

INVESTIGATION OF THE DIPOLE MOMENT AND RELAXATION
TIME OF ORGANIC MOLECULES

by

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INTRODUCTION

With the development of microwave equipment the frequency range over which dielectrics could be studied was extended to the wavelength region between 0.10 cm and 100.0 cm, or frequencies between 3×10^5 Mc./sec. and 3×10^2 Mc./sec. The two important techniques for obtaining data on the dielectric properties of materials were (1) the resonant cavity method and (2) the reflection method. The first method involved the comparison of the resonant frequency of an empty cavity to the resonant frequency of the cavity partially or completely filled with a dielectric. The other method consisted of the reflection of electromagnetic waves from a dielectric or conductor and the measurement of the attenuation experienced by the reflected wave. In order to obtain a complete analysis of a dielectric material, the loss term, k'' in the expression for the complex dielectric constant $k^* = k' - jk''$, has to be known. It is directly proportional to the attenuation factor α_2 , as the following equation shows,

$$k'' = \frac{2 \alpha_2^2 \beta_2^2}{1/\lambda_f^2},$$

in which β_2 is the phase factor of the waves in the dielectric medium and λ_f is the wavelength in free space.

Of the two methods mentioned only the reflection method gives data for the loss term. As the aim of the work was (1) to derive a more suitable expression for the attenuation factor and (2) to investigate the effect of increased concen-

tration of dipolar solute on the calculated value of the dipole moment and the relaxation time, the reflection method was employed. The relaxation time is defined as the time in which the induced polarization decreases to $1/e$ of its original value.

Lebye (1) derived an equation for the polarization, $P(\omega)$, in terms of the index of refraction n , Boltzmann constant k , the absolute temperature T , Avogadro's number N_0 , the electric dipole moment μ , the relaxation time τ , the molecular weight of the solute m_0 , and the density of the solute per unit volume of solvent g .

$$P(\omega) = \frac{n^2 - 1}{n^2 + 2} \frac{m_0}{g} + \frac{4\pi N_0 \mu^2}{9kT (1 + j\omega\tau)}$$

This equation has been used in the calculation of the dipole moment of gases, liquids in the vapour state and dilute solutions of polar compounds in a nonpolar solvent. Generally, in the past the dipole moment determined from dilute solutions has been obtained by extrapolation to infinitely dilute solution of the plot of the polarization versus the mole fraction of solute. It has been noticed that the calculated values of the dipole moment decreased as the concentration of the solution was increased. A study was made of this observation, using dimethylaminoazobenzene, acetonitrile, tetrahydrofuran and tetrahydropyran, each in a benzene solution, a nonpolar solvent.

THEORY

In the treatment of the theory the following symbols will be employed, the subscript (1) referring to air as the medium and (2) referring to a dielectric in the waveguide.

\underline{E}	electric field intensity
\underline{H}	magnetic field intensity
$k^* = k' - jk''$	complex dielectric constant
k''	loss part of the dielectric constant
A_{r1}	amplitude of the reflected E-wave
A_{i1}	amplitude of the incident E-wave
B_{i1}	amplitude of the incident H-wave
$Z_1 = \frac{A_{i1}}{B_{i1}}$	characteristic impedance of the waveguide
$\gamma = \alpha + j\beta$	propagation factor
λ_1	wavelength in the air-filled waveguide
λ_2	wavelength in the dielectric-filled waveguide
λ_f	wavelength in free space
m_2	number of molecules of solute per unit volume of solvent
ω	angular frequency

From the work of Debye (1), dealing with the dielectric behavior of materials, and from the equations concerning electromagnetic waves traveling in two adjoining media, derived by Von Hippel (2), the working equations needed in the calculation of the dipole moment μ , and the relaxation time τ , were obtained.

Solutions to the electromagnetic wave equations

$$(1) \quad \nabla^2 \underline{E} = e^* \mu^* \frac{\partial^2 \underline{E}}{\partial t^2}$$

$$(2) \quad \nabla^2 \underline{H} = e^* \mu^* \frac{\partial^2 \underline{H}}{\partial t^2}$$

can be written in the form

$$(3) \quad \begin{aligned} E_1(x) &= e^{j\omega t} (A_{11} e^{-\gamma_1 x} + A_{r1} e^{\gamma_1 x}) \\ &= A_{11} (e^{-\gamma_1 x} + r_0 e^{\gamma_1 x}) e^{j\omega t} \end{aligned}$$

$$(4) \quad H_1(x) = \frac{A_{11}}{z_1} (e^{-\gamma_1 x} - r_0 e^{\gamma_1 x}) e^{j\omega t}$$

The ratio of the amplitudes, A_{11} and A_{r1} , defines the reflection coefficient

$$(5) \quad r_0 = e^{-2\phi} = \frac{A_{r1}}{A_{11}}, \text{ where } \phi = \rho + j\psi$$

The terminating impedance in medium 1 of the waveguide at the interface of the two media, $x = 0$, is defined as

$$(6) \quad Z(0) = \frac{E_1(0)}{H_1(0)} = z_1 \left[\frac{1 + r_0}{1 - r_0} \right] = z_1 \coth(\rho + j\psi).$$

The first minimum in the air-filled waveguide occurs at a distance x_0 from the interface. At this point the incident and reflected waves are 180° out of phase. It has been shown

by Von Hippel (3), that

$$(7) \quad \frac{V_{\min}}{E_{\max}} \equiv E = \tan \rho = \frac{\sin \left(\frac{\pi \Delta x}{\lambda_1} \right)}{\left(2 - \cos^2 \left(\frac{\pi \Delta x}{\lambda_1} \right) \right)^{1/2}},$$

where Δx is the width of the minimum to the double power points. It follows then from (6) and (7), that

$$(8) \quad Z(0) = Z_1 \left[\frac{\tanh \rho - j \cot \psi}{1 - j \tanh \rho \cot \psi} \right] = Z_1 \left[\frac{E - j \tan \beta_1 x_0}{1 - j E \tan \beta_1 x_0} \right]$$

The terminating impedance, $Z(0)$, written in terms of the parameter in medium 2, will be

$$(9) \quad Z(0) = Z_2 \left[\frac{e^{\alpha_2 d} - e^{-\alpha_2 d}}{e^{\alpha_2 d} + e^{-\alpha_2 d}} \right] = Z_2 \tanh \gamma_2 d,$$

where Z_2 is the characteristic impedance in medium 2, and d is the length of the medium 2. In a rectangular waveguide $\gamma_2^{(2)}$ equals $\alpha_2^{(2)}$. Combining (8) and (9) produces

$$(10) \quad \frac{\tanh(\alpha_2 + j\beta_2)d}{(\alpha_2 + j\beta_2)} = \frac{E - j \tan \beta_1 x_0}{\beta_1 (1 - j E \tan \beta_1 x_0)}$$

By trigonometric expansion

$$\tanh(\alpha_2 + j\beta_2)d = \frac{\tanh \alpha_2 d + j \tan \beta_2 d}{1 + j \tanh \alpha_2 d \tan \beta_2 d}.$$

Assuming negligible attenuation in medium 1 allows the approximation $\beta_1 = j\beta_1$. Then by cross-multiplying equation (10)

one obtains

$$(11) \quad j\beta_1(1 - j\epsilon \tan\beta_1 x_0)(\tanh\alpha_2 d + j\tan\beta_2 d) = \\ (\epsilon - j\tan\beta_1 x_0)(\alpha_2 + j\beta_2)(1 + j\tanh\alpha_2 d \tan\beta_2 d).$$

Equating real and imaginary terms respectively and solving for $\tanh\alpha_2 d$ in each case, from the real part one obtains

$$(12) \quad \tanh\alpha_2 d = \frac{\epsilon\alpha_2 + \beta_2 \tan\beta_1 x_0 + \beta_1 \tan\beta_2 d}{\beta_1 \epsilon \tan\beta_1 x_0 + \beta_2 \epsilon \tan\beta_2 d - \alpha_2 \tan\beta_2 d \tan\beta_1 x_0}$$

and from the imaginary part

$$(13) \quad \tanh\alpha_2 d = \frac{\beta_2 - \alpha_2 \tan\beta_1 x_0 - \beta_1 \epsilon \tan\beta_2 d \tan\beta_1 x_0}{\beta_1 - \alpha_2 \epsilon \tan\beta_2 d - \beta_2 \tan\beta_2 d \tan\beta_1 x_0}.$$

The attenuation factor remains the only unknown quantity, since the phase factors, β_1 and β_2 , are determined from λ_1 , λ_2 and d ; x_0 and Δx , in the expression for L , may be measured directly. Either one of the two equations can be solved for the attenuation factor by successive approximations. As it turns out, only (13) may be solved consistently with success for α_2 to obtain proper values. With the values of d used, equation (12) gives incorrect values of $\tanh\alpha_2 d$ greater than one, due to inaccuracy in measuring $\tan\beta_1 x_0$ and $\tan\beta_2 d$, which are only of minor importance in (13). Examples of this are the extreme cases for $\tanh\alpha_2 d$, for which $\tan\beta_2 d$ goes to infinity or zero.

Case I, $\tan\beta_2 d \rightarrow \infty$, results in

$$(12a) \quad \tanh \alpha_2 d = \frac{\beta_1}{\beta_2^2 - \alpha_2 \tan \beta_1 x_0}$$

and (13a)

$$\tanh \alpha_2 d = \frac{\beta_1 \beta \tan \beta_1 x_0}{\alpha_2 \beta + \beta_2 \tan \beta_1 x_0} \approx \frac{\beta_1 \beta}{\beta_2},$$

since generally $\alpha_2 \beta \ll 1$. Using representative numerical values, one obtains

$$(12a) \quad \tanh \alpha_2 d = \frac{1.4}{.26} > 1 \quad \text{and} \quad (13a) \quad \tanh \alpha_2 d = \frac{.14}{2.6} < 1.$$

Case II, $\tan \beta_2 d = 0$, results in

$$(12b) \quad \tanh \alpha_2 d = \frac{1 \alpha_2 + \beta_2 \tan \beta_1 x_0}{1^2 \tan 1 x_0} \approx \frac{2.6}{.14} > 1$$

and (13b)

$$\tanh \alpha_2 d = \frac{\beta_2 - \alpha_2 \tan \beta_1 x_0}{\beta_1} \approx \frac{.26}{1.4} < 1$$

As $\tan(y)$ varies from zero to infinity, as y varies from zero to 1.571, any error in the variables $\beta_1 x_0$ and $\beta_2 d$ results in an equal or greater error in the value of $\tan \beta_1 x_0$ and $\tan \beta_2 d$. Because of the way in which the terms in (12) are arranged, the various products of the terms are usually of the same order of magnitude, causing α_2 to depend on the accuracy of all the quantities. By contrast equation (13) usually reduces to an expression relatively independent of $\tan \beta_1 x_0$ and $\tan \beta_2 d$. Only in the range of values $\tan \beta_2 d \approx 1$, will equation

(12) produce values for the attenuation factor in agreement with those obtained from equation (13). Equation (12) should be ignored, because of the uncertainties in its usefulness and its dependence on the type of data, and one should concern himself only with equation (13). Even though no explicit restrictions need to be placed on the value of d , when (13) is used, for various sets and types of data, which depend on the dielectric under investigation, certain values of d are more suitable and convenient for calculations than others. This one has to determine from the data on hand as one goes along in the study of various compounds.

Expressions for $k' = e'/e_0$ and $k'' = e''/e_0$ in terms of the waveguide parameters can be obtained from equations (3) and (4) and the boundary conditions for rectangular waveguides. The magnetic field must be parallel to the walls of the waveguide and the tangential electric field must be zero. The propagation factor in free space can be written as

$$\gamma_1' = j\omega(e''\mu'')^{1/2}.$$

From these stated conditions the following expression can be worked out,

$$(14) \quad \gamma_1 = \left[\gamma_1'^2 + \left(\frac{m_a \pi}{a}\right)^2 + \left(\frac{n_b \pi}{b}\right)^2 \right]^{1/2} \\ = \left[-\omega^2 e'' \mu'' + \left(\frac{m_a \pi}{a}\right)^2 + \left(\frac{n_b \pi}{b}\right)^2 \right]^{1/2},$$

where a and b are the width and the height respectively of the waveguide cross-section. The integers, m_a and n_b , denote the

mode of propagation, indicating the number of half wave lengths along the respective side of the waveguide wall.

For wave motion to exist within the waveguide, the propagation factor must be complex or imaginary, requiring that

$$\omega \cong \frac{1}{e^* \mu^*} \left[\left(\frac{m_a \pi}{a} \right)^2 + \left(\frac{n_b \pi}{b} \right)^2 \right].$$

This implies a minimum allowable frequency, the cut-off frequency, for waves to be propagated in any particular waveguide. As the relative permeability is nearly unity for non-magnetic media, one obtains for the cut-off frequency, f_c ,

$$f_c (e^*)^{1/2} = \frac{1}{\lambda_c} = \left[\left(\frac{n_a}{2a} \right)^2 + \left(\frac{n_b}{2b} \right)^2 \right]^{1/2}.$$

Making use of the wave velocity, $v = f \lambda_f = (e_o \mu_o)^{1/2}$, the expression of the complex dielectric constant in terms of the waveguide parameters equals

$$(15) \quad \frac{e^*}{e_o} \cong k^* = \frac{(1/\lambda_c)^2 - (\gamma_1/2\pi)^2}{(1/\lambda_c)^2 + (1/\lambda_1)^2}$$

The real and imaginary parts equal

$$(16) \quad k' = \frac{(1/\lambda_c)^2 - \frac{\alpha_2^2 - \beta_2^2}{4\pi^2}}{(1/\lambda_c)^2 + (1/\lambda_1)^2}$$

$$(17) \quad k'' = \frac{2\alpha_2\beta_2}{(1/\lambda_c)^2 + (1/\lambda_1)^2}.$$

Debye (1) derived the following equation for the polarization at high frequencies

$$(18) \quad \epsilon(\omega) = \frac{k' - 1}{k' + 2} \frac{m_0}{g} = \frac{n^2 - 1}{n^2 + 2} \frac{m_0}{g} + \frac{4\pi N_0 \mu^2}{9kT(1 + j\omega\tau)}$$

Crawford (4) solved this equation for the dipole moment, obtaining

$$(19) \quad \mu^2 = \frac{9kT}{4\pi m_2} (R - P)(1 + Q^2)$$

$$R = \frac{(k'^2 + k' + k''^2 - 2)}{(k' + 2)^2 + k''^2}$$

$$I = \frac{3k''}{(k' + 2)^2 + k''^2}$$

$$P = \frac{n^2 - 1}{n^2 + 2}$$

$$Q = \frac{I}{R - P} = \omega\tau$$

Thus the relaxation time will be

$$(20) \quad \tau = \frac{I}{(R - P)\omega}$$

A simpler expression for the relaxation time can be obtained directly from the original Debye equations (1), starting with

$$(21) \quad k' = n^2 + \frac{k_0 - n^2}{1 + X^2} \quad k'' = \frac{k_0 - n^2}{1 + X^2} X$$

$$X = \frac{k_0 + 2}{n^2 + 2}$$

By combining the equations for k' and k'' and eliminating X ,

the expression for the relaxation time is derived as

$$(22) \quad z = \frac{k''^2}{k' - n^2} \frac{n^2 + 2}{(k_0 + 2)\omega}$$

This expression is preferred to equation (20), because the various values are not as often repeated, thus diminishing the propagation of error.

If one assumes that $\frac{k_0 + 2}{n^2 + 2} \approx 1$, then equations (21) reduce to

$$(23) \quad k' = n^2 + \frac{k_0 - n^2}{1 + (\omega\tau)^2} \quad k'' = \frac{k_0 - n^2}{1 + (\omega\tau)^2}$$

When $\omega\tau \rightarrow \infty$, $k'' = 0$ and $k' = n^2$. When $\omega\tau \rightarrow 0$, $k'' = 0$ and $k' = k_0$. For $\omega\tau = 1$, the loss will become a maximum.

$$k''_{\max} = \frac{k_0 - n^2}{2} \quad \text{and} \quad k'_{\max} = \frac{k_0 + n^2}{2}$$

By combining the equations (23), for k' and k'' , and eliminating $\omega\tau$, the equation of a circle can be obtained with radius equal to k''_{\max} and the center on the axis of reals at k'_{\max} .

$$(24) \quad \left[k' - \frac{k_0 + n^2}{2} \right]^2 + k''^2 = \left[\frac{k_0 - n^2}{2} \right]^2$$

When the experimental values are plotted, frequently the curve will not be a semi-circle, but will have either less or more

curvature. Cole (5) has proposed an empirical correction factor, $(1 - \alpha)$, which appears as an exponent in

$$k'' = n^2 + \frac{k_0 - n^2}{1 + j(\omega\tau)^{1-\alpha}}$$

When the center of the arc is below the horizontal axis, the angle between the line joining the center of the arc and the point $(k' = n^2, 0)$ will be $\alpha\pi/2$.

From the original Debye equations, (21), a theoretical expression for k_0 can be obtained by combining equations (21), eliminating $\omega\tau$, and by dividing k'' by $(k' - n^2)$. Then the static dielectric constant becomes

$$(25) \quad k_0 = k' + \frac{k''^2}{k' - n^2}$$

APPARATUS

The major part of the equipment consisted of a microwave circuit, oscilloscope and amplifiers, (see plate I). The microwave circuit included x-band waveguide of cross-section 2.285 cm by 1.016 cm, suitable for the transmission of electromagnetic waves over the frequency range of 8,200 Mc./sec. to 12,000 Mc./sec. The source of power was a type 2K25 klystron, frequency modulated by a sawtooth waveform from a sweep voltage of a 551 Tektronix dual-beam oscilloscope. A variable attenuator and a transmission cavity wavemeter were

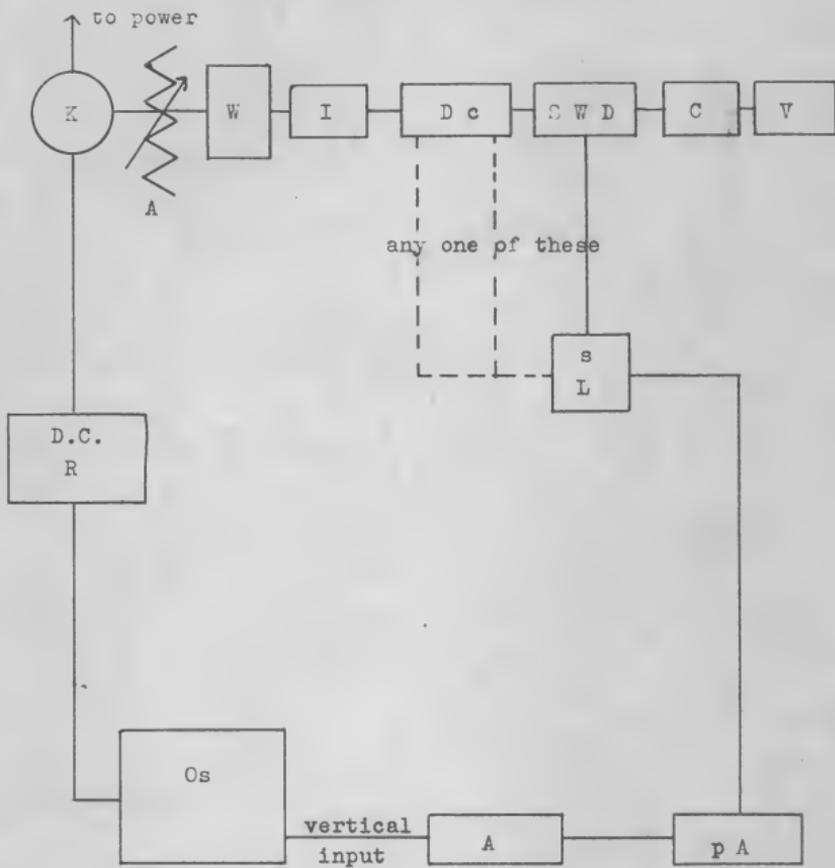
EXPLANATION OF PLATE I

General Microwave Circuit

K	2K25 klystron
A	Variable attenuator
W	Transmission cavity wave meter
I	Isolator
D c	Directional coupler
S W D	Standing wave detector
C	Dielectric sample cell
V	Vernier caliber and plunger drive mechanism
s L	Square-law 1N22 crystal detector
p A	Pre-amplifier
A	Amplifier
Os	Oscilloscope
D.C. R	D.C. restorer circuit

The square-law 1N22 crystal detector could be coupled to either end of the directional coupler to observe the reflected or incident wave.

PLATE I



connected in series with the klystron waveguide section. The attenuator was used to adjust the power output and to reduce the effect of the reflected wave on the klystron. The wavemeter consisted of a cylinder with one movable wall, to which a micrometer screw was connected. The wavemeter had been calibrated by the National Bureau of Standards. The operating frequency of 9,550 Mc./sec. corresponded to a wavemeter setting of 0.205 inches.

The isolator also helped to block out the reflected signal preventing it from returning to the power-source and interfering with the klystron performance. By means of the directional coupler it was possible to observe either the reflected or incident wave. The output from the directional coupler was 20 db. below the transmitted signal level.

The standing wave detector, Hewlett-Packard Model 809B, consisted of a slotted waveguide section into which an adjustable probe could be inserted, which fed the signal through a square-law 1N22 crystal detector and amplifiers to the oscilloscope for observation. The overall amplification of the signal by the amplifiers was approximately 10^5 .

The dielectric cell was sealed liquid tight at both ends, so that it could be placed in a horizontal position. One end was sealed off by a thin mica window, secured onto the waveguide flange with Fuller's adhesive, a milk-base liquid glue. This adhesive did not dissolve in benzene and could be washed off the flange with water. The adhesive dried to a thin film,

EXPLANATION OF PLATE II

Dielectric sample cell and plunger drive mechanism

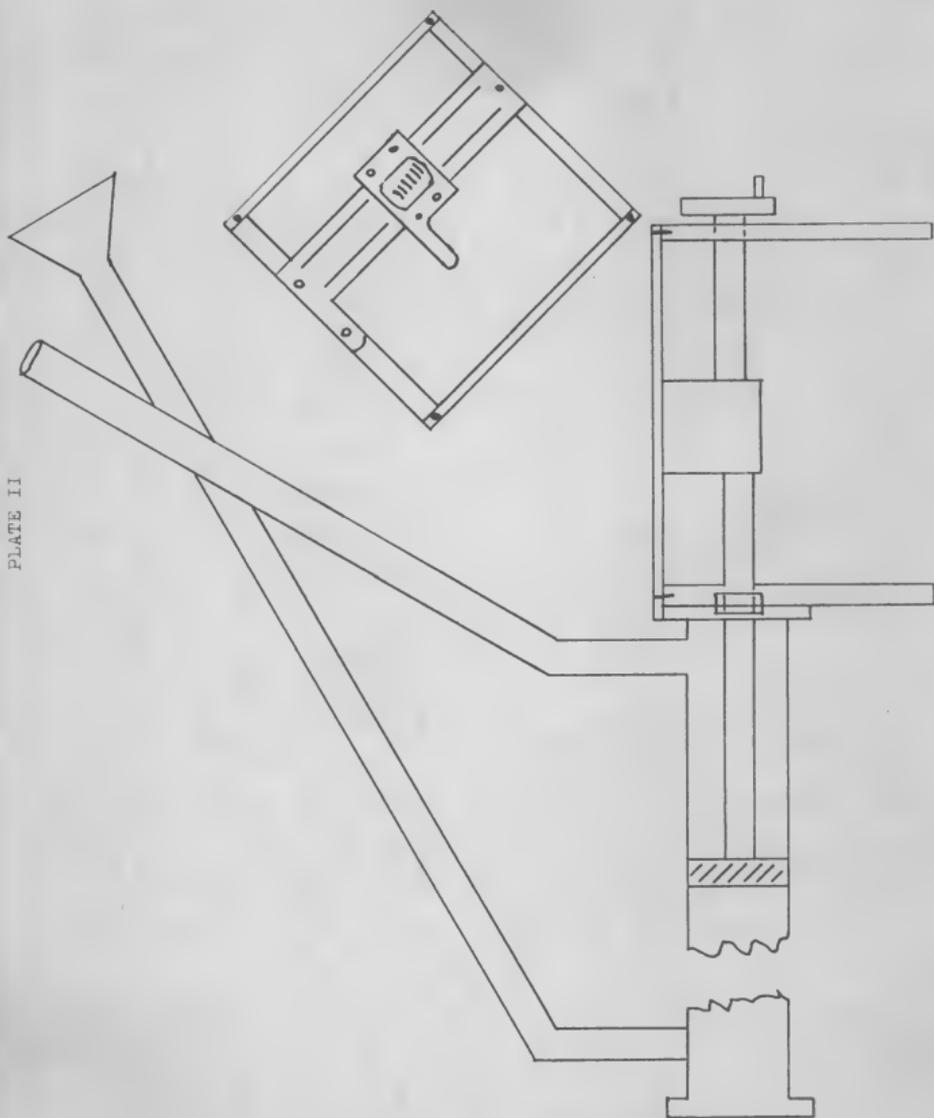


PLATE II

thus causing no objectionable discontinuity when the cell was coupled to the standing wave detector. The Teflon-adhesive initially used proved unsatisfactory, as it eventually dissolved in benzene, requiring frequent replacement of the mica window. The other end of the cell was sealed by a $3/8$ inch metal shaft sliding through an O-ring. To the metal rod a waveguide shorting section was attached causing a second reflection of the electromagnetic waves, contributing to the standing wave pattern. The other end of the shaft was connected to a vernier caliber and a drive mechanism to indicate the position of the short. (see Plate II)

At first an inferior type O-ring was used, which swelled up in benzene, braking the motion of the plunger. As a free motion of the plunger was essential for accurate settings, a better type O-ring, Goschen GRC27-8 larger in size and resistant to benzene, was obtained. It then became possible to use the equipment several hours at a time without braking action being introduced by the O-ring.

In order to fill the cell one had to hold it vertically, pouring the solution in slowly, to prevent air bubbles from remaining behind trapped in the liquid. It was impossible to accomplish this with the cell already in a horizontal position coupled to the standing wave detector.

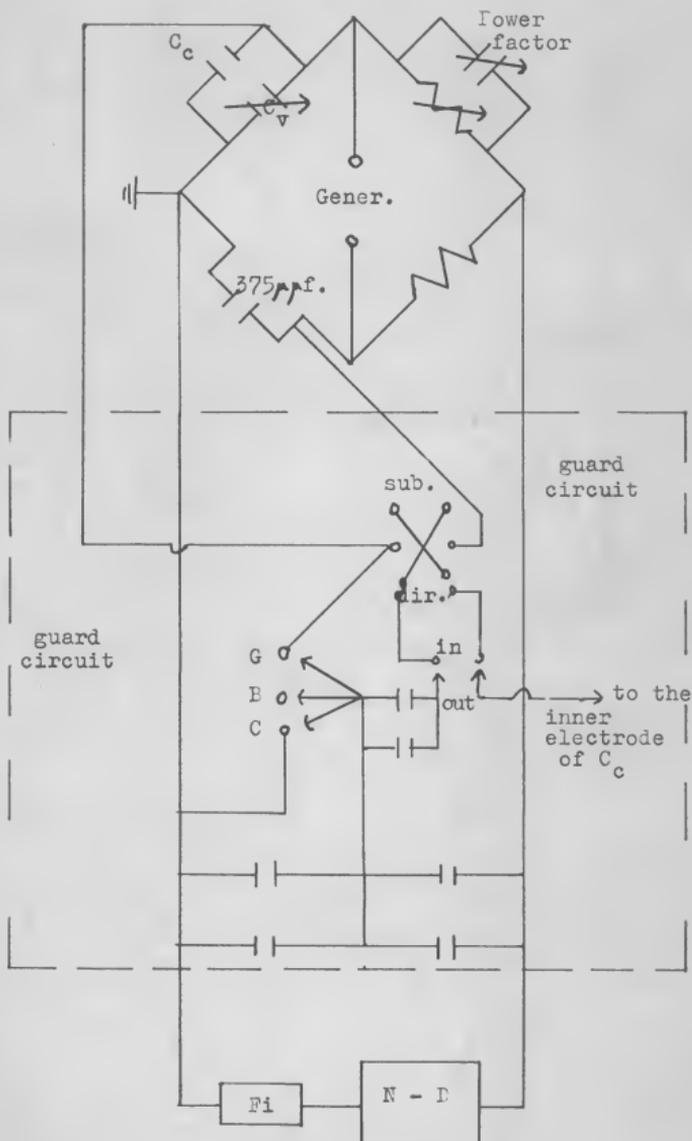
A cylindrical capacitor to be used in the determination of the dielectric constant at low frequencies was constructed from brass tubing. Guard rings were placed at the ends of the

EXPLANATION OF PLATE III

Capacitance Bridge and Guard Circuits

C_c	Cylindrical test capacitor
C_v	Variable bridge capacitor
sub.	Substitution method, for C_c less than $1000\mu\mu\text{f.}$
dir.	Direct method, for C_c greater than $1000\mu\mu\text{f.}$
in	connecting the guard circuit with the capacitance bridge
out	disconnecting the guard circuit
G	for balancing the guard circuit
B	for balancing the bridge circuit
C	for balancing the coupling circuit
Fi	Wave filter
N - D	Null-detector

PLATE III



inner electrode in order to eliminate fringe effects. The respective radii were 1.08 cm and 0.77 cm and the length of the inner electrode 13.60 cm. The measuring circuit, (see Plate III), included a General Radio type 716-A capacitance bridge, a type 716-F2 guard circuit, a null-detector, a type 1951- wave filter and a type 1330-A bridge oscillator. Because the capacitance of the cylindrical capacitor was only $31.0 \pm 0.5 \mu\text{f}$, the substitution method had to be used. An extensive system of grounding had to be arranged in order to eliminate A.C. pickup.

An Abbe refractometer was employed to measure the index of refraction of the various solutions.

PROCEDURE

Readings for λ_1 , λ_2 , x_0 and Δx were obtained with the microwave circuit. The wavelength in each medium was determined by locating the distance between successive nodes in the respective waveguide sections. The wave length in the air-filled part was found by shorting the slotted waveguide section and locating the nodes along it at positions x_n , which were expected to be $n\lambda_1/2$ cm from the electric short and occurring $\lambda_1/2$ cm apart. Because the zero point of the scale did not coincide with the position of the short, the values of x_n , the distance between the interface and the nth node, were slightly less than $n\lambda_1/2$. A correction factor of 0.030 cm was calculated and added to the readings taken along the standing

wave detector. The expression used in finding the correction factor could be written as

$$\frac{\sum_{n=4}^7 \frac{n\lambda_1}{2} - x_n}{4}$$

The integer n ran from four to seven, as those were the multiples of $\lambda_1/2$ that could be located along the standing wave detector.

The scale attachment to the plunger movement also required calibration. The empty sample cell was coupled to the standing wave detector and the plunger set for zero reading of the vernier caliber. Then the nodes along the standing wave detector were located at the positions x'_n . The correction factor to be added to the plunger setting in order to find the sample thickness was

$$\frac{\sum_{n=4}^7 x_n - x'_n}{4},$$

with x_n defined as above. The correction factor for the sample length was not a constant, because the cell was taken apart periodically for cleaning and polishing. It would have been advantageous to have been able to construct the cell and the plunger movement, so that no correction factor would have been required, as it would have decreased the uncertainties in the value of the sample thickness by about 0.010 cm. The uncertainties in the correction factor and the plunger setting

added to produce an error of about 0.015 cm. in d .

After the cell was filled with about 50 ml of solution and connected to the rest of the microwave circuit, the wavelength in the dielectric was determined. Generally, the probe and the crystal detector were coupled to the directional coupler to pick up the signal from the reflected wave only. Thus any phase effect due to interaction between the incident and reflected waves would have been omitted, providing more precise readings for λ_2 . However, as it turned out, the solutions caused high enough loss to decrease the height of the pulse on the oscilloscope making it difficult to locate the nodes accurately. The standing wave detector gave a pulse, whose height varied from a minimum of 0.10 cm to a maximum of 5.00 cm, but when the detector was connected to the directional coupler, the pulse height varied by not more than 0.20 cm over the same range. By leaving the probe on the standing wave detector and then changing the plunger position to successive nodes in the cell, readings for λ_2 were obtained. The pulse on the oscilloscope varied enough in height as the plunger was moved a distance of a quarter wavelength that it was possible to pinpoint the position of the nodes of the standing waves.

The wavelength λ_2 was determined for pure benzene having first the square-law detector coupled to the directional coupler and then to the standing wave detector. The values for the wavelength by either method were identical, indicating that either approach could be used for low loss solutions.

After the wavelength in the dielectric had been determined, the plunger was left at some arbitrary position and nodes along the slotted waveguide were located at x_n'' . Δx was determined by locating on either side of x_n'' points for which the signal displayed on the oscilloscope was twice the minimum. It was noted that the pulse at a minimum varied in height from 1.0 cm to 0.1 cm when d approached values of odd multiples and even multiples of $\lambda_2/4$, respectively. The pulse also showed variation with loss in the dielectric medium, increasing with loss when d approached even multiples and decreasing for odd multiples of $\lambda_2/4$. For very dilute and low loss solutions it was difficult to determine Δx accurately because the pulse was very low. When the vertical gain on the oscilloscope was turned up, high frequency noise pattern blanketed out the desired signal.

Of the two following equations, that one which produced a positive value was used to determine x_0 , the distance from the interface to the first minimum in medium 1.

$$x_0 = \frac{\sum_{n=4}^7 x_n'' + 0.03 - \frac{n\lambda_1}{2}}{4} \quad \text{or} \quad x_0 = \frac{\sum_{n=4}^7 x_n'' + 0.03 - \frac{(n-1)\lambda_1}{2}}{4}$$

The dielectric constant of the solutions was determined at 400 cps. using a General Radio type 716-A capacitance bridge and a guard circuit, (see Plate III). The values for the dielectric constant at 400 cps. were to be approximately equal to k_0 , the static dielectric constant. The ratio of the capacitances of the cylindrical capacitor filled with dielectric and air, equaled the dielectric constant. From equation (25)

k_0 was determined and when compared with the experimental results showed a deviation of about one percent.

CALCULATION

The general order of the calculation is summarized for convenience. The phase factors were determined from their definitions $\beta_2 = 2\pi/\lambda_2$ and $\beta_1 = 2\pi/\lambda_1$. When Δ was less than 0.10, it was determined from $\Delta = \pi\Delta x/\lambda_1$. Otherwise, equation (7)

$$E = \frac{\sin \frac{\pi \Delta x}{\lambda_1}}{\left[2 - \cos^2 \frac{\pi \Delta x}{\lambda_1} \right]^{1/2}}$$

had to be used. The attenuation term was calculated from equation (13)

$$\tanh \alpha_2 d = \frac{E\beta_2 - \alpha_2 \tan \beta_1 x_0 - \beta_1 E \tan \beta_2 d \tan \beta_1 x_0}{\beta_1 - \alpha_2 \tan \beta_2 d - \beta_2 \tan \beta_1 x_0 \tan \beta_2 d}$$

Then k' and k'' were evaluated from (16)

$$k' = \frac{1/\lambda_c^2 - \frac{\alpha_2^2 - \beta_2^2}{4\pi^2}}{1/\lambda_c^2 + 1/\lambda_1^2} \quad \text{and (17)} \quad k'' = \frac{2\alpha_2\beta_2}{1/\lambda_c^2 + 1/\lambda_1^2},$$

where at an operating frequency of 9,350 Mc./sec. and $\alpha_2^2 < 0.001$ these equations became

$$k' = \frac{0.04849 + 1/\lambda_2^2}{0.09722} \quad \text{and} \quad k'' = \frac{\alpha_2\beta_2}{1.920}$$

The number of molecules of solute per unit volume of solution, m_2 , was determined from $m_2 = N_0 E/m_0$, where N_0 was Avogadro's

number, m_0 the molecular weight of the solute and g the mass in grams of solute per unit volume of solvent, appearing in the equation for μ , equation (19)

$$\mu^2 = \frac{9kT}{4\pi m_2} (R - P)(1 + Q^2),$$

where m , P and Q were defined on page 10.

The relaxation time τ was calculated from (22)

$$\tau = \frac{k''^2}{k' - n^2} \left[\frac{n^2 + 2}{(k_0 + 2)\omega} \right]$$

The results for τ varied by about 1.0% from values determined from equation (20). The value of k_0 in equation (22) was found either experimentally or was determined from (25).

REGULAR

Following is a table showing the pertinent data and the results as obtained for the chemical compound dimethylaminoazobenzene used in solution with the nonpolar solvent benzene.

Table 1. Results of the electric dipole moment and the relaxation time.

Mole fraction	$^{\circ}\text{C}$	k'	$\tan\delta = \frac{k''}{k'}$	α_2	d cm	$\lambda_2/4$ cm	μ debye	$\tau_{10} \cdot 10^{-11}$ sec.
.0059	22.6	2.308	.012	.023	5.829	9.77	2.68	1.1
.0069	21.1	2.296	.015	.026	1.689	2.82	2.51	1.8
	24.1	2.293	.012	.020	5.830	9.73	2.36	1.9
.0078	24.0	2.323	.012	.020	5.830	9.82	2.32	1.1
	23.9	2.320	.010	.016	8.359	14.10	2.15	0.9
.0098	26.6	2.310	.013	.022	5.870	9.78	2.03	1.7
	22.3	2.328	.008	.014	5.630	9.63	2.14	2.2
.0117	23.9	2.342	.017	.029	1.689	2.86	2.29	1.1
	24.1	2.318	.014	.023	5.830	9.80	1.95	1.7
	23.6	2.323	.019	.032	5.829	9.81	2.29	2.1
.0136	24.0	2.337	.013	.022	5.829	9.85	1.98	1.1
	23.6	2.334	.016	.028	5.829	9.85	2.00	1.3
.0193	22.5	2.351	.021	.035	5.830	9.90	1.55	1.4
	19.0	2.361	.025	.043	5.870	10.00	2.05	1.4

RESULTS

Table 2. Results of the dipole moment and the relaxation time.

Mole fraction	°C	k'	$\tan\delta = \frac{k''}{k'}$	α_2	d cm.	$\lambda_D/4$ cm.	μ debye	$\tau_{10^{-12}}$ sec.
<u>Acetonitrile</u>								
.0178	27.4	2.438	.058	.100	2.368	4.11	3.35	11.7
	21.2	2.538	.053	.092	5.750	10.25	3.60	10.1
	23.4	2.443	.051	.087	6.350	11.04	3.20	10.2
<u>Tetrahydrofuran</u>								
.0172	17.7	2.361	.013	.022	3.540	6.02	2.20	4.1
	18.2	2.361	.006	.010	7.622	12.97	2.21	1.9
	17.4	2.365	.012	.021	6.180	13.94	2.26	3.7
	18.2	2.365	.006	.011	8.755	14.92	2.22	1.9
.0338	24.8	2.393	.010	.018	6.864	11.78	1.64	3.9
	25.2	2.391	.010	.016	9.809	16.98	1.76	2.5
	24.8	2.393	.014	.023	10.379	17.82	1.62	3.6
<u>Tetrahydropyran</u>								
.0086	21.3	2.308	.003	.006	11.321	19.00	2.28	2.0
	20.9	2.308	.005	.008	11.917	20.00	2.30	3.0
.0148	22.9	2.334	.009	.015	7.102	8.00	2.16	3.9
	28.1	2.330	.016	.028*	7.193	8.15	2.21	6.9
	28.4	2.376	.017	.029*	7.348	8.56	2.17	5.1
	28.1	2.331	.007	.011	7.701	9.06	2.14	2.8

* A possible error of about 0.02 in the value of Δx .

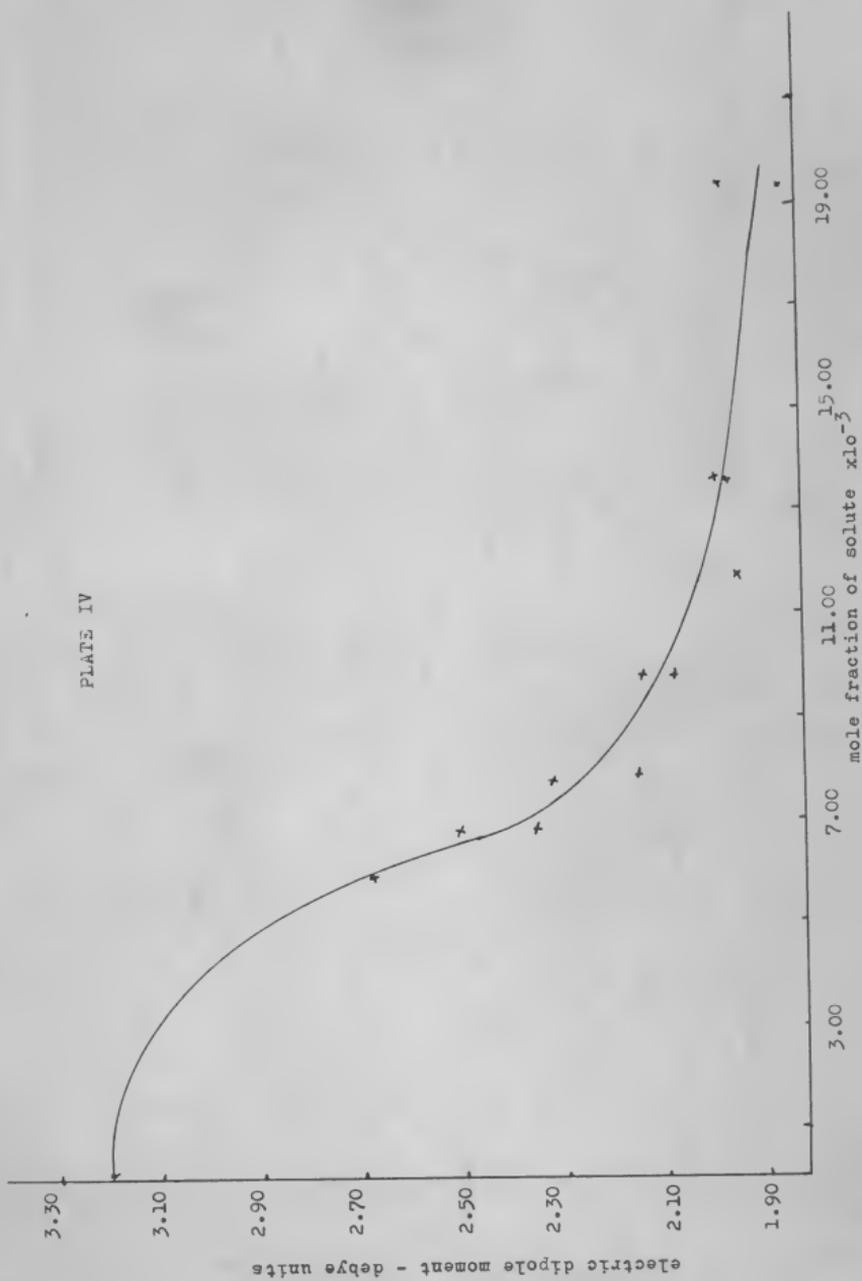
EXPLANATION OF PLATE IV

Dimethylaminoazobenzene

Electric dipole moment in units of debye
versus mole fraction of solute



PLATE IV



EXPLANATION OF PLATE V

Lebye plot

Plot 1

$$k_0 = 2.367$$

$$k_\infty = 2.289$$

$$k' = 2.334$$

$$k'' = 0.0383$$

$$\alpha = 0$$

Plot 2

$$k_0 = 2.340$$

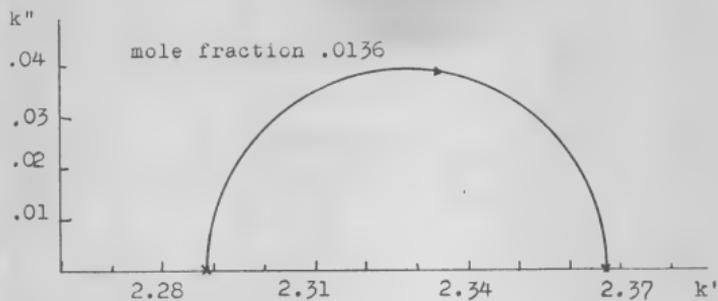
$$k_\infty = 2.268$$

$$k' = 2.230$$

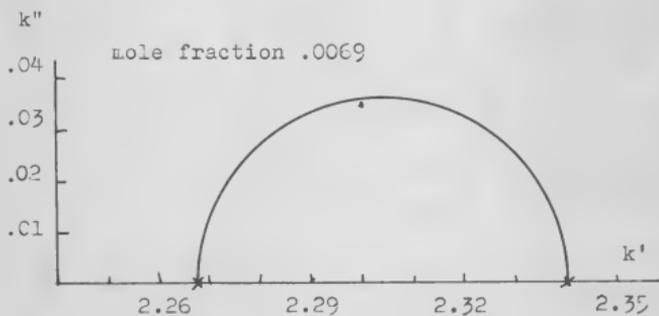
$$k'' = 0.0350$$

$$\alpha = 0$$

LATE V



dimethylaminoazobenzene



EXPLANATION OF PLATE VI

Lebye plot

Plot 1

$$k_0 = 2.439$$

$$k_{\infty} = 2.238$$

$$k' = 2.361$$

$$k'' = 0.0306$$

$$\alpha = 0.623$$

Plot 2

$$k_0 = 2.599$$

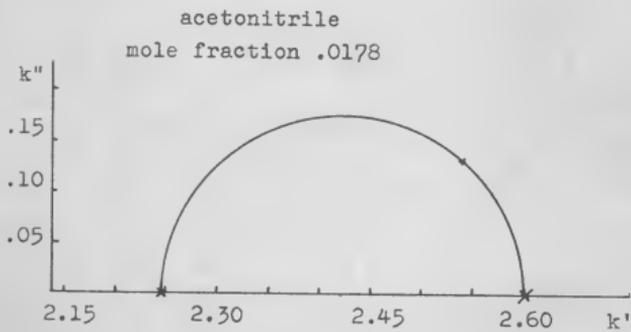
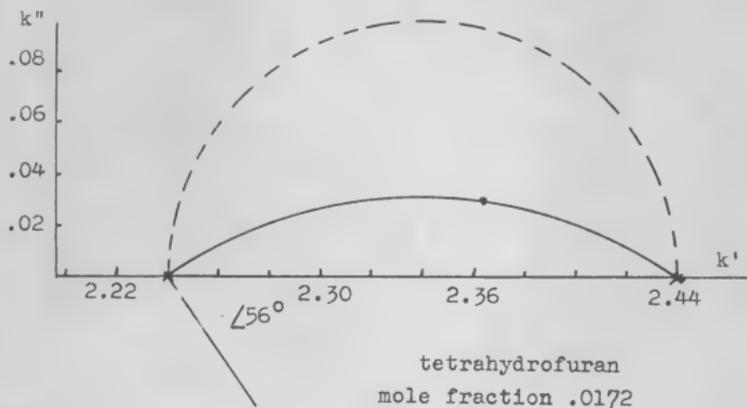
$$k_{\infty} = 2.244$$

$$k' = 2.538$$

$$k'' = 0.134$$

$$\alpha = 0$$

PLATE VI



DISCUSSION

Published values of the electric dipole moment have, generally, been determined from data extrapolated to infinitely dilute solutions. In these extrapolations the temperature has either been kept constant or varied in large steps of 20°C or so. Enough data for dimethylaminoazobenzene were gathered to be able to extrapolate the dipole moment to infinitely dilute solutions, obtaining a value of 3.10 debye. Campbell (6) gives a value of 3.22 ± 0.15 debye, thus showing satisfactory agreement.

The moment values for tetrahydrofuran and tetrahydropyran, as calculated by equation (19), did not agree with the published values, 1.64 (7) and 1.70 (8) for tetrahydrofuran and 1.94 (7) for tetrahydropyran. As no error could be found in the data nor in the calculations, some other explanation had to be found to explain the difference in the results. The discrepancy can be explained by assuming the presence of a positive solvent effect. Generally, the observed dipole moment for a chemical compound in solution is smaller than that for the vapour state by a factor between 0.9 and 0.7. At times, though, the opposite is true. The increased value of the dipole moment for the chemical in solution is explained as due to a positive solvent-solute interaction. It is here assumed that as the concentration increased, the dipole-dipole interaction appeared and gradually canceled the positive solvent effect decreasing the value of μ . As only a small amount of purified tetrahydrofuran

was available, no other concentrations could be made. Data of solutions at other concentrations will be needed in order to gain a better understanding of the solvent effect. It might prove fruitful to use also other solvents, as for example dioxane, n-heptane and carbon tetrachloride, and note the variation in k' , k'' , ν and τ .

The calculated relaxation time for acetonitrile was about four times as large as the value 2.8×10^{-12} sec. cited by Le Fevre (9). He used carbon tetrachloride as the solvent and a solution of mole fraction 0.00485 compared to 0.0178 as used by the author. The calculated moments, 3.20 to 3.60 debye, compared with the range of values 3.11 to 3.50 debye given by Le Fevre (9). In order to explain the variation in the two values for the relaxation time, it is assumed that the type of solvent used effected the value of the relaxation time. This assumption seems valid in view of the fact that the moment values have been found to vary with the type of solvent.

Most of the sets of calculated values of τ showed large fluctuation, the greatest being exhibited by the values for tetrahydrofuran. The values for dimethylaminoazobenzene seemed more consistent and showed a slight increase with concentration. No published values of τ for dimethylaminoazobenzene could be found. Holland and Smyth (8) give a value of 2.9×10^{-12} sec. measured at 5 Kc./sec. for tetrahydrofuran, which agrees in order of magnitude with the obtained values.

The fluctuations in the values of τ could be traced back

to corresponding variations in α_2 . The attenuation factor is expected to be a constant of the medium within the waveguide, independent of the sample length. However, it was observed that the calculated attenuation factor varied with $n\lambda_2/4$. The attenuation assumed large values, about 0.025, when evaluated from data obtained for the sample length equal to an even multiple of $\lambda_2/4$ and small ones, about 0.013, when evaluated at odd multiples of $\lambda_2/4$. These values seemed to vary with the integer n , apparently approaching a constant value of attenuation as n became large. Thus the relaxation time, directly proportional to k'' and α_2 through the equations (22) and (17), oscillated between extremes depending on the sample length. The extent of the variations in α_2 and ρ varied with the solute and was not always of the same magnitude. The variation of α_1 appeared to be caused by uncertainties in Δx , as explained on pp 25. Tetrahydrofuran and tetrahydropyran showed the largest fluctuation, believed to be closely related to the loss in the solution. Eventhough a large mole fraction of solute was used in the solutions of tetrahydrofuran and tetrahyropyran, which should have produced a large pulse height, the pulse height at a minimum, for $d = \lambda_2 n_{\text{even}}/2$, was extremely small, introducing error in Δx and ρ , thus also in α_2 . Some improvement could be achieved by increasing the number of significant figures in the readings of λ_1 , λ_2 , x_0 and Δx .

Cole (5) has made a study of the dielectric constant as a function of temperature. The temperature coefficient of the

dielectric constant is on the average about 0.003 units per degree. The values for the Debye plots, plates V and VI, were not temperature corrected, as the exact variation of k' and k'' with temperature was unknown, and as the corrections were at most of the order of the uncertainties of the measurements of k' and k'' . The Debye plots were accurate to within 2% and could have been improved not only by decreasing the uncertainties, but also by adding to the curves points for the values of k' and k'' at higher frequencies. By using only the minimum number of three points to draw the curves, the shape of the curves was approximate and might have turned out slightly different if more points had been plotted. Different microwave equipment would have to be set up in order to evaluate k' and k'' at higher frequencies.

Accurate plots are useful in the study of dielectrics, because a one to one correspondence exists between values of k' , k'' and the frequency. Cole (5) and Poley (10) have made use of the Debye plots in different ways. Cole drew curves using values of k' and k'' , which had been obtained by various workers, showing that discrepancies existed between the sets of the results, while the values by the same person were consistent within themselves. This shows the limitation in the preciseness of the plots. Poley studied the value of k' for nitrobenzene in the high frequency region of the Debye plot and noticed that the point of intersection, $(k_0, 0)$, of the curve and the k' axis did not agree with the other points in prescribing a circular arc. By Maxwell's relation of $n^2 = k_0$

k_0 would have been 2.43, but from the construction of a smooth arc a value of 4.07 was determined. The inequality of $n^2 = k_0$ would effect the calculated values of μ and τ , since the value of n^2 was substituted for k_0 in the respective equations pertaining to μ and τ . It can be seen from the Lebye plots in this particular case, (see plates V and VI), that k_0 could not have been much greater than n^2 and therefore the approximation $k_0 = n^2$ would have remained sufficiently accurate within one or two percent.

With a temperature bath built around the dielectric cell, an exact study of the dependence of k' , k'' and τ on the temperature could be made and a more accurate determination of the dependence of k' , k'' and τ on the concentration of the solution performed. Also one could calculate μ from a plot of the polarization, $P(\omega)$, versus $1/T$.

In order to be able to use successfully solutions of high concentration, one will have to find out whether or not the increased loss causes unsymmetric, distorted standing waves. For low loss materials the location of a node was well-defined, but became more uncertain with the increase in loss. For more concentrated solutions the value of Δx increased as it was determined further away from the interface of the two media. An increase in Δx was also observed when readings were taken at intervals of about twenty minutes, this indicating an increase in the loss, probably due to some heating effect.

Values of k' for tetrahydrofuran and mole fraction 0.0172

were found to be larger by 0.01 when compared to results given by Smyth (11). This small discrepancy could have been caused by experimental error in the two compared values. Otherwise it could be an indication, since k' is inversely proportional to λ_2 , that the technique used in measuring λ_2 , was valid for very low loss solutions only, but introduced slight inaccuracies in the value of λ_2 for the more concentrated solutions. The concentrations, at which the error in λ_2 becomes appreciable, would depend upon the compound used. It was also noted that the pulse height at a node in the air-filled waveguide was greater for a sample length of odd multiples of $\lambda_2/4$ than for even multiples. The observation that this had to occur in order to keep α_2 sufficiently constant gives no explanation as to the cause of the variation in pulse height. That α_2 did not remain constant in the work would indicate that the measured value of Δx was either too small in the case of d equal to odd multiples of $\lambda_2/4$ or too large in the case of d equal to even multiples of $\lambda_2/4$.

These observations should all be investigated more thoroughly in order to determine to what extent they influence the results pertaining to the dielectrics. One feels that the results compare on the whole in accuracy with that attained by other workers in the microwave region of the frequency spectrum.

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INVESTIGATION OF THE DIPOLE MOMENT AND RELAXATION
TIME OF ORGANIC MOLECULES

by

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AN ABSTRACT OF A THESIS

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At microwave frequencies the propagation factor provided information for the determination of the complex dielectric constant, $k^* = k' - jk''$, which then could be used to evaluate the electric dipole moment μ , and the relaxation time τ , of polar compounds in solution. Special attention was given to any possible dependence of the values of μ and τ on the concentration of the solutions. Diethylaminoazobenzene, acetonitrile, tetrahydrofuran and tetrahydropyran were dissolved in benzene at various concentrations, and the variation in the dielectric constant, the dipole moment and the relaxation time was studied.

The dielectric was retained in a liquid-tight waveguide, which was terminated by a shorting plunger, causing standing waves to be set up in the air- and dielectric-filled waveguide sections. The propagation factor, $\gamma = \alpha + j\beta$, was determined for the two media, where β , the phase factor, was evaluated from the wavelength λ according to $\beta = \frac{2\pi}{\lambda}$. Since no suitable, explicit expression for α_2 , the attenuation factor in the dielectric, existed an equation had to be worked out, the result being,

$$\tanh \alpha_2 d = \frac{E\beta_2 - \alpha_2 \tan \beta_1 x_0 - \beta_1 E \tan \beta_2 d \tan \beta_1 x_0}{\beta_1 - \alpha_2 E \tan \beta_2 d - \beta_2 \tan \beta_1 x_0 \tan \beta_2 d}$$

which was solved for α_2 by successive approximations.

The dipole moment was determined from a modified expression of the polarization.

$$P(\omega) = \frac{k^* - 1}{k^* + 2} \frac{m_0}{g} = \frac{n^2 - 1}{n^2 + 2} \frac{m_0}{g} + \frac{4\pi N_0 \mu^2}{9kT(1 + j\omega\tau)}$$

The relaxation time was calculated from the expression

$$\tau = \frac{k''^2}{k' - n^2} \left[\frac{n^2 + 2}{(k_0 + 2)\omega} \right].$$

The plot of k' versus k'' produced either a semi-circle with radius $\left[(k_0 - n^2)/2 \right]$ and the center at $\left[(k_0 + n^2)/2, 0 \right]$ or an arc with the same end points on the horizontal k' axis, but with the center of the curve below the k' axis. The results for the complex dielectric constant were fitted to the curve, enabling one to establish reliability of the experimental values of k^* . The value of the dipole moment was found to decrease with the increase in concentration for each compound studied. As seen from the results obtained for dimethylaminoazobenzene, the dipole moment approached a limiting value after an initial large decrease. The relaxation time showed a slight increase in value with concentration, and seemed to depend upon the solvent used.

The uncertainty in the dipole moment values was about 2%, and was caused by limiting conditions of the measuring equipment and temperature control.