a conventional electron-coupled triode oscillator using a 316A tube was used to make some check measurements at a wavelength of about 50 cm.

The measuring system was composed of a Lecher wire system having a thermocouple and galvanometer as detector (Fig 3). This system was designed by Dr. G. Potapenko, and has been used by him previously in studying dielectrics.

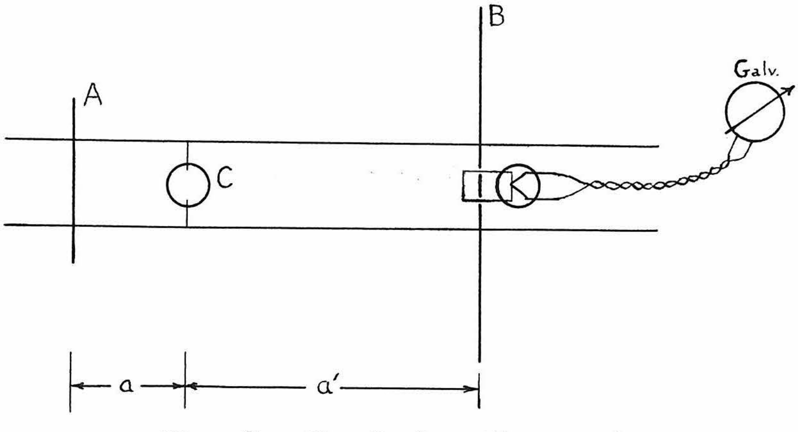
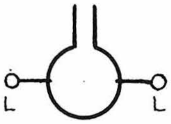


Fig. 3. The Lecher Wire System

The Lecher wires were of copper, each 0.20 cm in diameter and spaced 2.0 cm between centers. They were attached at one end to weighted levers to maintain constant tension in the wires. The working section of the Lecher system was bounded by two shorting bridges, A and B. Bridge A was the "fixed" bridge of the system. It was a copper disc with a radius of 2.5 cm having two holes in its face through which the Lecher wires ran, with short lengths of copper tubing soldered to the back of the disc in order to keep the plane of the disc perpendicular to the wires. It was supported only by the Lecher wires and could be slid along them by hand. Bridge B, the "movable" bridge, was a copper disc with a radius of 18.0 cm. It was mounted on a rigid carriage, which moved on tracks. The carriage as a whole was moved along the Lecher wires by a motor driven worm gear, and its position was determined by a scale engraved on one of the horizontal members of the carriage. This scale could be read to 0.01 cm with the aid of a vernier index mounted on the base of the system. In addition, a short end section of the carriage, including the bridge, could be moved with respect to the remainder of the carriage through a range of about one centimeter. This motion was effected by means of a precision worm gear, driven by hand, and the relative position of the two sections was indicated by a dial extensometer which was divided to 0.001 cm. The Lecher wires passed through small holes in the bridge, and good contact between the bridge and the wires was maintained by the use of small, knife-edged copper plates set into the plane of the disc and held against the Lecher wires by small coil springs.

The measuring condenser C (Fig 4) consisted of a spherical glass flask 1.0 cm in diameter into which a pair of platinum leads had been fused at opposite ends of a diameter. These leads were 0.05 cm in diameter and projected about 0.01 cm into the flask. No condenser plates were used. The outer ends of the leads were soldered into holes in the Lecher wires so that the flask was supported with its center in the plane of the Lecher wires and midway between them.



Scale: Full Size

L - L : Lecher Wires

Fig. 4. The Condenser

The detector was a vacuum thermocouple having a heater resistance of 1000 ohms. It was mounted in a copper box immediately behind bridge B, and was inductively coupled into the Lecher system by a small rectangular loop of wire lying in the plane of the Lecher wires and passing through holes in the face of the bridge. The thermocouple was connected through a shielded cable to a galvanometer with a sensitivity of 40 mm/$\mu$V in this circuit.

The whole Lecher system was partially shielded against external disturbance by a copper screen surrounding it at a distance of about 30 cm, but which was open at the ends.

The Lecher system was excited directly by radiation emitted by the generator tube. Bridge B being appreciably greater than a half wavelength in radius, coupling between the working section and the remainder of the apparatus behind B was negligible. Bridge A was smaller in order to permit coupling with the generator, which was placed beyond this end of the system, and somewhat above the plane of the Lecher wires. Coupling was varied simply by changing the distance between the generator and the measuring system, and was made as loose as was consistent with good galvanometer deflections.

Theory of the Apparatus

The basic equations used to calculate the dielectric constant and the absorption coefficient of the dielectric in Drude's second method are those derived by Coolidge(4) and extended for the case of an appreciable absorption by Potapenko(5). They are:

$$\delta_0 + \varepsilon'\delta = \frac{\lambda}{2}\left[\cot \alpha a_1 + \cot \alpha a_2\right] \qquad \underline{1}$$

$$\frac{\varkappa}{1-\varkappa^2} = \frac{d\gamma}{4\pi}\,\frac{\delta_0 + \varepsilon'\delta}{\varepsilon'\delta}\left[1 + \frac{\alpha a_1 \dfrac{\sin \alpha a_2}{\sin \alpha a_1} + \alpha a_2 \dfrac{\sin \alpha a_1}{\sin \alpha a_2}}{\sin \alpha (a_1 + a_2)}\right] \qquad \underline{2}$$

$$\delta_0 = 4\pi \ln \frac{S}{R} \cdot K_0 \quad ; \quad \delta = 4\pi \ln \frac{S}{R} \cdot K \qquad \underline{3}$$

where $\varepsilon'$ and $\varkappa$ are respectively the real part of the dielectric constant, and the absorption coefficient of the dielectric. S is the distance between the wires of the Lecher system, R is their radius, and $K_0$ and $\varepsilon' K$ are respectively the ballast capacity ( the portion of C which does not depend on $\varepsilon'$) and the working capacity (the portion of C which is proportional to $\varepsilon'$) of the condenser C in esu. $\alpha = \frac{2\pi}{\lambda}$ , and $\lambda$ is the wavelength in centimeters of the exciting radiation. $d\gamma$ is the change in the logarithmic damping decrement of the system due to the presence of the dielectric, and $a_1$ and $a_2$ are the distances from the condenser to the two voltage nodes on either side of it when the system is in resonance. $a_1$ and $a_2$ are slightly greater than the corresponding distances $a$ and $a'$ to the two bridges, due to the "bridge shortening"(7) of the system, so that we may write $a_1 = a + \beta_1$ , $a_2 = a' + \beta_2$ , and $\beta_1 + \beta_2 = \beta$ , where $\beta$ is the total bridge shortening.

Formula 1 implies the constancy of the expression $[\cot \alpha a_1 + \cot \alpha a_2]$ as a function of $a_1$ when working at a given wavelength with a given dielectric. This was found by many workers to be untrue, the first of these being Linnitschenko(8). Two attempts have been made to explain this variation with condenser position, the first by Romanoff(9), and a second by Slatis(10).

Romanoff based his derivation on the assumption that the cause of the variation was the reflection of the electromagnetic waves from the air-glass and glass-dielectric interfaces of the condenser, which resulted in the expression:

$$\delta_0 + \varepsilon'\delta = \frac{\lambda}{2}\,\frac{k_1 \sin\alpha d - \sqrt{1-k_1^2}\,\cos\alpha d}{\sin\alpha a_1 \;\sin\alpha(a_1+d)}$$

where $d = \frac{\lambda}{2} - (a_1 + a_2)$ and $k_1$ is a parameter which depends slightly upon $\varepsilon'$ and which must be experimentally determined. This can be more readily compared with the Coolidge equation (1) if we make the substitution $k_1 = \cos 2\alpha\eta$ which yields the form:

$$\delta_0 + \varepsilon'\delta = \frac{\lambda}{2}\left[\cot\alpha(a_1-\eta) + \cot\alpha(a_2-\eta)\right]\left[1 - \frac{\sin\alpha\eta \;\sin\alpha(a_1+a_2-\eta)}{\sin\alpha a_1 \;\sin\alpha a_2}\right] \qquad 4$$

Slatis pointed out that the observed variation of the correction factor with the distance of the condenser from the plane of the Lecher wires was inverse to that which would be expected if reflection from the condenser were the cause, and proposed instead that the effect be attributed to the inductance of the condenser leads. He considered two contributing causes; firstly, the mutual inductance between eddy currents in the condenser leads and neighboring portions of the Lecher system, which would have the effect of changing the propagation constant of the Lecher system in the vicinity of the condenser, and secondly, the effect of the self inductance of the condenser leads, which would make the potential difference across the condenser different from that across the ends of its leads. On the basis of these assumptions he derived the equations:

$$\delta_0 + \varepsilon' \delta = \frac{\lambda}{2} \frac{\ln S/R}{\ln S/R'} \cot(\varphi + \alpha \zeta)$$

$$\cot \varphi = \frac{\cot \alpha(a_1 - \vartheta) + \cot \alpha(a_2 - \vartheta) - 2\alpha\vartheta}{\ln \frac{S}{R} \Big/ \ln \frac{S}{R'}}$$

$$\vartheta = \frac{L_{12}^2}{L_{22} \cdot 4 \ln S/R}$$

where $L_{12}$ is the mutual inductance between each condenser lead and its neighboring Lecher wire, $L_{22}$ is the self inductance of the condenser leads, R' is the radius of the leads, and $\zeta$ is a length which is less than that of the condenser leads by an amount depending on R' and the configuration of the condenser. In the case that the center of the condenser is coplanar with the Lecher wires, so that the condenser leads are very short, as was true for the present experiments, then $\alpha\zeta$ becomes very small with respect to $\varphi$ and the term in $\zeta$ can therefore be neglected. From the work of Malov(11), who approaches the problem in a slightly different fashion, it can also be seen that the effect of potential drop along the leads due to their self inductance is very small for leads of the size used in this work. On dropping $\zeta$ , Slatis' equations simplify to:

$$\delta_0 + \varepsilon'\delta + 2\pi\vartheta = \frac{\lambda}{2}\left[\cot\alpha(a_1 - \vartheta) + \cot\alpha(a_2 - \vartheta)\right] \qquad \underline{5}$$

$$\vartheta = \frac{L_{12}^2}{L_{22}\cdot 4\ln S/R} \qquad \underline{6}$$

In our case we always had $\frac{\sin\alpha(a_1 + a_2 - \eta)}{\sin\alpha a_1 \ \sin\alpha a_2} < 1$ and $\sin\alpha\eta \ll 1$ Due to this the final factor in equation $\underline{4}$ could be dropped. The term $2\pi\vartheta$ in equation $\underline{5}$, being a constant, could be combined with $\delta_0$ This would make equations $\underline{4}$ and $\underline{5}$ identical except for the meaning of the constants. As a result of this, it was not possible in our case to distinguish between the two corrections, i.e. it was not possible to decide which meaning of the constants should be preferred.

A comparison of the two methods, carried out by Fradkina(12) with apparatus designed to exaggerate the possible causes of the deviations led to the conclusion that Slatis' formula was the more reliable. The Slatis theory has also been checked experimentally by Kalinin and Posadskaia(13), who came to the conclusion that a measurable effect due to the inductance of the leads does exist, but that under ordinary experimental conditions it should be negligible. On the basis of these results Slatis' form of the equation and his expression for the constant $\vartheta$ (6) may be assumed as the correct ones, but since it is extremely difficult to obtain accurate values of $L_{12}$ and $L_{22}$ from the configuration of the circuit, $\vartheta$ is treated as an empirical constant in the rest of this work.

A further correction to the basic equation for the case when the absorption of the dielectric is very high has been made by Sosinsky and Dmitriev(14) which leads to the form

$$\delta_0 + \varepsilon'\delta = \frac{\lambda}{2}\left[\cot \alpha a_1 + \frac{(1-m^2)\tan \alpha a_2}{m^2 + \tan^2 \alpha a_2}\right] \tag{7}$$

before the application of Slatis' correction factor. Here $m = \frac{\sin \alpha \Delta/2}{\sqrt{1 + \sin^2 \alpha \Delta/2}}$ and $\Delta$ is the width of the resonance curve at the point $I^2 = \frac{1}{2} I^2_{max.}$ . The absorption factor in this work was sufficiently small so that $m^2 < 0.001$ , in which case, neglecting $m^2$, 7 reduces to 1, so this correction need not be considered. Hence equation 5 remains the one which we shall use for the computation of $\varepsilon'$.

The effect which the introduction of Slatis' correction factor has on Potapenko's equation for the absorption coefficient (2) was not derived by Slatis in his paper, but since we need this result we will do so here. In the following derivation, the initial assumptions are those of Slatis, as also is a part of the method of attack.

Consider the Lecher wire system (Fig 5) bridged by a condenser of capacity C at z = 0 and bounded by two perfectly conducting bridges at $z = -a_1$ and $z = a_2$. Assume that the effect of eddy currents in the condenser leads is equivalent to a change of propagation constant of the Lecher system in the vicinity of the condenser, and further that this change can be represented with sufficient accuracy by considering that it exists only within the region $|z| < \delta$, so that if waves of period T have a wavelength $\lambda$ for $|z| > \delta$, they will have a wavelength $\lambda' = \lambda/k$ for $|z| < \delta$. Then the current in any section of the Lecher system can be represented by

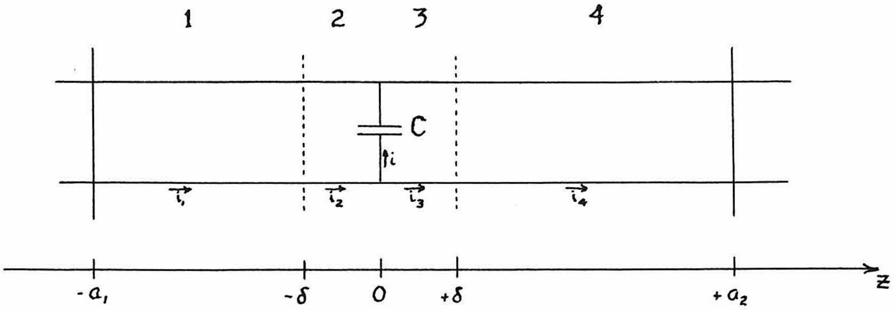


Fig. 5.

$$i_n = A_n e^{\xi\left(\frac{t}{T} - \frac{z}{\lambda_n}\right)} + B_n e^{\xi\left(\frac{t}{T} + \frac{z}{\lambda_n}\right)} \qquad \underline{8}$$

$[n = 1, 2, 3, 4]$

where $\lambda_1 = \lambda_4 = \lambda$ ; $\lambda_2 = \lambda_3 = \lambda/k$ and

$$\xi = -\gamma + 2\pi i \qquad \underline{9}$$

where $\gamma$ is the logarithmic damping decrement of the system.

$A_n$ and $B_n$ are complex constants to be determined from the boundary conditions. The boundary conditions to be satisfied are:

$$\text{at} \quad z = -a_1 : \quad \frac{\partial i_1}{\partial z} = 0$$

$$\text{at} \quad z = -\delta : \quad i_1 = i_2 \quad \text{and} \quad \frac{\partial i_1}{\partial z} = \frac{\partial i_2}{\partial z}$$

$$\text{at} \quad z = 0 : \quad i_2 - i_3 = i \quad \text{and} \quad \frac{\partial i_2}{\partial z} = \frac{\partial i_3}{\partial z}$$

$$\text{at} \quad z = \delta : \quad i_3 = i_4 \quad \text{and} \quad \frac{\partial i_3}{\partial z} = \frac{\partial i_4}{\partial z}$$

$$\text{at} \quad z = a_2 : \quad \frac{\partial i_4}{\partial z} = 0$$

For the current $i$ through the condenser, we have

$$i = C\frac{\partial V}{\partial t} + \frac{V}{W} \qquad \underline{10}$$

where V is the potential difference between the condenser plates and W is the resistance between the plates. When we neglect the potential drop along the condenser leads, V is also the potential difference between the Lecher wires, so that $V = 4qc^2 \ln S/R$, where q is the charge per unit length of the Lecher wires, S is their separation, and R their radius. Substituting this into equation 10 we have

$$i = 4c^2 \ln \frac{S}{R}\left[C\frac{\partial q}{\partial t} + \frac{q}{W}\right]$$

and substituting this into the first boundary condition at z = 0,

$$i_2 - i_3 = 4c^2 \ln \frac{S}{R}\left[C\frac{\partial q}{\partial t} + \frac{q}{W}\right]$$

In order to eliminate q from this relation, we differentiate with respect to time and make use of the equation$^{(15)}$ $\frac{\partial q}{\partial t} = -\frac{\partial i}{\partial z}$ giving as a boundary condition to replace $i_2 - i_3 = i$ the condition

$$\frac{\partial i_2}{\partial t} - \frac{\partial i_3}{\partial t} = -4c^2 \ln\frac{S}{R}\left[C\frac{\partial^2 i_3}{\partial t\,\partial z} + \frac{1}{W}\frac{\partial i_3}{\partial z}\right]$$

Substituting equation 8 into the boundary value relations, and making the abbreviation

$$\ell = 4c^2 \ln\frac{S}{R}\left[C + \frac{T}{\xi W}\right] \tag{11}$$

gives us the eight equations:

$$-A_1 e^{\frac{\xi a_1}{\lambda}} + B_1 e^{-\frac{\xi a_1}{\lambda}} = 0 \tag{12}$$

$$A_1 e^{\frac{\xi\delta}{\lambda}} + B_1 e^{-\frac{\xi\delta}{\lambda}} = A_2 e^{\frac{\xi\delta k}{\lambda}} + B_2 e^{-\frac{\xi\delta k}{\lambda}} \tag{13}$$

$$-A_1 e^{\frac{\xi\delta}{\lambda}} + B_1 e^{-\frac{\xi\delta}{\lambda}} = -kA_2 e^{\frac{\xi\delta k}{\lambda}} + kB_2 e^{-\frac{\xi\delta k}{\lambda}} \tag{14}$$

$$-A_2 + B_2 = -A_3 + B_3 \tag{15}$$

$$A_2 + B_2 - A_3 - B_3 = \ell\frac{\xi k}{\lambda}(A_3 - B_3) \tag{16}$$

$$A_3 e^{-\frac{\xi\delta k}{\lambda}} + B_3 e^{\frac{\xi\delta k}{\lambda}} = A_4 e^{-\frac{\xi\delta}{\lambda}} + B_4 e^{\frac{\xi\delta}{\lambda}} \tag{17}$$

$$-kA_3 e^{-\frac{\xi\delta k}{\lambda}} + kB_3 e^{\frac{\xi\delta k}{\lambda}} = -A_4 e^{-\frac{\xi\delta}{\lambda}} + B_4 e^{\frac{\xi\delta}{\lambda}} \tag{18}$$

$$-A_4 e^{-\frac{\xi a_2}{\lambda}} + B_4 e^{\frac{\xi a_2}{\lambda}} = 0 \tag{19}$$

Eliminating $A_1$ and $B_1$ from equations 12, 13, 14, and solving the result for the ratio $A_2/B_2$ gives

$$\frac{A_2}{B_2} = e^{-\frac{2\xi\delta k}{\lambda}} \frac{(k+1)\,e^{\frac{2\xi\delta}{\lambda}} + (k-1)\,e^{\frac{2\xi a_1}{\lambda}}}{(k-1)\,e^{\frac{2\xi\delta}{\lambda}} + (k+1)\,e^{\frac{2\xi a_1}{\lambda}}} \tag{20}$$

Following the same procedure to eliminate $A_4$ and $B_4$ from 17, 18, 19, we get

$$\frac{A_3}{B_3} = e^{\frac{2\xi\delta k}{\lambda}} \frac{(k+1)\,e^{\frac{2\xi a_2}{\lambda}} + (k-1)\,e^{\frac{2\xi\delta}{\lambda}}}{(k-1)\,e^{\frac{2\xi a_2}{\lambda}} + (k+1)\,e^{\frac{2\xi\delta}{\lambda}}} \tag{21}$$

In order to simplify the work, we make the following substitutions:

$$\left.\begin{aligned} e^{\frac{2\xi a_1}{\lambda}} &= \frac{x+1}{x-1} \;; & e^{\frac{2\xi a_2}{\lambda}} &= \frac{y+1}{y-1} \\ e^{\frac{2\xi\delta}{\lambda}} &= \frac{r+1}{r-1} \;; & e^{\frac{2\xi\delta k}{\lambda}} &= \frac{s+1}{s-1} \end{aligned}\right\} \tag{22}$$

Then 20 and 21 become

$$\frac{A_2}{B_2} = \frac{s-1}{s+1}\,\frac{kxr - k + x - r}{kxr - k - x + r} \tag{23}$$

$$\frac{A_3}{B_3} = \frac{s+1}{s-1}\,\frac{kyr - k - y + r}{kyr - k + y - r} \tag{24}$$

Making the further abbreviations

$$\frac{xr-1}{r-x} = u \;; \quad \frac{yr-1}{r-y} = v \tag{25}$$

we get

$$\frac{A_2}{B_2} = \frac{sk\mu - k\mu - s + 1}{sk\mu + k\mu + s + 1} \qquad \underline{26}$$

$$\frac{A_3}{B_3} = \frac{skv + kv + s + 1}{skv - kv - s + 1} \qquad \underline{27}$$

Adding and subtracting equations $\underline{15}$ and $\underline{16}$ give

$$2A_2 = 2A_3 + \frac{\ell\xi k}{\lambda}(A_3 - B_3) \qquad \underline{28}$$

$$2B_2 = 2B_3 + \frac{\ell\xi k}{\lambda}(A_3 - B_3) \qquad \underline{29}$$

The ratio of $\underline{28}$ to $\underline{29}$ gives

$$\frac{A_2}{B_2} = \frac{2\frac{A_3}{B_3} + \frac{\ell\xi k}{\lambda}\left(\frac{A_3}{B_3} - 1\right)}{2 + \frac{\ell\xi k}{\lambda}\left(\frac{A_3}{B_3} - 1\right)} \qquad \underline{30}$$

and, solving $\underline{30}$ for $\frac{\ell\xi k}{\lambda}$, we obtain

$$\frac{\ell\xi k}{\lambda} = 2\,\frac{\frac{A_3}{B_3} - \frac{A_2}{B_2}}{\left(\frac{A_3}{B_3} - 1\right)\left(\frac{A_2}{B_2} - 1\right)} \qquad \underline{31}$$

Substituting the values for $A_2/B_2$ and $A_3/B_3$ from equations $\underline{26}$ and $\underline{27}$ into $\underline{31}$ and simplifying gives

$$\frac{\ell\xi k}{\lambda} = -\frac{skv + 1}{kv + s} - \frac{sk\nu + 1}{k\mu + s} \qquad \underline{32}$$

From equation $\underline{22}$, $(x+1)/(x-1) = e^{\frac{2\xi a_1}{\lambda}}$, and therefore $x = (e^{\frac{2\xi a_1}{\lambda}} + 1)/(e^{\frac{2\xi a_1}{\lambda}} - 1) = -i\cot\left(\frac{-i\xi a_1}{\lambda}\right)$, and similar expressions obtain for y, r, and s, so that

$$\left.\begin{aligned}
x &= -i \cot\left(-\frac{i\xi a_1}{\lambda}\right)\\
y &= -i \cot\left(-\frac{i\xi a_2}{\lambda}\right)\\
r &= -i \cot\left(-\frac{i\xi \delta}{\lambda}\right)\\
s &= -i \cot\left(-\frac{i\xi \delta k}{\lambda}\right)
\end{aligned}\right\}\qquad \underline{33}$$

From 25 and 33

$$u = \frac{xr-1}{r-x} = -i\,\frac{\cot\left(-\frac{i\xi a_1}{\lambda}\right)\cot\left(-\frac{i\xi\delta}{\lambda}\right)+1}{\cot\left(-\frac{i\xi\delta}{\lambda}\right)-\cot\left(-\frac{i\xi a_1}{\lambda}\right)}$$

$$\left.\begin{aligned}
u &= -i \cot\left[-\frac{i\xi}{\lambda}(a_1-\delta)\right]\\
\text{and similarly}\qquad v &= -i \cot\left[-\frac{i\xi}{\lambda}(a_2-\delta)\right]
\end{aligned}\right\}\qquad \underline{34}$$

Substituting the values from 33 and 34 into 32 gives

$$\frac{\ell\xi k}{\lambda} = -\frac{k(-i)\cot\left(-\frac{i\xi\delta k}{\lambda}\right)\cdot(-i)\cot\left[-\frac{i\xi}{\lambda}(a_2-\delta)\right]+1}{k(-i)\cot\left[-\frac{i\xi}{\lambda}(a_2-\delta)\right]-i\cot\left(-\frac{i\xi\delta k}{\lambda}\right)} - \frac{k(-i)\cot\left(-\frac{i\xi\delta k}{\lambda}\right)(-i)\cot\left[-\frac{i\xi}{\lambda}(a_1-\delta)\right]+1}{k(-i)\cot\left[-\frac{i\xi}{\lambda}(a_1-\delta)\right]-i\cot\left(-\frac{i\xi\delta k}{\lambda}\right)}$$

$$\frac{\ell\xi}{\lambda} = i\left[\frac{\frac{1}{k}\cot\left(-\frac{i\xi\delta k}{\lambda}\right)\cot\left[-\frac{i\xi}{\lambda}(a_1-\delta)\right]-\frac{1}{k^2}}{\cot\left[-\frac{i\xi}{\lambda}(a_1-\delta)\right]+\frac{1}{k}\cot\left(-\frac{i\xi\delta k}{\lambda}\right)} + \frac{\frac{1}{k}\cot\left(-\frac{i\xi\delta k}{\lambda}\right)\cot\left[-\frac{i\xi}{\lambda}(a_2-\delta)\right]-\frac{1}{k^2}}{\cot\left[-\frac{i\xi}{\lambda}(a_2-\delta)\right]+\frac{1}{k}\cot\left(-\frac{i\xi\delta k}{\lambda}\right)}\right\}\qquad \underline{35}$$

But the effect of the leads should be small, so that we may consider $\xi\delta/\lambda \ll 1$. Then expanding the right hand side of 35 in a Maclaurin's series and neglecting powers of $\xi\delta/\lambda$ higher than the first, we obtain

$$\frac{\ell \xi}{\lambda} = i\left[\cot\left(-\frac{i\xi a_1}{\lambda}\right) + \cot\left(-\frac{i\xi a_2}{\lambda}\right)\right] + (1-k^2)\left[\cot^2\left(-\frac{i\xi a_1}{\lambda}\right) + \cot^2\left(-\frac{i\xi a_2}{\lambda}\right)\right]\frac{\xi\delta}{\lambda}$$

This can be rewritten in the form

$$\frac{\ell \xi}{\lambda} = i\left[\cot\left(-\frac{i\xi a_1}{\lambda}\right) + \cot\left(-\frac{i\xi a_2}{\lambda}\right) - i\left\{\csc^2\left(-\frac{i\xi a_1}{\lambda}\right) + \csc^2\left(-\frac{i\xi a_2}{\lambda}\right)\right\}\frac{\xi\delta(1-k^2)}{\lambda}\right] - \frac{2\xi\delta(1-k^2)}{\lambda} \qquad \underline{36}$$

Let us now consider the expression

$$\cot\left[-\frac{i\xi}{\lambda}\left\{a_1 - \delta(1-k^2)\right\}\right] + \cot\left[-\frac{i\xi}{\lambda}\left\{a_2 - \delta(1-k^2)\right\}\right]$$

Since it is also true that $(1-k^2)\xi\delta/\lambda \ll 1$ we can expand this expression in powers of $(1-k^2)\xi\delta/\lambda$ and, neglecting second and higher powers, obtain

$$\cot\left[-\frac{i\xi}{\lambda}\left\{a_1 - \delta(1-k^2)\right\}\right] + \cot\left[-\frac{i\xi}{\lambda}\left\{a_2 - \delta(1-k^2)\right\}\right] =$$

$$\cot\left(-\frac{i\xi a_1}{\lambda}\right) + \cot\left(-\frac{i\xi a_2}{\lambda}\right) - i\left\{\csc^2\left(-\frac{i\xi a_1}{\lambda}\right) + \csc^2\left(-\frac{i\xi a_2}{\lambda}\right)\right\}\frac{\xi\delta(1-k^2)}{\lambda} \qquad \underline{37}$$

Comparing the right hand side of this equation with the portion of $\underline{36}$ enclosed in square brackets, we find that they are identical, so that substituting $\underline{37}$ in $\underline{36}$ gives

$$\frac{\ell \xi}{\lambda} = i\left[\cot\left\{-\frac{i\xi}{\lambda}\left[a_1 - \delta(1-k^2)\right]\right\} + \cot\left\{-\frac{i\xi}{\lambda}\left[a_2 - \delta(1-k^2)\right]\right\}\right] - (1-k^2)\frac{2\xi\delta}{\lambda} \qquad \underline{38}$$

We define the constant $\vartheta$ by the relation $\vartheta = \delta(1-k^2)$ so that $\underline{38}$ becomes

$$\frac{(\ell + 2\vartheta)\xi}{\lambda} = i\left\{\cot\left[-\frac{i\xi}{\lambda}(a_1 - \vartheta)\right] + \cot\left[-\frac{i\xi}{\lambda}(a_2 - \vartheta)\right]\right\} \qquad \underline{39}$$

Substituting for $\ell$ and $\xi$ from 9 and 11 into this equation we obtain

$$-\frac{4c^2 C\gamma \ln\frac{S}{R}}{\lambda} - \frac{2\vartheta\gamma}{\lambda} + \frac{4c^2 T \ln\frac{S}{R}}{W\lambda} + i\left[\frac{8\pi c^2 C\ln\frac{S}{R}}{\lambda} + \frac{4\pi\vartheta}{\lambda}\right] =$$

$$i\left\{\cot\left[\frac{2\pi}{\lambda}(a_1-\vartheta)+\frac{i\gamma}{\lambda}(a_1-\vartheta)\right] + \cot\left[\frac{2\pi}{\lambda}(a_2-\vartheta)+\frac{i\gamma}{\lambda}(a_2-\vartheta)\right]\right\} \qquad \underline{40}$$

If we expand the right hand side of equation 40 in powers of $\gamma$, we can neglect powers of $\gamma$ higher than the first provided that the dielectric in the condenser has low enough losses so that the damping of the system remains small. In this case we obtain

$$\frac{-4c^2 C\gamma \ln\frac{S}{R} - 2\vartheta\gamma + \frac{4c^2 T}{W}\ln\frac{S}{R}}{\lambda} + i\left[\frac{8\pi c^2 C\ln\frac{S}{R} + 4\pi\vartheta}{\lambda}\right] =$$

$$i\left\{\cot\frac{2\pi}{\lambda}(a_1-\vartheta) + \cot\frac{2\pi}{\lambda}(a_2-\vartheta)\right\} + \frac{\frac{2\gamma}{\lambda}(a_1-\vartheta)\cot\frac{2\pi}{\lambda}(a_1-\vartheta)}{\sin\frac{4\pi}{\lambda}(a_1-\vartheta)} + \frac{\frac{2\gamma}{\lambda}(a_2-\vartheta)\cot\frac{2\pi}{\lambda}(a_2-\vartheta)}{\sin\frac{4\pi}{\lambda}(a_2-\vartheta)} \qquad \underline{41}$$

Equating real and imaginary parts of 41 separately, and making the abbreviation $2\pi/\lambda = \alpha$ gives

$$\frac{8\pi c^2 C\ln\frac{S}{R} + 4\pi\vartheta}{\lambda} = \cot\alpha(a_1-\vartheta) + \cot\alpha(a_2-\vartheta) \qquad \underline{42}$$

$$\frac{-4c^2 C\gamma\ln\frac{S}{R} - 2\vartheta\gamma + \frac{4c^2 T}{W}\ln\frac{S}{R}}{\lambda} = \frac{\frac{\alpha\gamma}{\pi}(a_1-\vartheta)\cot\alpha(a_1-\vartheta)}{\sin 2\alpha(a_1-\vartheta)} + \frac{\frac{\alpha\gamma}{\pi}(a_2-\vartheta)\cot\alpha(a_2-\vartheta)}{\sin 2\alpha(a_2-\vartheta)} \qquad \underline{43}$$

With the use of equation 3, and converting from e.m.u. to e.s.u., equation 42 becomes

$$\delta_0 + \varepsilon'\delta + 2\pi\vartheta = \frac{\lambda}{2}\left[\cot\alpha(a_1-\vartheta) + \cot\alpha(a_2-\vartheta)\right] \qquad \underline{5}$$

which is just Slatis' result.

Taking the ratio of equation 43 to 42 we obtain

$$-\frac{\gamma}{2\pi} + \frac{4c^2 T \ln\frac{S}{R}}{W\left(8\pi c^2 C \ln\frac{S}{R} + 4\pi\vartheta\right)} =$$

$$\frac{\alpha\gamma}{\pi}\,\frac{(a_1-\vartheta)\sin 2\alpha(a_2-\vartheta)\cot\alpha(a_1-\vartheta) + (a_2-\vartheta)\sin 2\alpha(a_1-\vartheta)\cot\alpha(a_2-\vartheta)}{\sin 2\alpha(a_1-\vartheta)\,\sin 2\alpha(a_2-\vartheta)\left[\cot\alpha(a_1-\vartheta) + \cot\alpha(a_2-\vartheta)\right]}$$

Simplifying this yields

$$\frac{T(\delta_0+\varepsilon'\delta)}{CW\gamma(\delta_0+\varepsilon'\delta+2\pi\vartheta)} - 1 = \alpha\,\frac{(a_1-\vartheta)\frac{\sin\alpha(a_2-\vartheta)}{\sin\alpha(a_1-\vartheta)} + (a_2-\vartheta)\frac{\sin\alpha(a_1-\vartheta)}{\sin\alpha(a_2-\vartheta)}}{\sin\alpha(a_1+a_2-2\vartheta)}$$

$$\frac{T}{WC} = \gamma\,\frac{\delta_0+\varepsilon\delta+2\pi\vartheta}{\delta_0+\varepsilon\delta}\left[1+\alpha\,\frac{(a_1-\vartheta)\frac{\sin\alpha(a_2-\vartheta)}{\sin\alpha(a_1-\vartheta)} + (a_2-\vartheta)\frac{\sin\alpha(a_1-\vartheta)}{\sin\alpha(a_2-\vartheta)}}{\sin\alpha(a_1+a_2-2\vartheta)}\right] \qquad \underline{44}$$

But

$$W = \frac{1}{4\pi\sigma k} = \frac{k_0+\varepsilon' k}{4\pi\sigma k c^2 C} = \frac{(k_0+\varepsilon' k)\lambda(1-\varkappa^2)}{4\pi k c C\varepsilon'\varkappa} = \frac{(\delta_0+\varepsilon'\delta)T(1-\varkappa^2)}{4\pi\varepsilon'\delta\varkappa C}$$

where $\sigma$ is the conductivity of the dielectric and $\varkappa$ is the absorption coefficient. From this

$$\frac{T}{WC} = \frac{4\pi\varepsilon'\delta\varkappa}{(\delta_0+\varepsilon'\delta)(1-\varkappa^2)} \qquad \underline{45}$$

so that, combining 44 and 45, and writing $d\gamma$ for $\gamma$ , we obtain

$$\frac{\varkappa}{1-\varkappa^2} = \frac{d\gamma}{4\pi}\,\frac{\delta_0+\varepsilon'\delta+2\pi\vartheta}{\varepsilon'\delta}\left[1+\alpha\,\frac{(a_1-\vartheta)\frac{\sin\alpha(a_2-\vartheta)}{\sin\alpha(a_1-\vartheta)} + (a_2-\vartheta)\frac{\sin\alpha(a_1-\vartheta)}{\sin\alpha(a_2-\vartheta)}}{\sin\alpha(a_1+a_2-2\vartheta)}\right] \qquad \underline{46}$$

Thus equation 46 is the one which the adoption of Slatis' assumptions requires us to use instead of equation 2 for the computation of $\varkappa$. The result, as we might have expected from the relation between equations 1 and 5, is that obtained by replacing $a_1$ by $a_1 - \vartheta$, $a_2$ by $a_2 - \vartheta$, and $\delta_0$ by $\delta_0 + 2\pi\vartheta$ in equation 2.

Alternative methods of computation, which are not simply modifications of equations 1 and 2 are offered by Abadie(16), and by Slatis in his second paper(17).

Abadie's original derivation was carried out for apparatus designed to utilize Drude's original second method, in which the condenser terminates the Lecher system and there is thus only one shorting bridge, as compared with Coolidge's modification utilizing two bridges with the condenser between. However we can attempt to modify Abadie's work to suit the Coolidge-type apparatus. In order to do so, we must replace Abadie's assumption concerning the resistance of the circuit with one appropriate to the changed circuit. Abadie assumed that the resistance of the circuit exclusive of the condenser was effectively constant, and could be represented with sufficient accuracy by a lumped resistance placed in series with the bridge. For the circuit with two bridges we may assume either that the total resistance of the circuit may still be represented as a single lumped resistance placed in series with one of the bridges, or that it must be divided and represented as lumped resistances in series with each bridge. The first of these assumptions leads to the equations

$$\delta_0 + \varepsilon'\delta = \frac{\lambda}{2}\left(\cot \alpha a_1 + C\right) \qquad 47$$

$$\frac{\varkappa}{1-\varkappa^2} = \frac{\lambda D}{2\varepsilon'\delta} \qquad 48$$

Here C and D are obtained by simultaneous solution of the equations

$$\begin{cases} \dfrac{C z^2 + (\rho^2 + 2\rho D + 1) z - C\rho^2}{C\rho^2 z^2 + (\rho^2 + 2\rho D + 1) z - C} = z_0^2 (m^2 - 1) + m^2 \\[2em] C z^2 - (C^2 + D^2 - 1) z - C = 0 \end{cases}$$

where $z = \cot \alpha a_2$, $z_0 = \cot \alpha y_0$, $y_0$ is the half-length of a horizontal chord of the resonance curve and $m$ is the ratio of the maximum current at resonance to the current in the Lecher system at points on this chord. $\rho$ is determined by

$$\rho = \frac{1}{\sqrt{z_0'^2 (m'^2 - 1) + m'^2}}$$

where the primed symbols have the same meanings as the corresponding unprimed ones except that they refer to measurements made with the condenser empty.

An attempt to apply these equations yielded results which were evidently incorrect. Table I compares the results of a few calculations made by this method with those obtained from equations 5 and 46. The $\varepsilon'$ values obtained with equation 47 are consistently

| Solutions of Acetic Acid in Benzene | | | | |
|---|---|---|---|---|
| Concentration in mol fractions of $CH_3COOH$ | From equations 5 and 46 | | From equations 47 and 48 | |
| | $\varepsilon'$ | $\frac{\kappa}{1-\kappa^2}$ | $\varepsilon'$ | $\frac{\kappa}{1-\kappa^2}$ |
| 0.323 | 3.12 | 0.029 | 2.98 | 0.316 |
| 0.618 | 4.15 | 0.068 | 4.02 | 0.254 |
| 1.000 | 5.64 | 0.104 | 5.55 | 0.203 |

Table I

lower than those obtained using equation 5, but there is nothing here to say which is the more correct set. However, the values of $\frac{\kappa}{1-\kappa^2}$ obtained from equation 48 are much too large at the low concentration end, and decrease with increasing concentration, which indicates that our initial assumption of a single lumped resistance is untenable. It is to be expected that an error of this type, dealing with the location of the energy dissipation of the circuit, would have a much greater effect on the absorption coefficient than on the dielectric constant, as was actually observed to be the case.

The alternative formula obtained by assuming the resistance of the circuit divided between the two bridges proved to be entirely too complex for purposes of calculation, in addition to which it requires a calibration measurement on a substance of known absorption coefficient, which makes it dependent on some other method. Therefore Abadie's treatment, although quite successful for the original Second Drude Method(18), is not convenient for application in the modification used in this work.

Slatis' second paper(17) is an attempt to eliminate the necessity for taking a full resonance curve for each measurement, and reduces the necessary data to a single reading of the position and amplitude of the maximum of the resonance curve. It assumes constancy of the applied emf, which was not sufficiently true in our case to apply this method, as the small changes in amplitude of the resonance curves due to solutions of low absorption were less than those due to the slow changes in output of the oscillator. Also the use of chord mid-points from a full resonance curve provides a much better determination of the position of the maximum in the cases of high absorption where the maxima are flat and hence difficult to fix exactly by a single reading. Therefore the full resonance curves were taken and Slatis' earlier expressions (Eqns. 5,46) were used, as previously specified.

## Calibration of the Apparatus

In order to use the above equations (5 and 46), the correction factors $\vartheta$ and $\beta$ and the capacities $\delta_0$ and $\delta$ must be experimentally determined. The bridge shortening $\beta$ was determined before the condenser was inserted in the system. This was done by measuring the distance between successive positions of the movable bridge at resonance, which gave the half-wavelength, and by measuring the distance between the two bridges at the shortest resonance separation. The difference between these two values gave the total bridge shortening. Repeated measurements of this quantity gave the average value $\beta$ = 0.110 cm. It was assumed that each of the bridges contributed equally to this, so that $\beta_1 = \beta_2 =$ 0.055 cm. The assumption $\beta_1 = \beta_2$ is probably not exactly correct, but it is nearly enough true as to introduce little error, and there is no simple method of separating the contributions of the two bridges. The principal cause of the bridge shortening is the self inductance of the bridge, and bridge A is large enough so that its self inductance should approach that of bridge B, the rate of change of inductance with respect to the radius becoming small as the radius becomes large.

$\beta$ having been measured, the condenser was inserted in the Lecher system, and the distance from the condenser to the zero position of the vernier scale of the movable bridge was determined.

This was measured by means of a set of copper gauge blocks and the vernier scale and precision extensometer of the movable bridge. These same copper gauge blocks were used throughout the experimental work to set the position of bridge A with respect to the condenser. The results of the above measurements gave the value $L_0$ , which is the reading that the vernier scale would have with the extensometer reading zero if the movable bridge were coincident with the center line of the condenser. This value was $L_0 = 67.567 - 0.0012(t - 20)$ where t is the temperature in $^{\circ}$C. The values of $a_2$ for use in equations 5 and 46 were thus obtained from the relation

$$a_2 = L_0 - L + E + \beta_2 \qquad \underline{49}$$

where L is the reading of the vernier scale and E is the extensometer reading when the system is in resonance. Values of E were obtained by taking resonance curves ( galvanometer deflection versus extensometer reading), plotting them, and using the average position of the midpoints of chords spaced 10% of maximum deflection apart, from 30% of maximum deflection upward.

To obtain $\vartheta$ , $a_2$ was measured as a function of $a_1$ for a range of values of the latter from about 1 cm to 4.5 cm, the largest value permitted by the apparatus. The procedure, necessitated by the limited range of E and the relative inaccuracy of L, was as follows: $a_2$ was obtained for one setting of $a_1$, then $a_1$ was shifted by about 0.5 cm and $a_2$ measured again without shifting L. Then L was changed and the same resonance curve taken again, and the whole process was repeated as often as necessary to cover the desired range. The repetition of resonance curves before and after changing L, without changing $a_1$ made possible the adjustment of the values of L to make the series of readings consistent. The necessary adjustment was never greater than 0.007 cm, which is about the limiting accuracy to which L could be read. The adjustments were made in such a fashion that their mean was zero, and since there were about ten readings, the resulting values of $a_2$ should be correct to about 0.001 cm. From the resulting pairs of values of $a_1$ and $a_2$ the right hand side of equation 5 was computed for several trial values of $\vartheta$, and by linear interpolation, the value of $\vartheta$ which gave the least mean square deviation was computed. The results of several repetitions of this process, using both air and benzol as dielectrics in the condenser, gave the value $\vartheta = 0.011$ cm. The effect of this correction factor on the constancy of $\delta_0 + \epsilon'\delta$ can be seen from the example given in Table II.

| $\lambda = 25.550$ cm. Dielectric: Benzene | | | |
|---|---|---|---|
| | | $\delta_0 + \epsilon'\delta$ in cm | |
| $a_1$ in cm. | $a_2$ in cm. | $\vartheta = 0$ | $\vartheta = 0.011$ |
| 1.180 | 11.571 | 0.902 | 1.696 |
| 1.580 | 11.135 | 1.262 | 1.700 |
| 2.080 | 10.578 | 1.451 | 1.692 |
| 2.580 | 10.009 | 1.564 | 1.715 |
| 3.080 | 9.444 | 1.569 | 1.673 |
| 3.580 | 8.870 | 1.613 | 1.688 |
| 4.080 | 8.317 | 1.578 | 1.647 |

Table II

$\delta_0'$ and $\delta$ could be determined from the data used to get $\vartheta$, but it was desirable to include a greater range of values of $\varepsilon'$ in the determination, and for this purpose the benzol-acetone mixtures standardized by Drude(19) were used. The results of twelve series of calibrations gave the values $\delta_0 = 0.562 \pm .075$, $\delta = 0.462 \pm .016$ cm. The large random error in $\delta_0$ is due principally to errors in L, which affect $\delta_0$ more than they do $\delta$ in this type of run, since L was kept constant for each run over the range of $\varepsilon'$.

This completed the calibration of the apparatus.

### Procedure

For each resonance curve, galvanometer deflections, which were proportional to the squate of the current in the Lecher system, were observed as a function of the position of the movable bridge as measured by the extensometer. The galvanometer was read with the aid of a telescope and scale, the deflections being readable to the nearest 0.1 mm and maximum deflections were of the order of ten centimeters. Points were ordinarily taken for bridge positions spaced 0.25 mm apart, which gave from 15 to 30 points per resonance curve, depending on the amount of absorption in the system. On some of the curves taken for calibration purposes points were taken every 0.10 mm.

The galvanometer deflections were reduced to percent of maximum deflection for each curve and the resulting resonance curve was plotted. The maximum was determined by taking the midpoints of chords, as described above. If the curve was properly symmetrical these midpoints lay within a range of about 0.02 mm and the position of the maximum was taken as the center of their range, to the nearest 0.01 mm.

The value of the logarithmic damping decrement $\gamma$ was obtained for each curve by the use of Bjerknes' formula$^{(20)}$

$$\gamma = \frac{2\pi}{\lambda} \Delta l \sqrt{\frac{R^2}{1-R^2}} \qquad \underline{50}$$

where $\Delta l$ is the length of a horizontal chord of the resonance curve and R is the ratio of the current in the Lecher system at points on this chord to the maximum current at resonance. Three chords, at positions corresponding to values of $R^2$ of 0.40, 0.50, and 0.60 were measured, and $\gamma$ was computed for each of the three levels and the results averaged. The value of $d\gamma$ used in equation 46 was the difference in the $\gamma$ values of the solution under investigation and the pure solvent.*

The general procedure for each run was as follows: the generator was first permitted to run for half an hour or more to achieve equilibrium. The half-wavelength of the oscillations was then measured. Then, without further changing the value of L, resonance curves were taken at the first maximum with substances in the condenser in the following order: Air, Solvent, 1st Sample, 2nd Sample, Solvent, 3rd Sample, 4th Sample, Solvent, Air. This sequence was repeated as often as necessary. Data for two or three resonance curves were taken in immediate succession for each substance in order to avoid observational errors. Generally in the

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* Sample resonance curves, together with illustrations of these calculations as well as numerical examples for all important subsequent calculations are given in the Appendix.

course of one run, several samples were tested from each solution. at the end of the run, the half-wavelength of the oscillations was remeasured. The repeated measurements on the pure solvent and on the empty condenser provided a fairly continuous check of the constancy of the generator and the reproducibility of the measurements. Any variations which were large enough to be observable in the course of taking the data terminated the run. Smaller variations were not great enough to invalidate the data.

The repeated measurements on the pure solvent and on the empty condenser also served a more important purpose, as they gave sufficient data for the calibration of the condenser. It was found impractical to substitute the well calibrated values of $\delta_0$ and $\delta$ into equation 5 to obtain $\varepsilon'$, since in order for the result to be meaningful to the accuracy desired, each resonance curve would have had to be retaken many times with different resettings of L in order to remove the inaccuracy resulting from our inability to read this value to as many places as the remainder of the data. The method adopted was therefore to make the runs with L kept always constant, and use values of $\delta_0$ and $\delta$ computed from data taken during that same run on substances of known $\varepsilon'$ to compute the unknown values of $\varepsilon'$ for that run. The justification of this procedure follows in the next section.

## Elimination of Systematic Errors

Let us first consider the effect of any systematic errors in $a_1$ and $a_2$ on the value of $\varepsilon'$. If we make the abbreviation $\delta_0 + 2\pi\vartheta = \delta_0'$, equation 5 can be rewritten in the form

$$\varepsilon' = \frac{\lambda}{2\delta}\left[\cot\alpha(a_1-\vartheta) + \cot\alpha(a_2-\vartheta)\right] - \frac{\delta_0'}{\delta}$$

and therefore

$$d\varepsilon' = -\frac{\alpha\lambda}{2\delta}\left[\frac{da_1}{\sin^2\alpha(a_1-\vartheta)} + \frac{da_2}{\sin^2\alpha(a_2-\vartheta)}\right] \qquad \underline{51}$$

If, however, we use the method outlined above of computing $\delta_0'$ and $\delta$ from data from the same run, we have

$$\delta_0' + \varepsilon_1'\delta = \frac{\lambda}{2}\left[\cot\alpha(a_1-\vartheta) + \cot\alpha(a_{2_1}-\vartheta)\right]$$

$$\delta_0' + \varepsilon_2'\delta = \frac{\lambda}{2}\left[\cot\alpha(a_1-\vartheta) + \cot\alpha(a_{2_2}-\vartheta)\right]$$

$$\delta_0' + \varepsilon_3'\delta = \frac{\lambda}{2}\left[\cot\alpha(a_1-\vartheta) + \cot\alpha(a_{2_3}-\vartheta)\right]$$

where $\varepsilon_1'$ and $\varepsilon_2'$ are known dielectric constants and $\varepsilon_3'$ is the value to be determined. Then eliminating $\delta_0'$ and $\delta$ and solving for $\varepsilon_3'$ gives

$$\varepsilon_3' = \frac{\varepsilon_2'\left[\cot\alpha(a_{2_3}-\vartheta) - \cot\alpha(a_{2_1}-\vartheta)\right] - \varepsilon_1'\left[\cot\alpha(a_{2_3}-\vartheta) - \cot\alpha(a_{2_2}-\vartheta)\right]}{\cot\alpha(a_{2_2}-\vartheta) - \cot\alpha(a_{2_1}-\vartheta)}$$

and since we are considering only systematic errors, so that $da_{2_1} = da_{2_2} = da_{2_3} = da_2$, we get

$$d\varepsilon_3' = (\varepsilon_2' - \varepsilon_1')\frac{\left[\cot\alpha(a_{2_3}-\vartheta) - \cot\alpha(a_{2_1}-\vartheta)\right]\left[\cot\alpha(a_{2_3}-\vartheta) - \cot\alpha(a_{2_2}-\vartheta)\right]\alpha\, da_2}{\cot\alpha(a_{2_1}-\vartheta) - \cot\alpha(a_{2_2}-\vartheta)} \qquad \underline{52}$$

It is first to be noticed that this form is independent of $a_1$, and since $a_1$ was never disturbed after being set at the beginning of each run, any error in setting it must be systematic for the run, and will therefore to a first approximation have no effect on the value of $\varepsilon'$.

If we substitute sets of typical values into equations 51 and 52 we get the following comparative results:

$$\text{For } \varepsilon' \sim 2.5 \begin{cases} \text{From } \underline{51} : & d\varepsilon' = -48.7\, da_1 - 42.0\, da_2 \\ \text{From } \underline{52} : & d\varepsilon' = \qquad\qquad\qquad - 0.002\, da_2 \end{cases}$$

$$\text{For } \varepsilon' \sim 5.7 \begin{cases} \text{From } \underline{51} : & d\varepsilon' = -48.7\, da_1 - 42.5\, da_2 \\ \text{From } \underline{52} : & d\varepsilon' = \qquad\qquad\qquad - 0.104\, da_2 \end{cases}$$

It is seen that the second method discussed, which is the one actually adopted for computing $\varepsilon'$, results in a considerable reduction in the error due to any systematic error in $a_2$. This means that any errors in the determination of $\beta_2$ and $\vartheta$, and those introduced by the inability to read L precisely are largely nullified by this method of computation. However it does somewhat increase the possibility of random error, as the constants involved are based on fewer data than those of the first method.

Next considering the same type of error with regard to equation 46 for $\frac{\varkappa}{1-\varkappa^2}$, there is the question of whether to substitute the independently measured values of $\delta_0'$ and $\delta$, or those obtained to compute $\varepsilon'$ for the same run. Neglecting the change of $\varepsilon'$ with $a_2$, for constant $\delta_0'$ and $\delta$ we get from equation 46

$$d\left(\frac{\varkappa}{1-\varkappa^2}\right) = \frac{d\gamma}{4\pi}\,\frac{\delta_0'+\varepsilon'\delta}{\varepsilon'\delta}\left\{\left[\frac{\sin\alpha(a_2-\vartheta)}{\sin\alpha(a_1-\vartheta)\sin\alpha(a_1+a_2-2\vartheta)} - \frac{\alpha(a_1-\vartheta)}{\sin^2\alpha(a_1-\vartheta)} + \frac{\alpha(a_1+a_2-2\vartheta)}{\sin^2\alpha(a_1+a_2-2\vartheta)}\right]\alpha\, da_1 + \right.$$

$$\left.\left[\frac{\sin\alpha(a_1-\vartheta)}{\sin\alpha(a_2-\vartheta)\sin\alpha(a_1+a_2-2\vartheta)} - \frac{\alpha(a_2-\vartheta)}{\sin^2\alpha(a_2-\vartheta)} + \frac{\alpha(a_1+a_2-2\vartheta)}{\sin^2\alpha(a_1+a_2-2\vartheta)}\right]\alpha\, da_2\right\} \qquad \underline{53}$$

whereas if $\delta_0'$ and $\delta$ are considered as functions of $a_1$ and $a_2$ we get, neglecting $\left[\cot\alpha(a_1-\vartheta)+\cot\alpha(a_{2_3}-\vartheta)\right]\left[\cot\alpha(a_1-\vartheta)+\cot\alpha(a_{2_2}-\vartheta)\right]$ with respect to $\csc^2\alpha(a_1-\vartheta)$

$$d\left(\frac{\varkappa}{1-\varkappa^2}\right) = \frac{d\gamma}{4\pi}\,\frac{\delta_0'+\varepsilon'\delta}{\varepsilon'\delta}\left\{\left[\frac{\sin\alpha(a_2-\vartheta)}{\sin\alpha(a_1-\vartheta)\sin\alpha(a_1+a_2-2\vartheta)} - \frac{\alpha(a_1-\vartheta)}{\sin^2\alpha(a_1-\vartheta)} + \frac{\alpha(a_1+a_2-2\vartheta)}{\sin^2\alpha(a_1+a_2-2\vartheta)}\right]\alpha\, da_1 + \right.$$

$$\left.\left[\frac{\sin\alpha(a_1-\vartheta)}{\sin\alpha(a_2-\vartheta)\sin\alpha(a_1+a_2-2\vartheta)} - \frac{\alpha(a_2-\vartheta)}{\sin^2\alpha(a_2-\vartheta)} + \frac{\alpha(a_1+a_2-2\vartheta)}{\sin^2\alpha(a_1+a_2-2\vartheta)}\right]\alpha\, da_2\right\} +$$

$$\left[-\frac{\alpha\varkappa(\delta_0'+\varepsilon'\delta)\,da_1}{\varepsilon'\delta(1-\varkappa^2)\sin^2\alpha(a_1-\vartheta)} - \frac{\alpha\varkappa(\delta_0'+\varepsilon'\delta)\,da_2}{\varepsilon'\delta(1-\varkappa^2)\sin^2\alpha(a_1-\vartheta)}\right] \qquad \underline{54}$$

Substituting numerical values for a typical case

From $\underline{53}$ : $\quad d\left(\frac{\varkappa}{1-\varkappa^2}\right) = 1.33\, da_1 + 1.32\, da_2$

From $\underline{54}$ : $\quad d\left(\frac{\varkappa}{1-\varkappa^2}\right) = 0.18\, da_1 + 0.17\, da_2$

The improvement by the use of the second method is not as marked in this case, but it nevertheless represents a reduction in the systematic error. Therefore values of $\delta_0$ and $\delta$ obtained during the course of each run will be used in both equation $\underline{5}$ and equation $\underline{46}$.

The general accuracy of the data will not be discussed until we have considered the forms in which it is to be used. For this discussion refer to page 47.

## Method of Calculating the Radius of the Dipole and Dipole Moment

The molar polarization of substances whose molecules have a permanent dipole moment, when the substance is subjected to an alternating electric field of angular frequency $\omega$ is given by the formula due to Debye(21)

$$P = \frac{\varepsilon - 1}{\varepsilon + 2}\frac{M}{\rho} = \frac{4\pi N}{3}\left[\alpha_0 + \frac{\mu^2}{3kT}\frac{1}{1+i\omega\tau}\right] \qquad \underline{55}$$

Here P is the molar polarization, which in this case is a complex quantity, and $\varepsilon$ is the complex dielectric constant, M is the molecular weight and $\rho$ is the density of the fluid. $\alpha_0$ is the distortion polarizability of the molecules, $\mu$ is their dipole moment, and $\tau$ is their relaxation time, i.e. the time required for a non-random distribution of the molecular orientations to drop to 1/e of its initial non-random character. N is Avogadro's number, k is the Boltzmann constant, and T is the absolute temperature.

The complex dielectric constant $\varepsilon$ can be related to our measured quantities $\varepsilon'$ and $\varkappa$ , respectively the real dielectric constant and the absorption coefficient, in the following way. We can write

$$\varepsilon = \varepsilon' - i\varepsilon'' \qquad \underline{56}$$

where $\varepsilon''$ is the imaginary part of the dielectric constant. The complex index of refraction is given by

$$n = r(1 - i\varkappa) \qquad \underline{57}$$

where r is the real refraction index and $\varkappa$ the absorption coefficient. But the complex dielectric constant is equal to the square of the complex index of refraction, $\varepsilon = n^2$ , so that substituting from 56 and 57,

$$\varepsilon' - i\varepsilon'' = r^2(1 - i\varkappa)^2 = r^2(1 - \varkappa^2) - 2ir^2\varkappa$$

Therefore

$$\varepsilon' = r^2(1 - \varkappa^2)$$

$$r^2 = \frac{\varepsilon'}{1 - \varkappa^2}$$

and

$$\varepsilon'' = 2r^2\varkappa = \frac{2\varepsilon'\varkappa}{1 - \varkappa^2}$$

so that if we substitute this value for $\varepsilon''$ into equation 56 we obtain

$$\varepsilon = \varepsilon' - i\,\frac{2\varepsilon'\varkappa}{1 - \varkappa^2} = \varepsilon'\left(1 - i\,\frac{2\varkappa}{1 - \varkappa^2}\right) \qquad 58$$

If we assume a spherical molecular model, and further assume, as was done by Debye, that Stokes' law holds for molecular dimensions, then the relaxation time $\tau$ is related to the molecular radius a by the formula(21)

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad 59$$

where $\eta$ is the viscosity of the surrounding liquid.

This equation has been modified by Perrin(22) to take into account ellipsoidal molecular models. His result can be written in the form

$$\tau = \frac{4\pi\eta f a_1 a_2 a_3}{kT} \qquad 60$$

for the special case that the permanent electric moment of the molecule lies approximately along the direction of one of the axes of the ellipsoid. Here $a_1, a_2, a_3$ are the semi-axes of the ellipsoid and $f$ is a factor which depends on the shape of the ellipsoid, and which is approximately equal to one for many cases. Tables of this factor $f$ have been computed by Budo, Fischer, and Miyamoto$^{(23)}$.

Equation 55 was derived with the aid of the Clausius-Mosotti hypothesis, according to which the force acting upon a molecule in a polarizable medium equals $E + \frac{4\pi}{3}P$, i.e., it is larger than the force E of the applied field. In our case this assumption means in effect that there must be no interaction between the permanent dipoles of the fluid. This condition was fulfilled by working with dilute solutions of polar liquids in non-polar solvents. For a mixture of two liquids, the first part of equation 55 becomes

$$P_{12} = P_1 f_1 + P_2 f_2 = \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \frac{M_1 f_1 + M_2 f_2}{\rho_{12}} \qquad \underline{60}$$

where

$$f_1 = \frac{n_1}{n_1 + n_2} \quad ; \quad f_2 = \frac{n_2}{n_1 + n_2} \qquad \underline{61}$$

so that $f_1 + f_2 = 1$. Here n represents number of mols, the subscript 1 refers to the non-polar solvent, the subscript 2 to the polar solute, and the double subscript to the mixture, and hence $f_1$ and $f_2$ are mol fractions of the solvent and solute respectively. Then since $P_1$ is a constant, and at high dilution where there is no dipolar interaction $P_2$ has a constant value,which we will represent by $P_{2\infty}$, the expression $P_{12} = P_1 + (P_2 - P_1) f_2$ is a linear function of $f_2$ for small values of $f_2$. Hence if we plot $P_{12}$ as a function of $f_2$, we can obtain $P_1$ from the intercept at $f_2 = 0$ and the slope in the neighborhood of this intercept will give us $P_{2\infty} - P_1$ and hence $P_{2\infty}$. Since $P_{12}$ is complex, this process will have to be carried out separately for the real and imaginary parts. In order to obtain expressions for these in terms of our measured values of $\varepsilon'_{12}$ and $\frac{\varkappa_{12}}{1-\varkappa_{12}^2}$ we substitute $P = P_R - i P_I$ and equation 58 into equation 60. Upon separating real and imaginary parts, and making the abbreviation

$$\frac{2\varkappa}{1-\varkappa^2} = c \qquad \underline{62}$$

we obtain the results:

$$\left.\begin{aligned} P_{R_{12}} &= \frac{\varepsilon_{12}'^2 + \varepsilon_{12}' - 2 + c_{12}^2 \varepsilon_{12}'^2}{\varepsilon_{12}'^2 + 4\varepsilon_{12}' + 4 + c_{12}^2 \varepsilon_{12}'^2} \; \frac{M_1 f_1 + M_2 f_2}{\rho_{12}} \\ P_{I_{12}} &= \frac{3 c_{12} \varepsilon_{12}'}{\varepsilon_{12}'^2 + 4\varepsilon_{12}' + 4 + c_{12}^2 \varepsilon_{12}'^2} \; \frac{M_1 f_1 + M_2 f_2}{\rho_{12}} \end{aligned}\right\} \qquad \underline{63}$$

By plotting the values of $P_{R_{12}}$ and $P_{I_{12}}$ thus obtained as functions of $f_2$, we can obtain $P_{R_{2\infty}}$ and $P_{I_{2\infty}}$ by the process described above.

A number of workers in this field have proposed modifications of this process of extrapolation to infinite dilution, or have raised objections to it based on the invalidity of the Clausius-Mosotti hypothesis. Hedestrand(24), by differentiating equation 60 with respect to $f_2$ and then letting $f_2 \to 0$, obtains the relation

$$P_{2\infty} = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \; \frac{M_2 - \beta_1 M_1}{\rho_1} + \frac{3 M_1 \alpha_1 \varepsilon_1}{\rho_1 (\varepsilon_1 + 2)^2} \qquad \underline{64}$$

where $\alpha_1$ and $\beta_1$ are the limiting values of $\alpha = \frac{\varepsilon_{12} - \varepsilon_1}{f_2}$ and $\beta = \frac{\rho_{12} - \rho_1}{f_2}$ as $f_2 \to 0$. A similar expression was derived by Maybaum(25). Equation 64 represents no theoretical change in relation to equation 60, but simply a change in calculating practice, involving the extrapolation of the $\varepsilon_{12} - f_2$ and $\rho_{12} - f_2$ curves rather than the $P_{12} - f_2$ curves. This avoids the difficulty of computing $P_{12}$ for each set of data, but, from equation 60, the linearity of the $P_{12} - f_2$ curve implies the non-linearity of the $\varepsilon_{12} - f_2$ curve, and the extrapolation of $\varepsilon_{12}$ is therefore less reliable. For this reason, this method of computation was not used.

Several attempts have been made to improve equation 55 by taking the interaction of the dipoles into account. A semi-empirical correction proposed by vanArkel and Snoek(26), which has been well supported by experiment, consists in substituting $(3kT + Cn\mu^2)$ in place of $3kT$ in the denominator of the right hand side of equation 55. Here n represents the number of dipoles per unit volume of the liquid, and C is a constant, the physical meaning of which has been elucidated by Bottcher(27). Bottcher's work was based on the theory developed earlier by Onsager(28) for treating concentrated solutions, where the Clausius-Mosotti hypothesis no longer holds. In our case n is small, since dilute solutions of polar liquids in non-polar ones were used. Therefore the correcting term $Cn\mu^2$ is negligible compared to $3kT$, and the equation 55 can be used in its original form.

If $P_2$ is calculated using the relation $P_2 = P_1 + \frac{P_{12} - P_1}{f_2}$ and plotted as a function of $f_2$, then it should be a constant for small values of $f_2$ if the Clausius-Mosotti hypothesis is correct. It has been frequently observed that the values of $P_2$ thus obtained increase markedly with decreasing $f_2$ at very small values of $f_2$. It is very unlikely that association should be the cause of this, since the phenomenon occurs at high dilution. In attempting to explain this, Rodebush and Eddy(29) show that in certain circumstances, Onsager's theory should not reduce to the Debye theory at high dilution, and develop a semi-empirical formula for application to dilute solutions. They compare values of dipole moment computed from their results with those obtained from Debye theory, using values of dipole moment obtained from measurements on vapors as a standard. The results differ, but no particular preference is shown for either method. A more probable explanation is the one due to Halverstadt and Kumler(30) who point out that just such an increase in $P_2$ would be obtained if the dielectric constant of the solvent used in the solutions were slightly higher than that of the pure solvent, due to the presence of absorbed water. This would occur due to the much greater time of exposure to the air of the solvent used in making up the solutions compared to that used for the pure solvent measurements. They state that the phenomenon occurs most frequently in the literature for the most hygroscopic solvent, dioxane, and least for hexane, which is the least hygroscopic of the common solvents. Also for the measurements of Linton(31) and of Maryott(32), in which special precautions to eliminate water have been taken by drying the solutions after their preparation, the effect is entirely absent, Maryott's work being particularly convincing, as his values for the alcohols agree with those of other workers for moderately small values of $f_2$ and differ only in not showing any rise in $P_2$ at very high dilution. The method which Halverstadt and Kumler use to eliminate this, the linear extrapolation of the $\epsilon_{12}-f_2$ curve while ignoring the point obtained with the pure solvent, is inconsistent with their use of Hedestrand's formula based on the Debye-Clausius-Mosotti theory, and the more correct method of extrapolating the $P_{12}-f_2$ curve linearly, still ignoring the point obtained with the pure solvent, would seem to be preferable. Since the effect is a small one, being observable only when the $P_{12} - P_1$ difference becomes very small, we do not affect the value of $P_{2\infty}$ greatly by using the extrapolated rather than the measured value for $P_1$. Therefore in this work equations 63 will be used without modification, and $P_{R_{2\infty}}$ and $P_{I_{2\infty}}$ will be obtained by extrapolating the $P_{R_{12}} - f_2$ and $P_{I_{12}} - f_2$ curves linearly, ignoring the point at $f_2 = 0$.

We now wish to determine values of $a_1 a_2 a_3$ and $\mu$ from the values of $P_{R_{2\infty}}$ and $P_{I_{2\infty}}$ which we have obtained for our polar liquid at infinite dilution. We will drop the subscripts $_{2\infty}$ for convenience, as we are not concerned in what follows with the fact that these values were derived from dilute solutions. If we make the abbreviations

$$P_A = \frac{4\pi N}{3} \alpha_0 \qquad 65$$

$$P_D = \frac{4\pi N \mu^2}{9kT} \qquad 66$$

equation 55 assumes the form

$$P = P_A + P_D \frac{1}{1 + i\omega\tau} \qquad 67$$

If we let $P_0$ be the value of the molar polarization for very low frequencies ($\omega\tau << 1$) we obtain

$$P_0 = P_A + P_D \qquad 68$$

and substituting this back into equation 67 to eliminate $P_A$ gives

$$P = P_0 - P_D + P_D \frac{1}{1 + i\omega\tau}$$

If we write as before $P = P_R - i P_I$ and separate real and imaginary parts, we have the two relations

$$P_R = P_o - P_D \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \qquad \underline{69}$$

$$P_I = P_D \frac{\omega \tau}{1 + \omega^2 \tau^2} \qquad \underline{70}$$

Solving these simultaneously for $P_D$ and $\tau$ gives

$$P_D = \frac{P_I^2 + (P_o - P_R)^2}{P_o - P_R} \qquad \underline{71}$$

$$\tau = \frac{1}{\omega} \frac{P_o - P_R}{P_I} \qquad \underline{72}$$

Alternatively, if we substitute equation 68 into 71 and 72 and eliminate $P_o$ we obtain

$$P_D = \frac{P_I^2 + (P_R - P_A)^2}{P_R - P_A} \qquad \underline{73}$$

$$\tau = \frac{1}{\omega} \frac{P_I}{P_R - P_A} \qquad \underline{74}$$

Equations 59 and 66 taken together with either 71 and 72 or 73 and 74 serve to determine both $a_1 a_2 a_3$ and $\mu$ from a single determination of the complex polarization plus a knowledge of either $P_o$ or $P_A$ and the inner friction constant $\eta$ of the solvent.

If we plot $P_R$ and $P_I$ as functions of $\omega\tau$ by using equations 69 and 70, we get the curves shown in Figure 6. As can be seen from this figure, $P_I$ is small except in the neighborhood of $\omega\tau = 1$. Since $\tau$ is the quantity we are primarily interested in measuring, and $\tau$ depends directly on $P_I$ (Eqn. 72 or 74), it is necessary to

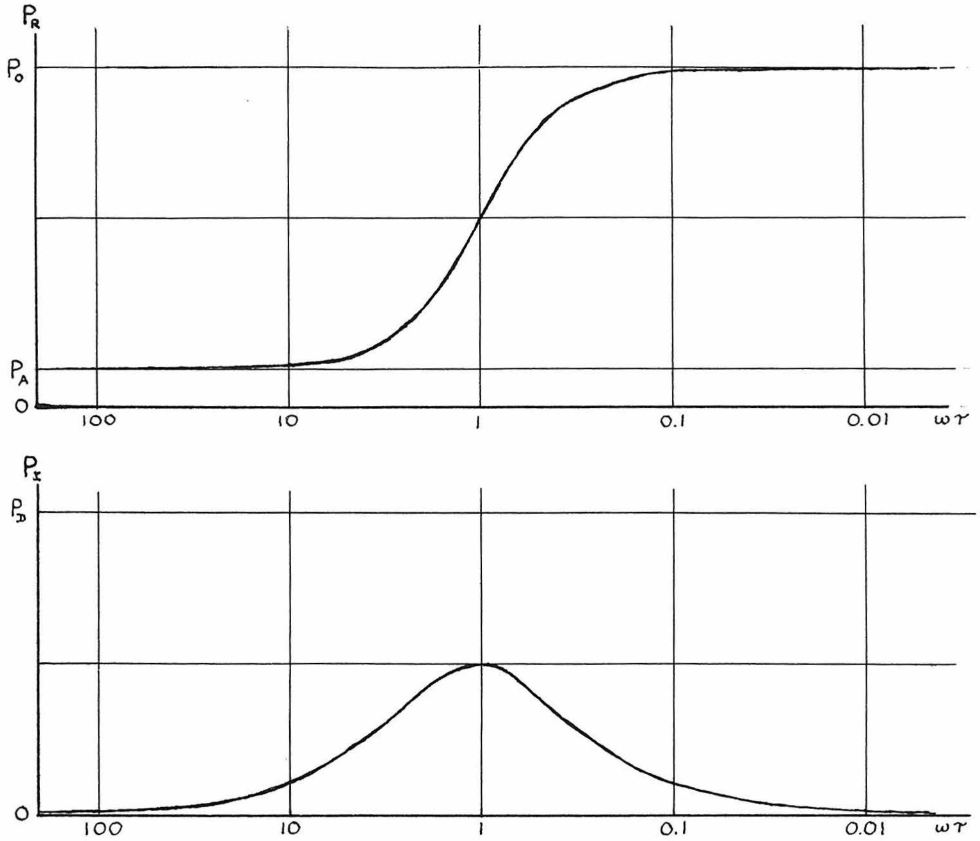


Fig. 6.

obtain $P_I$ values which are sufficiently large for accurate calculation. This means that our measurements must be made at a frequency near that determined by $\omega\tau = 1$. Since $\tau$ is of the order of $10^{-10}$ sec. for ordinary substances, this requires frequencies of the order of $10^9$/sec., and it is for this reason that the experiment had to be carried out at ultra-high frequencies.

The determination of the value of $\mu$ without making measurements of the temperature dependence of P always involves the necessity of knowing an additional constant, which for the methods most prevalent at present is the atomic polarization $P_A$, and for the method here presented may be either $P_o$ or $P_A$. Equations 71 and

72 using $P_o$ are much to be preferred to 73 and 74 using $P_A$, since $P_o$ values are more reliable, being subject to direct measurement, whereas $P_A$ values are extremely difficult to obtain by direct measurement, as this requires extremely high frequencies. In general $P_A$ is obtained by extrapolation of the values of the molar refraction measured in the infra-red region, or, even less reliably by the extrapolation of the molar refraction measured in the visible spectrum, neglecting the possibility of anomalous dispersion in the infra-red. This makes the available $P_A$ values less reliable than $P_o$ values.

Let us examine the relative accuracy of equations 71,72 and 73,74. Taking differentials and solving for the relative error, we obtain from 71 and 72

$$\left.\begin{aligned} \left.\frac{dP_D}{P_D}\right]_{P_o} &= \frac{2}{1+\omega^2\tau^2}\,\frac{dP_I}{P_I} + \frac{1-\omega^2\tau^2}{1+\omega^2\tau^2}\,\frac{P_R}{P_o-P_R}\,\frac{dP_R}{P_R} \\ \left.\frac{d\tau}{\tau}\right]_{P_o} &= -\frac{dP_I}{P_I} - \frac{P_R}{P_o-P_R}\,\frac{dP_R}{P_R} \end{aligned}\right\} \quad \underline{75}$$

and from 73 and 74

$$\left.\begin{aligned} \left.\frac{dP_D}{P_D}\right]_{P_A} &= \frac{2\omega^2\tau^2}{1+\omega^2\tau^2}\,\frac{dP_I}{P_I} + \frac{1-\omega^2\tau^2}{1+\omega^2\tau^2}\,\frac{P_R}{P_R-P_A}\,\frac{dP_R}{P_R} \\ \left.\frac{d\tau}{\tau}\right]_{P_A} &= \frac{dP_I}{P_I} - \frac{P_R}{P_R-P_A}\,\frac{dP_R}{P_R} \end{aligned}\right\} \quad \underline{76}$$

The coefficients involved are all of the order of unity or less, except for the factors $P_R/(P_o - P_R)$ in equations 75 and $P_R/(P_R - P_A)$ in equations 76. Examination of Fig 6 shows that for small $\omega\tau$, $(P_o - P_R) << P_R$, and therefore equations 71 and 72 using $P_o$ as a standard are very sensitive to errors in $P_R$ in this region. Conversely, for large $\omega\tau, (P_R - P_A) << P_R$, so that in this case equations 73 and 74 using $P_A$ as a standard are very sensitive to errors in $P_R$.

In our case $\omega\tau$ is appreciably less than 1, so that any preference for equations 71 and 72 due to the greater reliability of $P_0$ over $P_A$ may be outweighed by their sensitivity to errors in $P_R$. We will continue to use both sets of equations in this work whenever possible, keeping in mind the above differences.

From the viewpoint of the above equations (75,76), the ideal region in which to make measurements of this kind would be in the neighborhood of $\omega\tau = 10$, since here $P_I$ would still be large enough for accurate determination, so that using $P_0$ as our standard, we would have a very small dependence of $P_D$ on both $P_I$ and $P_R$, and small dependance of $\tau$ on $P_R$. However this would require wavelengths of less than a centimeter so that the practical difficulties would be very large.

## Accuracy of the Results

The discussion of the accuracy of the results can be divided into two sections, the first section dealing with the $P_{12}$ values, which are obtained by direct calculation from the original data, and the second with the final results, which are computed from the extrapolations of the $P_{12} - f_2$ curves.

The observational data used to compute $P_{12}$ consist of values of $a_1$ as set with the copper gauge blocks, $a_2$ and $\gamma$ as taken from the resonance curves, $\lambda$, $f_1$ and $f_2$, $\rho_{12}$ and T.

The settings of $a_1$ were correct to about 0.01 cm. Since these settings were never changed during a run, and ordinarily not disturbed between runs, this represents a systematic error which, from the discussion on pages 33-36, should have no effect on $\epsilon'$, and very little effect on $c$.

The values of $a_2$ were reproducible to 0.001 cm over short time intervals, with a possible systematic error of about 0.01 cm. Here also the systematic error should have negligible effect, as discussed on the pages cited above. Over long time intervals the values of $a_2$ sometimes changed by several thousandths of a centimeter due to changes in $\lambda$, but since a fairly continuous check on $\lambda$ was kept by repeated measurements on the empty condenser, this error was correctible.

Values of $\gamma$ were only consistent to about 2%. Since at very low concentrations $d\gamma$ was only about 1% of $\gamma$ we have the possibility of errors of several hundred percent in the value of $d\gamma$ at these low concentrations. This required considerable repetition of readings to get results of any validity.

Values of $\lambda$, $f_1$ and $f_2$, and $\rho_{12}$ were all accurate to at least 0.1% and should thus have negligible effect on the results compared to other errors. The temperature does not enter into the calculation of $P_{12}$, but the values of $P_{12}$ are temperature dependent and they were plotted without making any temperature correction, so it must be considered. All measurements were carried out at room temperature, which did not vary more than 0.2 °C during any one run. Most of the work was performed at 23 °C, and this was the temperature used for the calculations of the final results. Some of the runs were taken at temperatures ranging 3 °C either side of the mean. These were about equally distributed so that they should average out, but they account for part of the spread of the $P_{12}$ values before the averaging is done.

The computed values of $\varepsilon'$ depend primarily on the changes in the $a_2$ values rather than the $a_2$ values themselves. Thus an error of 0.001 cm in $a_2$ can produce an error of 1% in the computed $\varepsilon'$ value. Further, since $a_2$ was only measured to 0.001 cm, only a discrete set of values for $\varepsilon'$ was possible, so that a perfectly measured value might be off by 0.5%. This, combined with the variations due to temperature differences, accounts for the range of about 1.5% either side of the mean actually observed for the $\varepsilon'$ values.

In computing $c$, the variations of $d\gamma$ far outweigh any other sources of error. This produces errors of a single measurement ranging from several hundred percent at low concentrations to about 25% at $f_2 \sim 0.10$. The data obtained show fairly good normal distributions about the mean values so that the results obtained by statistical treatment should give a good measure of the reliability of these averages. For examples of the distributions obtained refer to pg. 73 of the Appendix, where the examples are given for $P_I$, which is principally dependent upon $c$ (see below).

The dependence of $P_{R_{12}}$ and $P_{I_{12}}$ on $\varepsilon'$ and $c$ is indicated in equations 77 which have been obtained by differentiating equations 63 and substituting typical values.

$$\left.\begin{aligned} \frac{dP_{R_{12}}}{P_{R_{12}}} &= 1.02\,\frac{d\varepsilon'}{\varepsilon'} + 0.001\,\frac{dc}{c} \\ \frac{dP_{I_{12}}}{P_{I_{12}}} &= -0.15\,\frac{d\varepsilon'}{\varepsilon'} + 1.00\,\frac{dc}{c} \end{aligned}\right\} \qquad \underline{77}$$

We see that $P_{R_{12}}$ is almost directly dependent on $\varepsilon'$ with very slight dependence on $c$, while $P_{I_{12}}$ is directly dependent on $c$ with appreciable dependence on $\varepsilon'$ also. We therefore expect the same accuracy in $P_{R_{12}}$ that we had in $\varepsilon'$, and for $P_{I_{12}}$ about the same as for $c$, since $c$ is much less accurate than $\varepsilon'$ and errors in $\varepsilon'$ will therefore increase the range of $P_{I_{12}}$ values very little.

The $P_{R_{12}}$ and $P_{I_{12}}$ values were averaged for each concentration before plotting, and the computed probable errors of the means are indicated on the $P_{12} - f_2$ curves which show the results of our measurements ( Figs 9 - 12). The observed ranges of the results are about what we would expect from our above consideration of the sources of the errors.

We must now consider the extrapolation of these values to infinite dilution. The method used was that of finding the straight line with the best least square fit in the low concentration range. The probable errors of the resulting values of $P_{R_{2\infty}}$ are from 2 to 3 percent, and for $P_{I_{2\infty}}$ are from 3 to 7 percent. This magnitude of several percent for the probable error in $P_{R_{2\infty}}$ is the basis for our preference of the results of equations 73, 74 over those of equations 71, 72, as will be discussed later.

Finally, substituting typical values into equations 76, we have

$$\frac{dP_D}{P_D} = .07\,\frac{dP_I}{P_I} + 1.12\,\frac{dP_R}{P_R}$$

$$\frac{d\tau}{\tau} = 1.00\,\frac{dP_I}{P_I} - 1.21\,\frac{dP_R}{P_R}$$

Since $P_D \propto \mu^2$ and $\tau \propto a_1a_2a_3$, this shows that we should expect values for the probable error to be about 1 to 2% for $\mu$ and 4 to 10% for $a_1a_2a_3$. This is a very high probable error for our $a_1a_2a_3$ values, but as will be seen when we consider our results, this uncertainty is still small enough so that our conclusions are not affected by it.

## Substances Investigated

Measurements were made on solutions of formic, acetic, propionic, and n-butyric acids in dioxane. Benzene was used for calibrating purposes.

The acids used were obtained from Baker's of New Jersey, and were kept in containers sealed with wax to exclude moisture. Thiophene-free benzene and water-free dioxane were obtained from the California Institute Chemistry department. The dioxane was also kept in a sealed container, while the bezene was kept water-free by having a number of thin flakes of metallic sodium on the bottom of the container.

To prepare the solutions, the liquids were decanted into smaller containers from which the solutions were made up volumetrically, using a 0.5 ml pipette. They were made up in test tubes, which were kept well corked, and they were ordinarily prepared fresh before each run, during the time that the apparatus was warming up, so that they were used almost immediately. Other pipettes were used for filling and emptying the condenser.

The condenser was cleaned by repeated rinsing with pure benzene.

## Results

After preliminary measurements, the investigation of dilute solutions of the lowest members of the fatty acid series in dioxane was undertaken. Dioxane was chosen as the solvent because it is the only non-polar liquid in which formic acid, the first member of the series, will dissolve to any large extent. Benzene could not be used as the solvent, because formic acid is soluble in benzene to mol fractions of the order of 0.001 only, and such a concentration is too small to permit accurate measurements with the method outlined above.

The fact that dioxane is non-polar is to be expected from the symmetry of its structure (Fig 8), and this has been confirmed by several investigators(33,34,35).

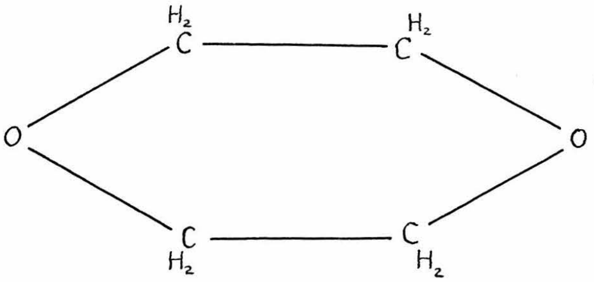


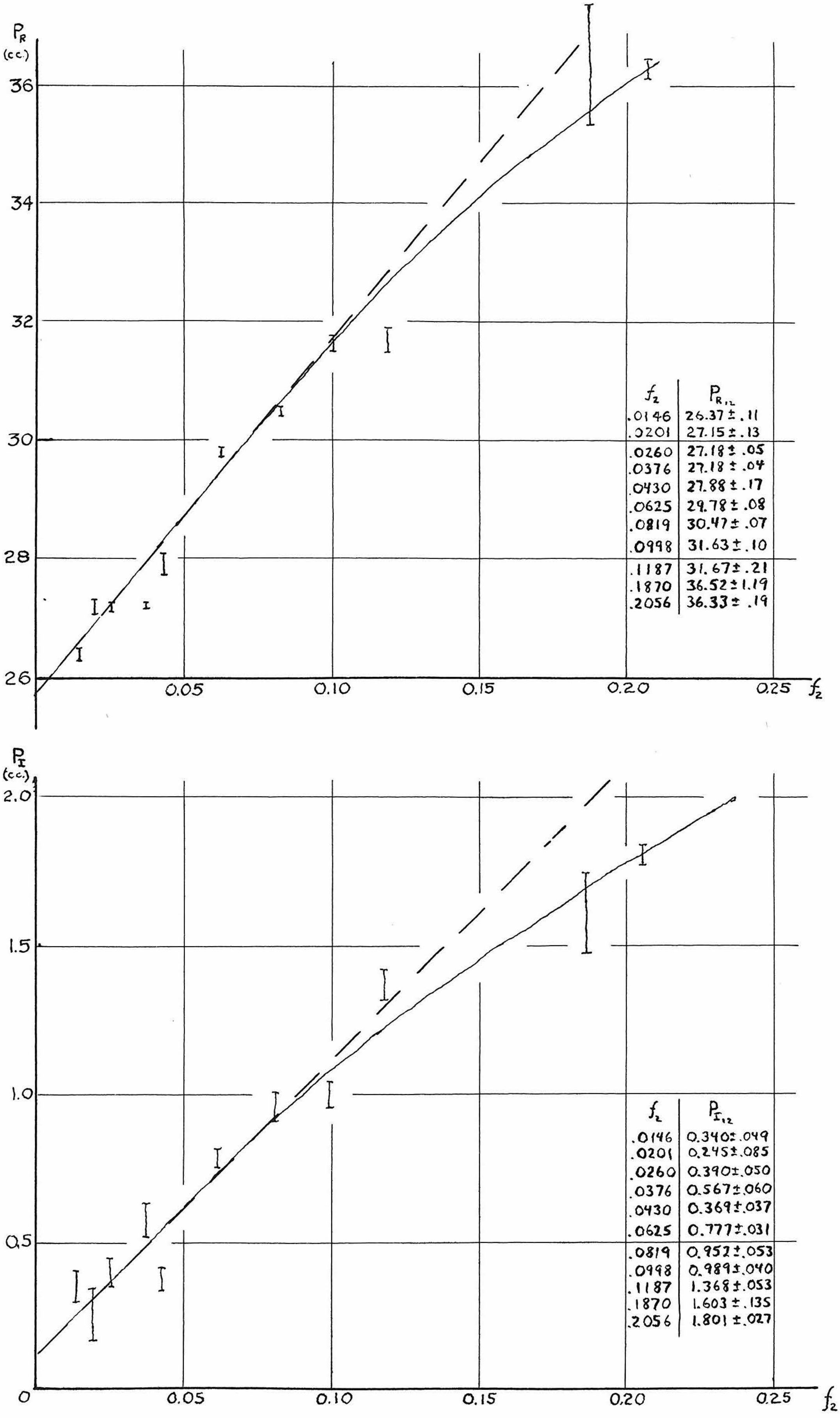
Fig. 8. The Dioxane Molecule; $C_4H_8O_2$

For the study of the fatty acids, dioxane has an additional important advantage over other non-polar solvents. Fatty acid molecules in solution in most non-polar solvents exist to a great extent in the form of polymers, even in very dilute solutions(36,37,38). Dioxane exerts a strong dissociating effect(39,40), so that in it the fatty acids exist as single molecules. Dioxane's possession of this dissociating property, which is normally a characteristic of polar solvents, may be attributed to the fact that, while the dioxane molecule as a whole has no dipole moment, the individual C - O bond moments within it are fairly large, creating local fields which are strong enough to disrupt the polymer-forming hydrogen bonds. Thus the use of dioxane gives us data on the single molecules without the complication of polymerization.

The results of the measurements on the fatty acid solutions are shown in Figures 9 - 12, which illustrate the $P_{12} - f_2$ curves for each of the substances studied. Each of the plotted points represents the mean of a number of observations, about twenty for points in the region of high dilution, and fewer with increasing concentration. The vertical range indicated for each of the plotted points represents the probable error of the value, as computed from the statistical fluctuations of the data averaged, rather than from estimates involving the sources of error.

The dotted straight lines shown on these curves are the lines which give the best fit for points in the low concentration range (not exceeding $f_2 = 0.10$) as computed by the method of least squares. The extrapolated values of $P_{2\infty}$ obtained from these lines are listed in Table III, together with values of $P_o$ as determined by Wilson and Wenzke(40) from dioxane solutions, and values of $P_A$ computed by extrapolation of the molar refraction from values measured at optical frequencies.

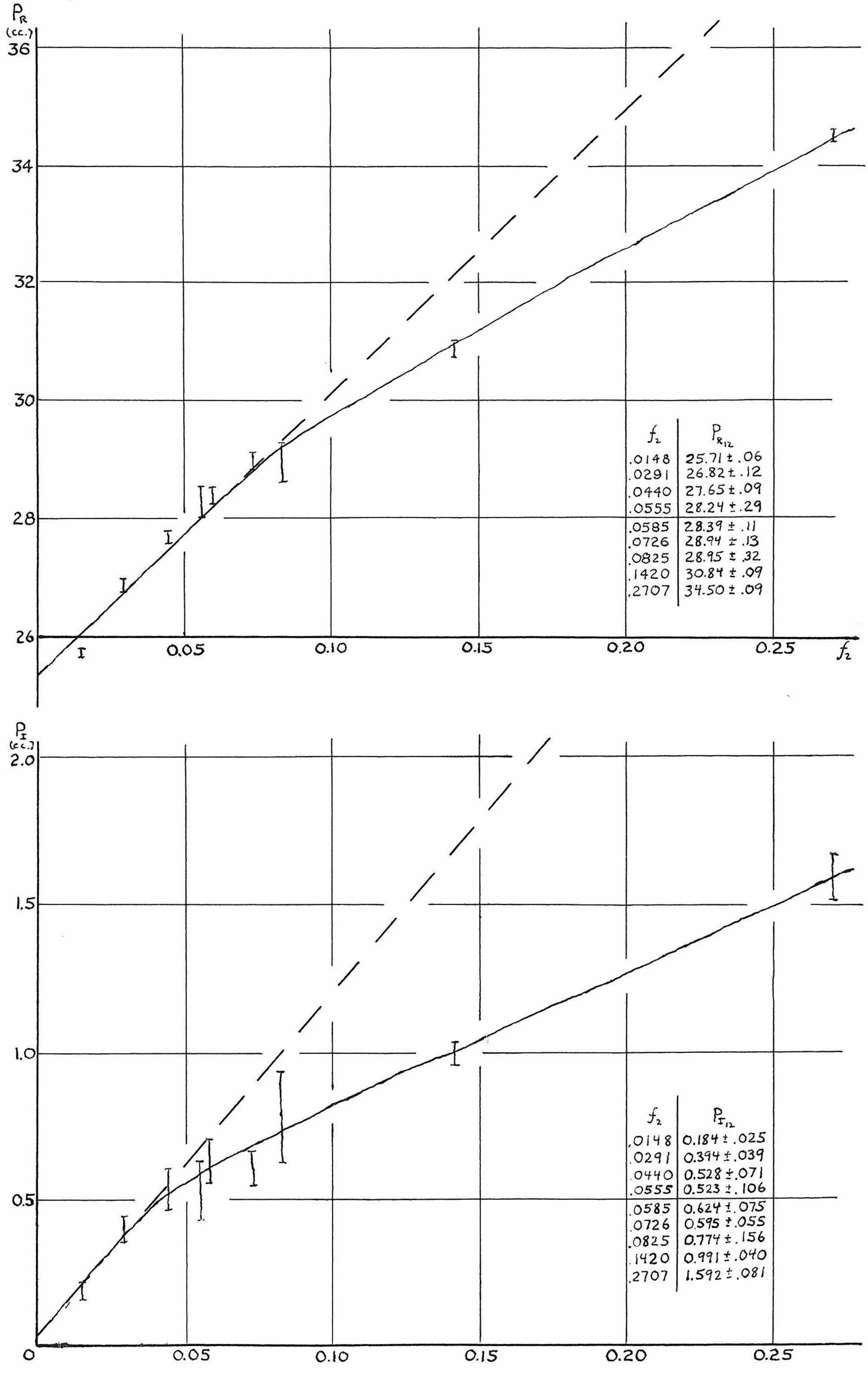
Also listed in Table III are the values of $P_D$ and $\tau$, as computed both from equations 71 and 72 using $P_o$, and from equations 73 and 74 using $P_A$. The results obtained by the two methods differ widely. Let us examine whether this difference indicates a significant error in our measurements.



| $f_2$ | $P_{R_{12}}$ |
|---|---|
| .0146 | 26.37 ± .11 |
| .0201 | 27.15 ± .13 |
| .0260 | 27.18 ± .05 |
| .0376 | 27.18 ± .04 |
| .0430 | 27.88 ± .17 |
| .0625 | 29.78 ± .08 |
| .0819 | 30.47 ± .07 |
| .0998 | 31.63 ± .10 |
| .1187 | 31.67 ± .21 |
| .1870 | 36.52 ± 1.19 |
| .2056 | 36.33 ± .19 |

| $f_2$ | $P_{I_{12}}$ |
|---|---|
| .0146 | 0.340 ± .049 |
| .0201 | 0.245 ± .085 |
| .0260 | 0.390 ± .050 |
| .0376 | 0.567 ± .060 |
| .0430 | 0.369 ± .037 |
| .0625 | 0.777 ± .031 |
| .0819 | 0.952 ± .053 |
| .0998 | 0.989 ± .040 |
| .1187 | 1.368 ± .053 |
| .1870 | 1.603 ± .135 |
| .2056 | 1.801 ± .027 |

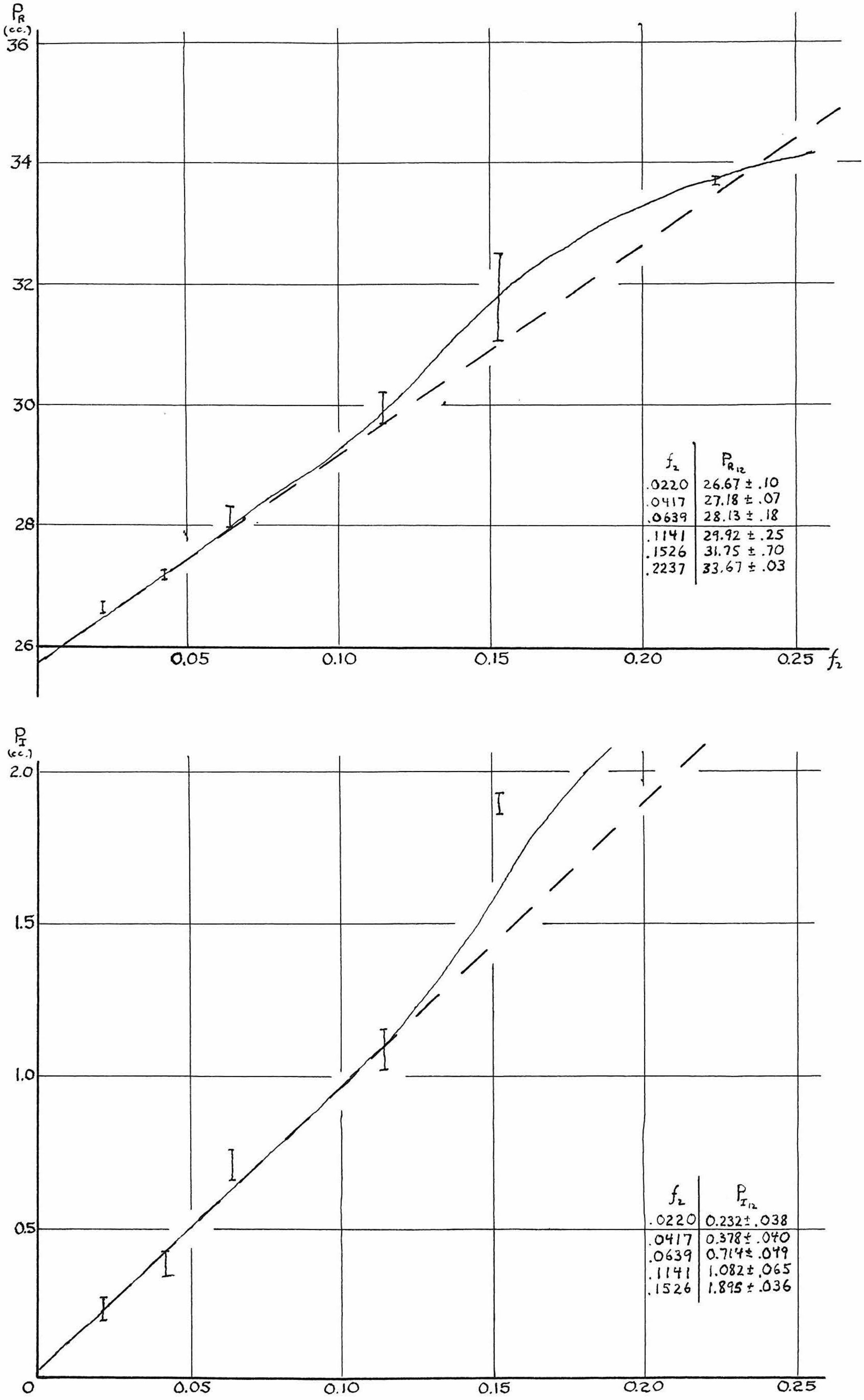
Fig. 9. *Polarization Curves:* Formic Acid in Dioxane



| $f_2$ | $P_{R_{12}}$ |
|---|---|
| .0148 | 25.71 ± .06 |
| .0291 | 26.82 ± .12 |
| .0440 | 27.65 ± .09 |
| .0555 | 28.24 ± .29 |
| .0585 | 28.39 ± .11 |
| .0726 | 28.94 ± .13 |
| .0825 | 28.95 ± .32 |
| .1420 | 30.84 ± .09 |
| .2707 | 34.50 ± .09 |

| $f_2$ | $P_{I_{12}}$ |
|---|---|
| .0148 | 0.184 ± .025 |
| .0291 | 0.394 ± .039 |
| .0440 | 0.528 ± .071 |
| .0555 | 0.523 ± .106 |
| .0585 | 0.624 ± .075 |
| .0726 | 0.595 ± .055 |
| .0825 | 0.774 ± .156 |
| .1420 | 0.991 ± .040 |
| .2707 | 1.592 ± .081 |

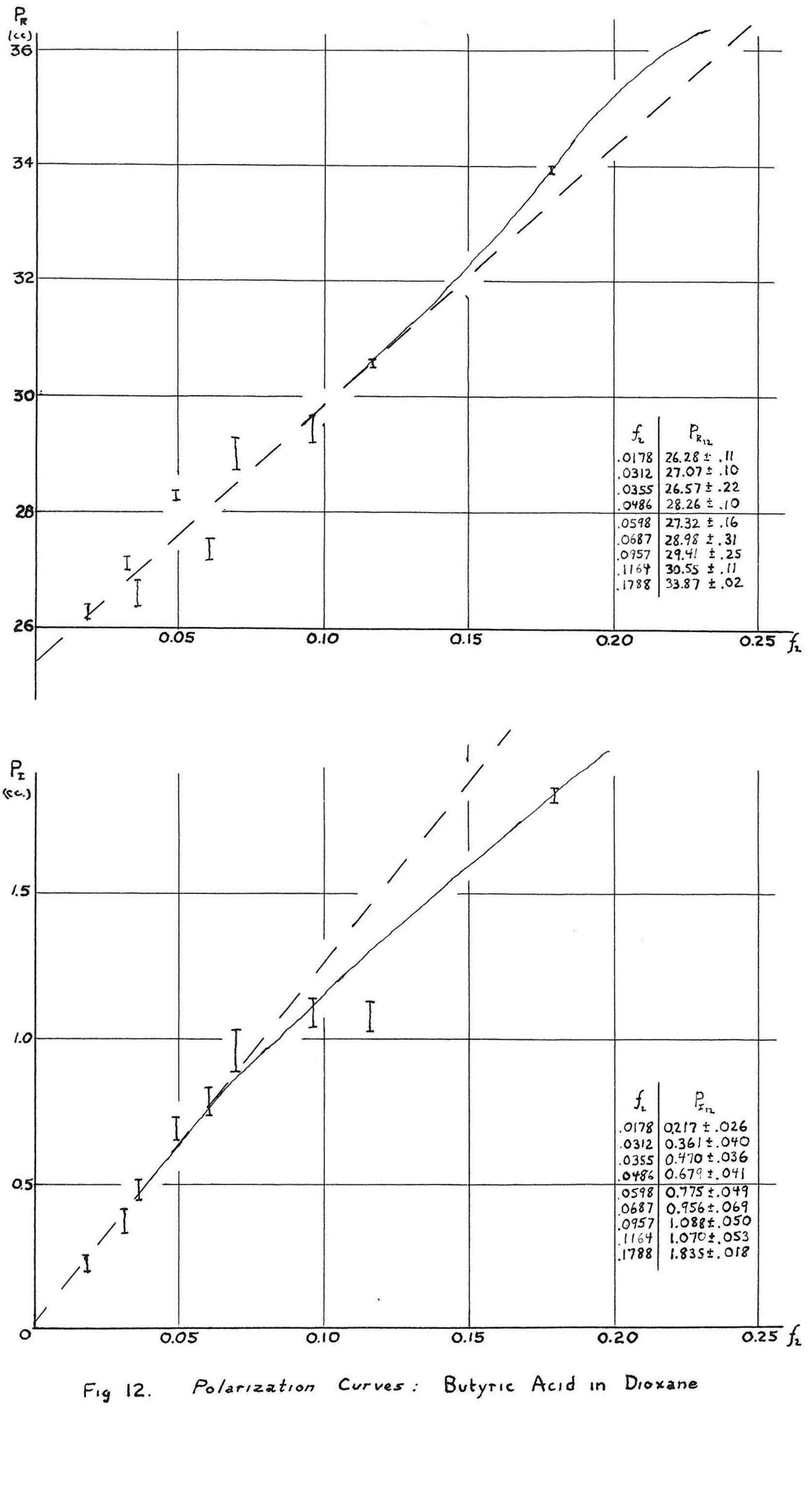
Fig. 10. *Polarisation Curves:* Acetic Acid in Dioxane



| $f_2$ | $P_{R_{12}}$ |
|---|---|
| .0220 | 26.67 ± .10 |
| .0417 | 27.18 ± .07 |
| .0639 | 28.13 ± .18 |
| .1141 | 29.92 ± .25 |
| .1526 | 31.75 ± .70 |
| .2237 | 33.67 ± .03 |

| $f_2$ | $P_{I_{12}}$ |
|---|---|
| .0220 | 0.232 ± .038 |
| .0417 | 0.378 ± .040 |
| .0639 | 0.714 ± .049 |
| .1141 | 1.082 ± .065 |
| .1526 | 1.895 ± .036 |

Fig. 11. *Polarization Curves :* Propionic Acid in Dioxane



| $f_2$ | $P_{R_{12}}$ |
|---|---|
| .0178 | 26.28 ± .11 |
| .0312 | 27.07 ± .10 |
| .0355 | 26.57 ± .22 |
| .0486 | 28.26 ± .10 |
| .0598 | 27.32 ± .16 |
| .0687 | 28.98 ± .31 |
| .0957 | 29.41 ± .25 |
| .1164 | 30.55 ± .11 |
| .1788 | 33.87 ± .02 |

| $f_2$ | $P_{I_{12}}$ |
|---|---|
| .0178 | 0.217 ± .026 |
| .0312 | 0.361 ± .040 |
| .0355 | 0.470 ± .036 |
| .0486 | 0.679 ± .041 |
| .0598 | 0.775 ± .049 |
| .0687 | 0.956 ± .069 |
| .0957 | 1.088 ± .050 |
| .1164 | 1.070 ± .053 |
| .1788 | 1.835 ± .018 |

Fig 12. *Polarization Curves:* Butyric Acid in Dioxane

| | | $HCOOH$ | $CH_3COOH$ | $C_2H_5COOH$ | $C_3H_7COOH$ |
|---|---|---|---|---|---|
| | $P_{R_{200}}$ (c.c.) | 88.42 | 73.95 | 62.02 | 70.50 |
| | $P_{I_{200}}$ (c.c.) | 10.14 | 11.77 | 9.45 | 12.58 |
| | $P_0$ (c.c.) | 90.52 | 75.91 | 80.78 | ——— |
| | $P_A$ (c.c.) | 8.56 | 13.00 | 17.50 | 22.25 |
| From Eq'ns 71, 72 | $P_D$ (c.c.) | 51.2 | 72.6 | 23.5 | ——— |
| | $\tau$ (sec.) | $0.278 \times 10^{-10}$ | $0.224 \times 10^{-10}$ | $2.665 \times 10^{-10}$ | ——— |
| From Eq'ns 73, 74 | $P_D$ (c.c.) | 81.2 | 63.2 | 46.5 | 51.5 |
| | $\tau$ (sec.) | $0.171 \times 10^{-10}$ | $0.260 \times 10^{-10}$ | $0.285 \times 10^{-10}$ | $0.350 \times 10^{-10}$ |

Table III

The condition for consistency of the results obtained by the two methods is gotten by equating the expressions for $\tau$ given by equations 72 and 74, which gives

$$\frac{1}{\omega}\,\frac{P_0 - P_R}{P_I} = \frac{1}{\omega}\,\frac{P_I}{P_R - P_A}$$

$$P_I^2 = (P_0 - P_R)(P_R - P_A) \qquad 78$$

In our discussion of the relative accuracy of equations 71,72 and 73,74 on pp. 33-36, we showed that for $\omega\tau < 1$ equations 71,72 were particularly sensitive to small errors in $P_R$. Let us assume then that our values for $P_I$ are correct, and calculate from equation 78 the values of $P_R$ which would make our results consistent. The results of these calculations are shown in Table IV.

| | $P_R$ in cc. Measured | $P_R$ in cc. From Eq'n 78 | % Difference |
|---|---|---|---|
| $HCOOH$ | 88.42 | 89.24 | 0.92 |
| $CH_3COOH$ | 73.95 | 73.62 | 0.45 |
| $C_2H_5COOH$ | 62.02 | 79.33 | 27.9 |

Table IV

Thus we see that for the cases of formic and acetic acids, an error of less than 1% in $P_R$ would account for the discrepancy between the two methods, and as we have seen that the probable error for our values of $P_R$ is several percent, this deviation of 1% can easily arise from the lack of precision of the method used, and the discrepancy is not a significant one. In the case of propionic acid the difference is too large to be accounted for in this way, and it represents a fundamental inconsistency between this work and that of Wilson and Wenzke.

For formic and acetic acids, although the adjustment in $P_R$ necessary to produce consistency between the two methods is small, the values of $P_D$ and $\tau$ actually computed differ considerably, and there remains the question of which ones to adopt. Taking formic acid as an example, as it exhibits the larger differences, if we calculate $P_D$ and $\tau$ using the adjusted value of $P_R$ obtained from equation 78, we obtain the values $P_D = 81.9$ cc, $\tau = 0.169 \times 10^{-10}$ sec. using either method. These results differ by about 1% from the values obtained with equations 73,74, and by a large amount from those obtained with 71,72. This is in agreement with our prediction that small changes in $P_R$ would affect 71,72 to a much greater extent than 73,74 in the region $\omega\tau < 1$. We came to the conclusion earlier that equations 71,72, because of their use of $P_o$ rather than $P_A$ as a basis, are to be preferred to 73,74 when $\omega\tau$ is sufficiently large. In our case we see that their use is not justified because the smallness of $\omega\tau$, and hence the smallness of $P_o - P_R$, makes them unreliable.

We will extend our acceptance of the unreliability of 71,72 to include the case of propionic acid. We do not have the same check in this case as for formic and acetic acids, but the value of $\tau$ obtained from these equations for propionic acid differs by a factor of 10 from the order of magnitude of the results for the other acids, and this difference is so unlikely to be correct that we will discard equations 71,72 in the case of propionic acid also, in consistency with our decision for the lighter acids.

In the above discussion we have assumed errors in $P_R$ to be the only source of our observed discrepancies, but an equal error in $P_o$ would have the same effect, as can be seen from the symmetry of occurrence of $P_o$ and $P_R$ in equations 71,72. In addition errors of $P_I$ and $P_A$ would have a contributing, but much smaller effect. Therefore there is no reason to assume that the values of $P_D$ and $\tau$ obtained with the adjusted values of $P_R$ from equation 78 are the correct ones. Hence the values obtained directly from equations 73,74 using the experimental data will be the only ones which will be used as a basis for our further discussion.

Substituting the values of $\tau$ shown in the last line of Table III into equation 59, and using the value $\eta = 1.34$ cP for dioxane(41), we obtain the values of $a_1a_2a_3$ listed in the first column of Table V.

| | $a_1a_2a_3$ in Å$^3$ | | Ratio: $\frac{a_1a_2a_3\ \text{Exp.}}{a_1a_2a_3\ \text{Struc.}}$ |
|---|---|---|---|
| | Experimental | From Structure | |
| $HCOOH$ | 4.12 | 10.6 | 0.389 |
| $CH_3COOH$ | 6.26 | 16.1 | 0.389 |
| $C_2H_5COOH$ | 6.86 | 19.2 | 0.357 |
| $C_3H_7COOH$ | 8.43 | 23.5 | 0.358 |
| | | Average: | 0.37 |

Table V

Let us compare these results with those obtained from the accepted structures of the molecules. Figure 13 illustrates models of the molecules of the four acids studied, drawn to scale with the outer envelope determined by the van der Waals radii of the atoms. The radii, bond lengths and bond angles used for these models were taken from Pauling(42). Taking the dimensions of these molecules along their three principal axes, and computing the value of $a_1a_2a_3$ for each, we obtain the results given in the second column of Table V.

We first observe that the experimental results are consistently smaller than those computed from the structure. However the agreement is as good as we should expect, since equation 59 was derived for macroscopic phenomena, and it is not to be expected that it will hold exactly for molecular dimensions. In particular, the derivation assumes that there is no slipping between the rotating body and the immediately adjacent layer of the liquid, so that the result depends only on the properties of the liquid itself, whereas for the molecular case, undoubtedly an appreciable part of the "slipping" takes place between the rotating molecules

Bond Lengths in Å

C - C : 1.54
C - H : 1.07
C - O : 1.43
C = O : 1.27
O - H : 0.96

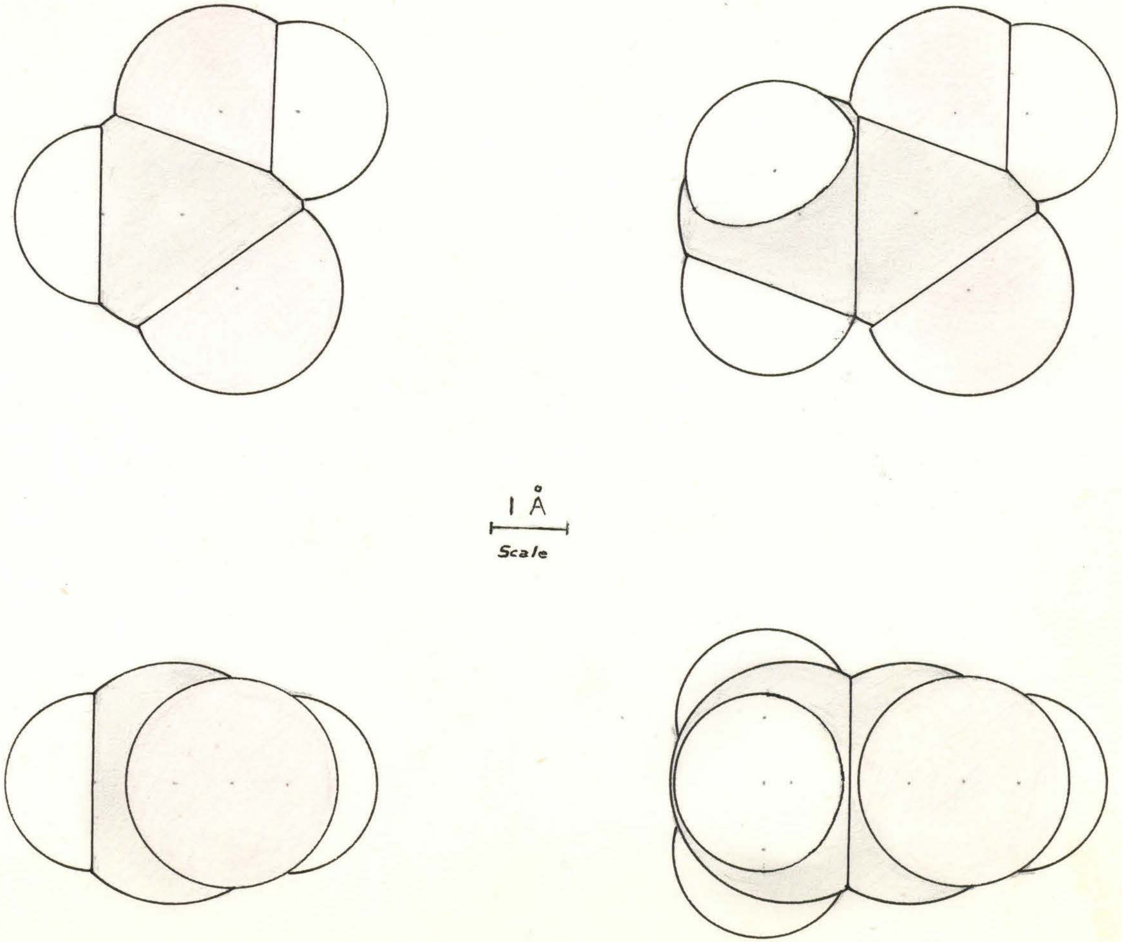
Bond Angles

H - C - H : 110°
H - C - C : 110°
C - C - O : 110°
C - C = O : 125°
O - C = O : 125°
C - O - H : 110°

Van der Waals
Radii in Å

C: 1.6
O: 1.4
H: 1.2

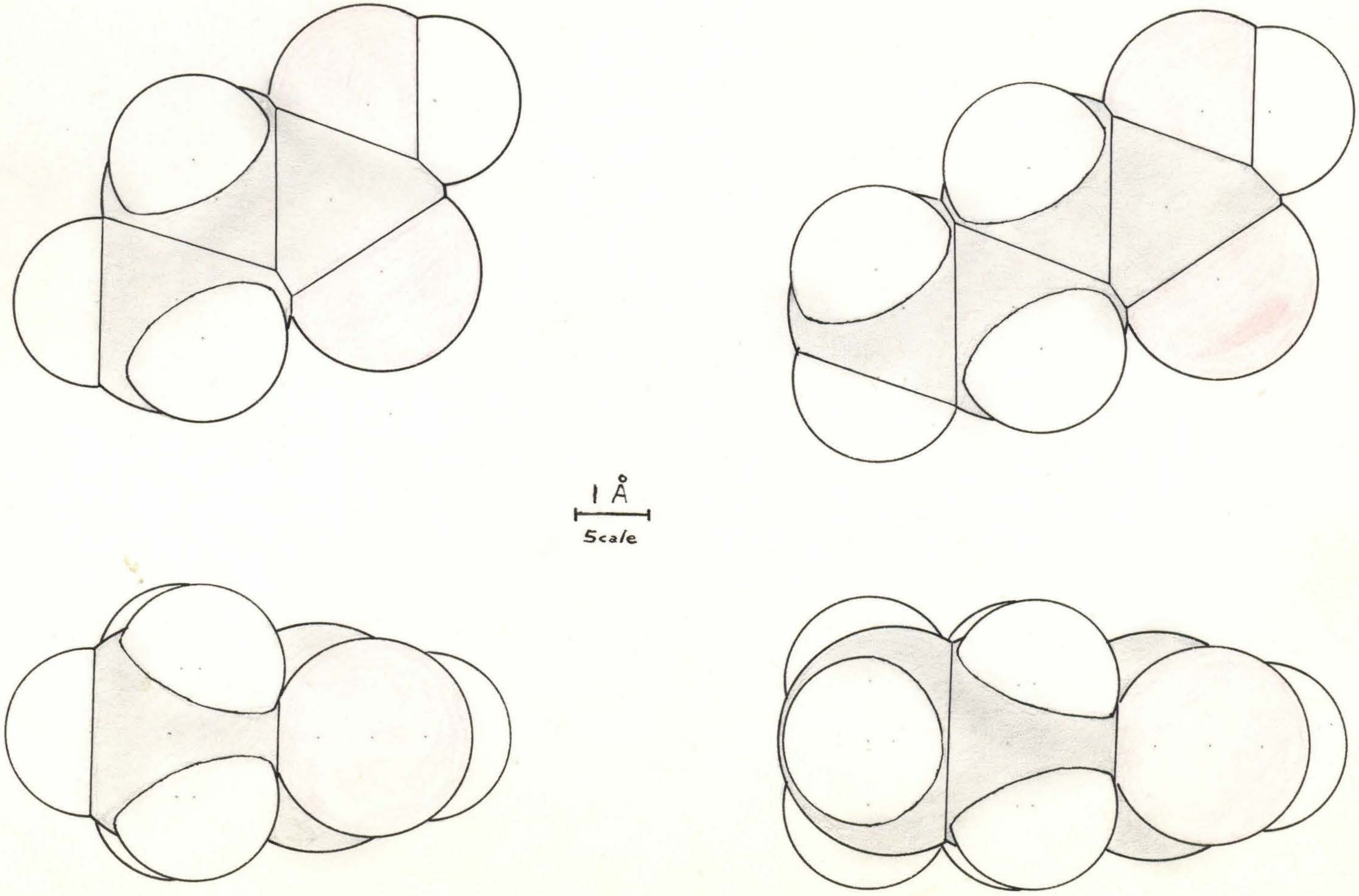
○ - Hydrogen
● - Carbon
◉ - Oxygen



Formic Acid: $HCOOH$

Acetic Acid: $CH_3COOH$

Fig. 13a. Molecular Models



Propionic Acid: $C_2H_5COOH$

n- Butyric Acid: $C_3H_7COOH$

Fig. 13b. Molecular Models

and the adjacent molecules of the liquid, and thus depends on the interaction forces between the unlike molecules. The effect of this can be expressed formally by replacing $\eta$ by a new value $\eta'$ which would be a function of both the solvent and the solute. In our case, for the homologous series of fatty acids, $\eta'$ must be approximately constant for the series in a given solvent, since the interaction forces will be of the same type for the different members of the series, depending largely on the forces between the dipoles of the solute and the solvent molecules. Therefore, while the absolute magnitudes of our results are of little value, their relative magnitudes must be significant.

If we examine the ratio of the experimental values of $a_1 a_2 a_3$ to those computed from the structure (Table V, column 3), we find that this ratio is approximately constant, with a value of about 0.37*. Thus the experimentally determined size of the rotating group is proportional to the size of the molecule, and this will only be true if the whole molecule rotates. Therefore we must conclude that the COOH group does not rotate independently of the aliphatic chain, at least in the case of the lighter fatty acids measured, but that the whole molecule rotates as a unit.

The values of the ratio given in the third column of Table V range about 5% either side of their mean, which is within the

---

* It is of interest to note that Fischer(43) obtained nearly this same value, actually $\eta' = 0.36\eta$, for series of ketones and alkyl chlorides in benzene. He advanced the hypothesis that this value should hold for all solutions of polar substances in non-polar solvents.

range of probable error predicted for the computed values of $a_1a_2a_3$. The values of $a_1a_2a_3$ obtained from the structure are equally likely to be in error, since the molecular dimensions are not known very precisely, and the method used in obtaining $a_1a_2a_3$ is itself very inaccurate. In view of this, the agreement obtained is very good. The increase of $a_1a_2a_3$ by more than a factor of two in going from formic to n-butyric acids is much too large to be attributed to anything but a real increase in the size of the rotating group.

If we compare the results obtained by Keutner and Potapenko for the alcohols, which are given in Table VI, we see that there is not a constant ratio of experimental to structural values of $a_1a_2a_3$. Instead, the experimental values remain approximately constant, from which they concluded that only the OH group rotated, since the volume of the rotating section remains constant for increasing chain length.

| | $a_1a_2a_3$ in Å$^3$ | | Ratio: $\frac{a_1a_2a_3\ \text{Exp.}}{a_1a_2a_3\ \text{Struc.}}$ |
|---|---|---|---|
| | Experimental | From Structure | |
| $CH_3OH$ | 9.5 | 9.5 | 1.00 |
| $C_2H_5OH$ | 11.2 | 12.0 | 0.93 |
| $C_3H_7OH$ | 11.2 | 13.8 | 0.81 |
| $C_4H_9OH$ | 10.9 | 16.5 | 0.66 |

Table VI

The fact that the alcohols and fatty acids give different results in this fashion, even though both series consist in an aliphatic chain terminated by a group possessing a permanent moment which is directed at right angles to the axis of the chain, may be explained by considering the natures of the polar groups.

The principal forces acting to prevent independent rotation of the polar groups are, for the alcohols, the repulsion between the hydrogen atom of the hydroxyl group and the hydrogen atoms of the neighboring alkyl group; and for the acids, the attractions between the oxygen atoms of the carboxyl group and the hydrogen atoms of the neighboring alkyl group. The effective positive charges of the hydrogen atoms of the alkyl chain is very small, as is indicated by the fact that they do not ordinarily form hydrogen bonds. The local polarization produced by the hydrogen atom~~s~~ of the hydroxyl group decreases this effective charge, while the local polarization produced by the oxygen atoms of the carboxyl group increases the effective charge. The distances involved are about the same in either case. Therefore the electrostatic forces will be greater in the acids than in the alcohols. In addition there are two such forces in the acids, contributed by the two oxygen atoms in the carboxyl group, while there is only one rotating hydrogen in the hydroxyl group. Therefore the forces hindering independent rotation of the carboxyl group must be more than twice as great as those for the hydroxyl group. This inequality of the forces hindering the independent rotation of the respective groups is evidently sufficient to mean the difference between free rotation for the OH group and binding to the rest of the molecule for the COOH group, as the measurements indicate.

For higher members of the fatty acid series, a rotation about a C — C bond at some distance along the chain from the carboxyl group, where the rotational hindrance would be small, is quite possible.

A check on our work can be obtained by computing the values of $\mu$ for the acid molecules, since several good determinations have been made of these values by low frequency measurements. By substituting the values of $P_D$ given in Table III into equation 66 we get the values of $\mu$ given in Table VII, where also are listed for comparison the results of Zahn(44) from measurements on the vapors; Wilson and Wenzke(40) from dioxane solutions; and Pohl, Hobbs, and Gross(45) from benzene solutions.

| | $\mu \times 10^{18}$ in e.s.u. | $\mu \times 10^{18}$ in e.s.u. | | |
|---|---|---|---|---|
| | | [Zahn] | [Wilson + Wenzke] | [Pohl, Hobbs, + Gross] |
| $HCOOH$ | 1.98 | 1.51 | 2.07 | 1.82 |
| $CH_3COOH$ | 1.75 | 1.73 | 1.74 | 1.68 |
| $C_2H_5COOH$ | 1.50 | 1.74 | 1.75 | 1.68 |
| $C_3H_7COOH$ | 1.58 | —— | —— | 1.65 |

Table VII

We see that all of our values are in agreement with these earlier determinations, with the possible exception of propionic acid, which is low, but still of the correct order of magnitude. This check renders a good support in favor of the validity of our results for $a_1 a_2 a_3$ computed earlier.

# Appendix

## Sample Calculations

To illustrate the calculations, we will carry a single curve from the original data through a complete set of calculations, bringing in the results of similar calculations on other portions of the data as we need them.

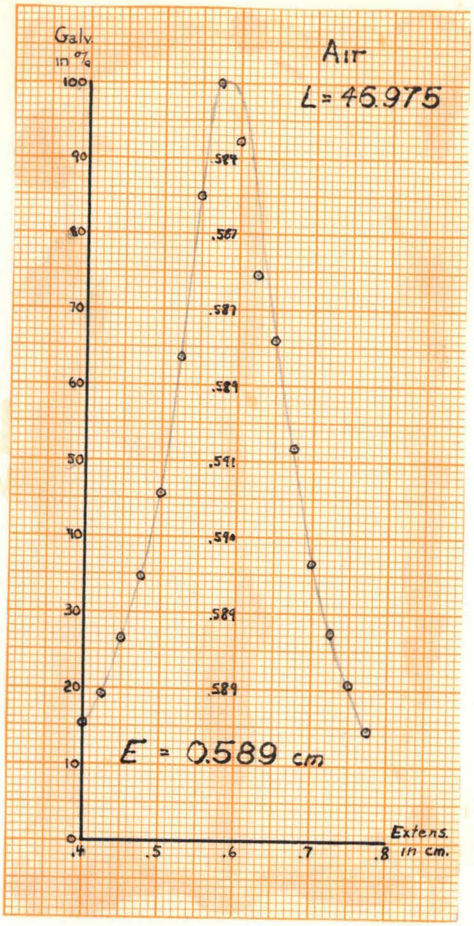
The data used is from a run taken March 28, 1943 on solutions of formic acid in dioxane. In the course of this run, four curves were taken with air in the condenser at $L \sim 47$ cm, eight curves were taken with air in the condenser at $L \sim 60$ cm, and sixteen curves were taken with pure dioxane in the condenser. The average values of the various constants of these curves were used to standardize and calibrate the run, giving values of $\lambda, \delta_0', \delta$ and $\gamma$. From these calibrating curves, one of each type has been chosen, such that the constants for the chosen curves are exactly the same as for the average curves of the corresponding types. These curves are used to illustrate the calculation of the various constants for the run, as needed, but it is to be remembered that they are representative curves, and that ordinarily average values are used for computing the constants.

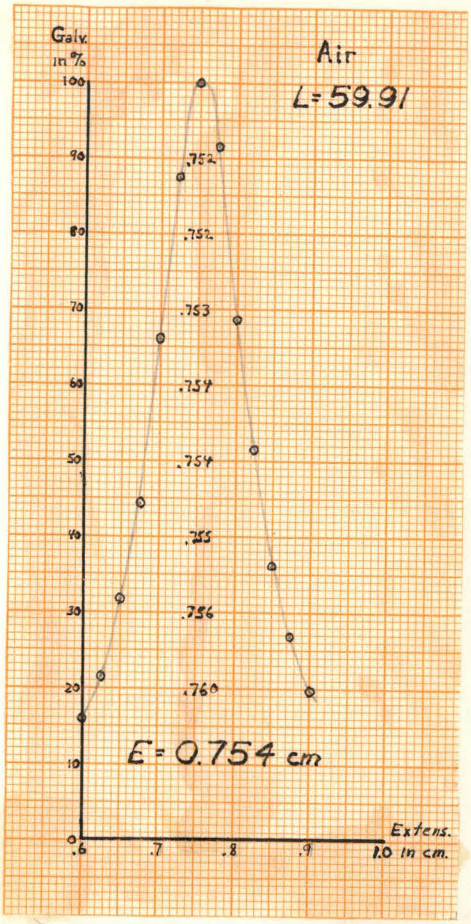
The abbreviations used for the column headings on the data given below are: E for the extensometer reading in centimeters, G for the galvanometer scale reading in millimeters, and % for the galvanometer scale reading reduced to percent of maximum deflection.

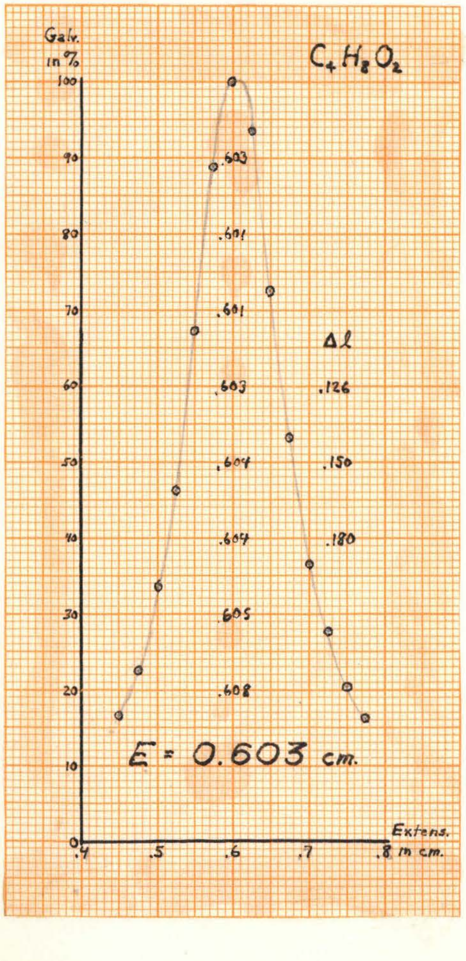
T = 23.6 °C          $a$ = 4.00 cm.

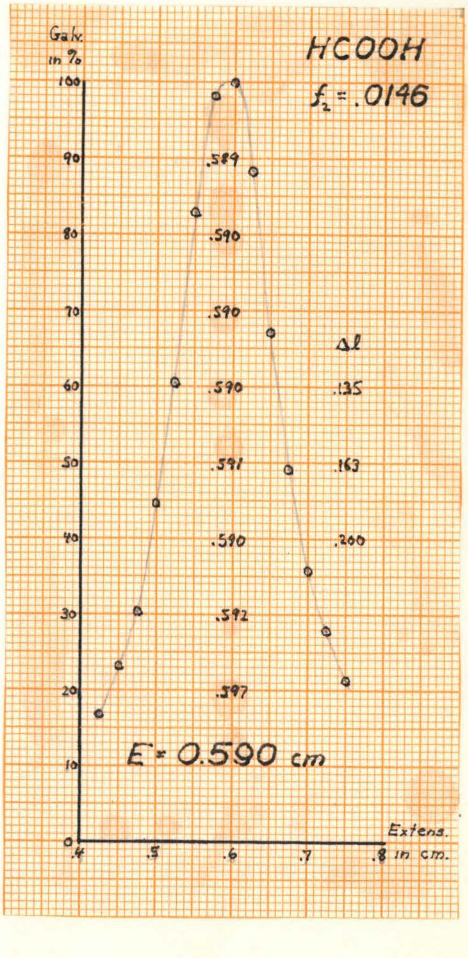
| Condenser contents: | Air | | Air | | Dioxane | | HCOOH<br>$f_2$ = .0146 | |
|---|---|---|---|---|---|---|---|---|
| L : | 46.975 | | 59.91 | | 59.91 | | 59.91 cm. | |
| $E \times 10^3$ | G | % | G | % | G | % | G | % |
| 400 | 20.7 | 15.3 | | | | | | |
| 425 | 26.0 | 19.2 | | | | | 18.2 | 16.9 |
| 450 | 35.9 | 26.5 | | | 23.0 | 16.7 | 25.1 | 23.2 |
| 475 | 46.8 | 34.6 | | | 31.0 | 22.5 | 32.8 | 30.4 |
| 500 | 61.9 | 45.7 | | | 46.0 | 33.3 | 48.1 | 44.5 |
| 525 | 86.2 | 63.7 | | | 63.7 | 46.2 | 65.3 | 60.5 |
| 550 | 115.0 | 85.0 | | | 92.8 | 67.3 | 89.4 | 82.8 |
| 575 | 135.2 | 100 | | | 122.7 | 88.8 | 106.1 | 98.2 |
| 600 | 124.8 | 92.1 | 24.1 | 159 | 138.0 | 100 | 108.0 | 100 |
| 625 | 101.0 | 74.6 | 32.9 | 21.6 | 129.2 | 93.5 | 95.4 | 88.3 |
| 650 | 89.1 | 65.9 | 48.2 | 31.7 | 100.0 | 72.5 | 72.5 | 67.1 |
| 675 | 70.0 | 51.7 | 67.2 | 44.2 | 73.5 | 53.2 | 53.2 | 49.2 |
| 700 | 49.2 | 36.4 | 100.3 | 66.0 | 50.4 | 36.5 | 38.7 | 35.8 |
| 725 | 37.1 | 27.4 | 133.1 | 87.5 | 37.5 | 27.7 | 30.0 | 27.8 |
| 750 | 28.0 | 20.7 | 152.0 | 100 | 28.1 | 20.4 | 23.0 | 21.3 |
| 775 | 19.7 | 14.6 | 139.0 | 91.5 | 22.4 | 16.2 | | |
| 800 | | | 104.0 | 68.4 | | | | |
| 825 | | | 78.1 | 51.4 | | | | |
| 850 | | | 54.9 | 36.1 | | | | |
| 875 | | | 40.7 | 26.8 | | | | |
| 900 | | | 30.1 | 19.8 | | | | |

From these data we plot the resonance curves (% vs E) as shown on the next page. On these curves, chord midpoints and chord lengths are marked. The mean midpoint is entered on the base of the curve as E for the curve.


Air
L = 46.975
Galv. in %
100
90
80
70
60
50
40
30
20
10
0
.589
.587
.587
.589
.591
.590
.589
.589
E = 0.589 cm
Extens. in cm.
.4
.5
.6
.7
.8


Air
L = 59.91
Galv. in %
100
90
80
70
60
50
40
30
20
10
0
.752
.752
.753
.754
.754
.755
.756
.760
E = 0.754 cm
Extens. in cm.
.6
.7
.8
.9
1.0


$C_4H_8O_2$
Galv. in %
100
90
80
70
60
50
40
30
20
10
0
.603
.601
.601
.603
.604
.604
.605
.608
Δl
.126
.150
.180
E = 0.603 cm.
Extens. in cm.
.4
.5
.6
.7
.8


HCOOH
$f_2$ = .0146
Galv. in %
100
90
80
70
60
50
40
30
20
10
0
.589
.590
.590
.590
.591
.590
.592
.597
Δl
.135
.163
.200
E = 0.590 cm
Extens. in cm.
.4
.5
.6
.7
.8

We obtain $a_1$ and $a_2$ from the relations

$$a_1 = \alpha + \beta_1$$

$$a_2 = L_0 - L + E + \beta_2$$ 49

and we have

$$L_0 = 67.567 - .0012(t - 20) = 67.563 \text{ cm.}$$

so that $a_1 = 4.00 + .055 = 4.055$ cm.

Air (L = 46.975): $a_2 = 67.563 - 46.975 + .589 + .055 = 21.232$ cm.

Air (L = 59.91): $a_2 = 67.563 - 59.91 + .754 + .055 = 8.462$ cm.

Dioxane: $a_2 = 67.563 - 59.91 + .603 + .055 = 8.311$ cm.

HCOOH ($f_2 = .0146$): $a_2 = 67.563 - 59.91 + .590 + .055 = 8.298$ cm.

The difference between the $a_2$ values obtained from successive maxima with air in the condenser is $\lambda/2$

$$\frac{\lambda}{2} = 21.232 - 8.462 = 12.77 \text{ cm.}$$

$$\alpha = \frac{2\pi}{\lambda} = .24601$$

We now use

$$\delta_0' + \varepsilon'\delta = \frac{\lambda}{2}\left[\cot\alpha(a_1 - \vartheta) + \cot\alpha(a_2 - \vartheta)\right]$$ 5

to compute $\varepsilon'$.

$$a_1 - \vartheta = 4.044 \quad ; \quad \alpha(a_1 - \vartheta) = .9949$$

$$\sin\alpha(a_1 - \vartheta) = .8387 \; ; \quad \cot\alpha(a_1 - \vartheta) = .6493$$

| | Air | Dioxane | HCOOH ($f_2 = .0146$) |
|---|---|---|---|
| $a_2 - \vartheta$ | 8.451 | 8.300 | 8.278 |
| $\alpha(a_2 - \vartheta)$ | 2.0790 | 2.0419 | 2.0387 |
| $\cot\alpha(a_2 - \vartheta)$ | - .5570 | - .5094 | - .5053 |
| $\cot\alpha(a_1 - \vartheta) + \cot\alpha(a_2 - \vartheta)$ | .0923 | .1399 | .1440 |
| $\delta_0' + \varepsilon'\delta$ | 1.179 | 1.787 | 1.839 |

Using air and dioxane as standards to compute $\delta_0'$ and $\delta$

$$\delta_0' + \delta = 1.179$$

$$\delta_0' + 2.235\delta = 1.787$$

$$\therefore \quad \delta_0' = 0.687$$

$$\delta = 0.492$$

Then for HCOOH ( $f_2 = .0146$): $.687 + .492\,\varepsilon' = 1.839$

$$\varepsilon' = 2.342$$

The formula for $\gamma$ is

$$\gamma = \frac{2\pi}{\lambda}\,\Delta l\,\sqrt{\frac{R^2}{1-R^2}}$$ 50

so, for $R^2 = 0.60 \; : \; \gamma_{.6} = .3013\,(\Delta l)_{.6}$

$R^2 = 0.50 \; : \; \gamma_{.5} = .2460\,(\Delta l)_{.5}$

$R^2 = 0.40 \; : \; \gamma_{.4} = .2008\,(\Delta l)_{.4}$

We now compute $c = \frac{2\varkappa}{1-\varkappa^2}$ from the formula

$$\frac{\varkappa}{1-\varkappa^2} = \frac{\delta_0' + \varepsilon'\delta}{\varepsilon'\delta}\,\frac{d\gamma}{4\pi}\left(1 + \frac{\alpha(a_1-\vartheta)\frac{\sin\alpha(a_2-\vartheta)}{\sin\alpha(a_1-\vartheta)} + \alpha(a_2-\vartheta)\frac{\sin\alpha(a_1-\vartheta)}{\sin\alpha(a_2-\vartheta)}}{\sin\alpha(a_1+a_2-2\vartheta)}\right)$$ 46

| | Dioxane | HCOOH ($f_2 = .0146$) |
|---|---|---|
| $(\Delta l)_{.6}$ | .126 | .135 |
| $(\Delta l)_{.5}$ | .150 | .163 |
| $(\Delta l)_{.4}$ | .180 | .200 |
| $\gamma_{.6}$ | .0380 | .0407 |
| $\gamma_{.5}$ | .0369 | .0401 |
| $\gamma_{.4}$ | .0362 | .0402 |
| $\gamma$ | .0370 | .0403 |
| $d\gamma$ | | .0033 |
| $\sin\alpha(a_2-\vartheta)$ | | .8925 |
| $\alpha(a_1+a_2-2\vartheta)$ | | 3.0336 |
| $\sin\alpha(a_1+a_2-2\vartheta)$ | | .1078 |

$$\frac{x}{1-x^2} = \frac{1.839}{1.152}\;\frac{.0033}{12.57}\left(1 + \frac{.9949\,\frac{.8925}{.8387} + 2.0387\,\frac{.8387}{.8925}}{.1078}\right)$$

$$c = .0232$$

Then we can compute $P_{R_{12}}$ and $P_{I_{12}}$ by the formulas

$$\left.\begin{aligned} P_{R_{12}} &= \frac{\varepsilon_{12}'^{2} + \varepsilon_{12}' - 2 + c_{12}^2\varepsilon_{12}'^{2}}{\varepsilon_{12}'^{2} + 4\varepsilon_{12}' + 4 + c_{12}^2\varepsilon_{12}'^{2}}\;\frac{M_1f_1 + M_2f_2}{\rho_{12}} \\ P_{I_{12}} &= \frac{3c_{12}\varepsilon_{12}'}{\varepsilon_{12}'^{2} + 4\varepsilon_{12}' + 4 + c_{12}^2\varepsilon_{12}'^{2}}\;\frac{M_1f_1 + M_2f_2}{\rho_{12}} \end{aligned}\right\}\quad \underline{63}$$

$$P_{R_{12}} = \frac{(2.342)^2 + 2.342 - 2 + (.0232\times 2.342)^2}{(2.342)^2 + 4\times 2.342 + 4 + (.0232\times 2.342)^2}\;\frac{.9854\times 88.10 + .0146\times 46.02}{1.0364}$$

$$P_{I_{12}} = \frac{3\times .0232\times 2.342}{(2.342)^2 + 4\times 2.342 + 4 + (.0232\times 2.342)^2}\;\frac{.9854\times 88.10 + .0146\times 46.02}{1.0364}$$

$$P_{R_{12}} = 26.20 \text{ cc.}$$

$$\text{at } f_2 = .0146$$

$$P_{I_{12}} = 0.731 \text{ cc.}$$

These results are then averaged together with all similar values obtained for the same concentration, and the probable deviation of the mean computed. Tabulations of some of these sets of results are given on the following pages, to show the distribution at some low concentration points. The representation of all of the results at this point is given by Figs 9 - 12 in the main part of this work.

In the following examples the values have been rearranged in order of descending magnitude, so that values of $P_{R_{12}}$ and $P_{I_{12}}$ are not paired according to their position.

I HCOOH $f_2 = .0146$

| | $P_{R_{12}}$ | $\Delta$ | $\Delta^2$ | $P_{I_{12}}$ | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|---|
| | 26.92 | .55 | .3025 | .731 | .391 | .1529 |
| | 26.92 | .55 | .3025 | .580 | .240 | .0576 |
| | 26.89 | .52 | .2704 | .548 | .208 | .0433 |
| | 26.65 | .28 | .0784 | .391 | .051 | .0026 |
| | 26.48 | .11 | .0121 | .353 | .013 | .0002 |
| | 26.23 | −.14 | .0196 | .352 | .012 | .0001 |
| | 26.20 | −.17 | .0289 | .176 | −.164 | .0269 |
| | 26.17 | −.20 | .0400 | .133 | −.207 | .0428 |
| | 25.81 | −.56 | .3136 | .107 | −.233 | .0543 |
| | 25.47 | −.90 | .8100 | .024 | −.316 | .0999 |
| Sum | 263.74 | | 2.1780 | 3.395 | | .4806 |
| Mean | 26.37 | | .2178 | .340 | | .04806 |

Prob. error of mean: $\frac{.6745}{3}\sqrt{.2178} = .11$ $\frac{.6745}{3}\sqrt{.04806} = .049$

$P_{R_{12}} = 26.37 \pm .11$ $P_{I_{12}} = .340 \pm .049$

II $CH_3COOH$ $f_2 = .0148$

| | $P_{R_{12}}$ | $\Delta$ | $\Delta^2$ | $P_{I_{12}}$ | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|---|
| | 26.01 | .30 | .0900 | .354 | .170 | .0289 |
| | 26.01 | .30 | .0900 | .347 | .163 | .0266 |
| | 26.00 | .29 | .0841 | .309 | .125 | .0156 |
| | 25.92 | .21 | .0441 | .265 | .081 | .0066 |
| | 25.81 | .10 | .0100 | .221 | .037 | .0014 |
| | 25.81 | .10 | .0100 | .215 | .031 | .0010 |
| | 25.78 | +.08 | .0064 | .170 | −.014 | .0002 |
| | 25.70 | −.01 | .0001 | .145 | −.039 | .0015 |
| | 25.62 | −.09 | .0081 | .139 | −.045 | .0020 |
| | 25.56 | −.15 | .0225 | .095 | −.089 | .0079 |
| | 25.24 | −.47 | .2209 | .000 | −.184 | .0339 |
| | 25.07 | −.64 | .4096 | −.050 | −.234 | .0548 |
| Sum | 308.53 | | .9958 | 2.210 | | .1804 |
| Mean | 25.71 | | .0830 | .184 | | .01503 |

Prob. error of mean $\frac{.6745}{3.317}\sqrt{.0830} = .06$ $\frac{.6745}{3.317}\sqrt{.01503} = .025$

$P_{R_{12}} = 25.71 \pm .06$ $P_{I_{12}} = .184 \pm .025$

III $C_2H_5COOH$ $f_2 = .0220$

| | $P_{R_{12}}$ | $\Delta$ | $\Delta^2$ | $P_{I_{12}}$ | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|---|
| | 27.72 | 1.05 | 1.1025 | .525 | .293 | .0858 |
| | 27.47 | .80 | .6400 | .525 | .293 | .0858 |
| | 27.18 | .51 | .2601 | .455 | .223 | .0497 |
| | 26.97 | .30 | .0900 | .398 | .166 | .0276 |
| | 26.84 | .17 | .0289 | .380 | .148 | .0219 |
| | 26.80 | .13 | .0169 | .354 | .112 | .0125 |
| | 26.80 | .13 | .0169 | .335 | .103 | .0106 |
| | 26.75 | .08 | .0064 | .259 | .027 | .0007 |
| | 26.52 | -.15 | .0225 | .215 | -.017 | .0003 |
| | 26.52 | -.15 | .0225 | .196 | -.036 | .0013 |
| | 26.45 | -.22 | .0484 | .082 | -.150 | .0225 |
| | 26.38 | -.29 | .0841 | -.019 | -.251 | .0630 |
| | 26.20 | -.47 | .2209 | -.038 | -.270 | .0729 |
| | 25.92 | -.75 | .5625 | -.082 | -.314 | .0986 |
| | 25.50 | -1.17 | 1.3689 | -.088 | -.320 | .1024 |
| Mean | 26.67 | | .2994 | .232 | | .0437 |

$P_{R_{12}} = 26.67 \pm .10$ $P_{I_{12}} = .232 \pm .038$

IV $C_3H_7COOH$ $f_2 = .0178$

| | $P_{R_{12}}$ | $\Delta$ | $\Delta^2$ | $P_{I_{12}}$ | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|---|
| | 27.98 | 1.70 | 2.8900 | .496 | .279 | .0778 |
| | 27.84 | 1.56 | 2.4336 | .427 | .210 | .0441 |
| | 26.81 | .53 | .2809 | .401 | .184 | .0339 |
| | 26.60 | .32 | .1024 | .357 | .140 | .0196 |
| | 26.55 | .27 | .0729 | .318 | .101 | .0102 |
| | 26.51 | .23 | .0529 | .299 | .082 | .0067 |
| | 26.24 | -.04 | .0016 | .299 | .082 | .0067 |
| | 26.22 | -.06 | .0036 | .274 | .057 | .0032 |
| | 26.19 | -.09 | .0081 | .255 | .038 | .0014 |
| | 26.15 | -.13 | .0169 | .210 | -.007 | .0000 |
| | 25.96 | -.32 | .1024 | .159 | -.058 | .0034 |
| | 25.81 | -.47 | .2209 | .134 | -.083 | .0069 |
| | 25.80 | -.48 | .2304 | .134 | -.083 | .0069 |
| | 25.79 | -.49 | .2401 | .127 | -.090 | .0081 |
| | 25.79 | -.49 | .2401 | .102 | -.115 | .0132 |
| | 25.72 | -.56 | .3136 | .102 | -.115 | .0132 |
| | 25.63 | -.65 | .4225 | -.045 | -.262 | .0686 |
| | 25.43 | -.85 | .7225 | -.134 | -.351 | .1232 |
| Mean | 26.28 | | .4642 | .217 | | .0248 |

$P_{R_{12}} = 26.28 \pm .11$ $P_{I_{12}} = .217 \pm .026$

The next step consists in the extrapolation of the $P_{12} - f_2$ curves. This was done by fitting a straight line, $P_{12} = a + bf_2$ to the points in the low concentration range. We take HCOOH as our example. From Fig 9 we observe that the points are roughly linear up through $f_2 = .0819$

|  | $f_2$ | $P_R$ | $P_I$ | $f_2^2 \times 10^6$ | $P_R f_2 \times 10^4$ | $P_I f_2 \times 10^4$ |
|---|---|---|---|---|---|---|
|  | .0146 | 26.37 | .340 | 213 | 3850 | 49.6 |
|  | .0201 | 27.15 | .245 | 404 | 5457 | 49.2 |
|  | .0260 | 27.18 | .390 | 676 | 7067 | 101.4 |
|  | .0376 | 27.18 | .567 | 1414 | 10596 | 213.2 |
|  | .0430 | 27.88 | .369 | 1849 | 11988 | 158.7 |
|  | .0625 | 29.78 | .777 | 3906 | 18612 | 485.6 |
|  | .0819 | 30.47 | .952 | 6708 | 24955 | 779.7 |
| Sum | .2857 | 197.02 | 3.640 | 15170 | 82525 | 1837.4 |

Then for $P_R$
$$\begin{cases} 7a + .2857b = 197.02 \\ .2857a + .01517b = 8.2525 \end{cases}$$

whence $a = 25.69$ ; $b = 60.23$

$$P_{R_{12}} = 25.69 + 60.23 f_2$$

$$P_{R_{2\infty}} = 85.92 \text{ cc.}$$

for $P_I$
$$\begin{cases} 7a + .2857b = 3.640 \\ .2857a + .01517b = .18374 \end{cases}$$

whence $a = .1105$ ; $b = 10.03$

$$P_{I_{12}} = .1105 + 10.03 f_2$$

$$P_{I_{2\infty}} = 10.14 \text{ cc.}$$

These are the values listed in Table III. From this point on the calculations are simple substitutions in equations 71 - 74, 59, and 66 and as all results at each stage are tabulated in the body of this work they will not be repeated here.

# Acknowledgment

I wish to express here my gratitude to Prof. G. Potapenko for suggesting the problem for this thesis and for his continued helpful advice toward the solution of difficulties connected with it.

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