MICROWAVE MEASUREMENTS OF THE ELECTRIC DIPOLE MOMENT AND OTHER DIELECTRIC PROPERTIES OF SOME ORGANIC COMPOUNDS

BY

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INTRODUCTION

In recent years microwave frequencies have been used extensively for making physical measurements, such as measuring the complex dielectric constant and loss tangent of materials. Most of this work has been done with resonance cavity measurements and some by measurements of reflection properties.

Some of the original experiments using the latter method were made by Roberts and von Hippel (13) using cylindrical wave guide. In this work it was shown that the complex dielectric constant of a material could be determined by measurements of the standing wave in front of the dielectric of known thickness, from which a high frequency electromagnetic wave had been reflected. Variations and refinements of the method of Roberts and von Hippel have been used by several workers (3)(4)(7)(9)(10)(15). Most of these works were aimed at either simplifying the mathematical calculations or improving the experimental techniques.

The theory developed by Debye (5) showing the functional relationship between the complex dielectric constant, the electric dipole moment, and the relaxation time has been used (3)(7) to determine the latter two quantities from the complex dielectric constant. These quantities are of particular interest to the chemists in the study of molecular structure.

The method described in this paper is a variation of the theory of Roberts and von Hippel. An electronic digital computer[1] is used for the solution of the impedance equations, then for the calculation of the complex dielectric constant, the electric dipole moment, and the relaxation time.

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[1] The computer used is an IBM Type 650 Magnetic Drum Data Processing Machine with floating decimal arithmetic and index registers.

This method requires fewer measurements and fewer approximations than the methods used by some workers (3)(7). The method allows any thickness of dielectric to be used, elminates the necessity for approximations in making calculations, and saves much calculation time. A statistical treatment of data, which would be prohibitive with hand calculations, is made possible by using this method.

THEORY

In general, when a wave strikes an interface between two media, the wave will be partially or totally reflected. This results in a standing wave pattern being set up in the first medium. In particular, when high frequency electromagnetic waves being propagated in the positive X direction in an air filled wave guide (medium 1) strike the surface of a dielectric (medium 2) at $x = 0$, a partial reflection occurs. If in addition, the dielectric is terminated by a metal short which causes total reflection at $x = d$, a standing wave pattern is set up in both media.

By expressing the intrinsic impedance at $x = 0$, that is the terminating impedance, first in terms of the dielectric parameters of medium 1 and then in terms of those of medium 2, Roberts and von Hippel (13) obtained the following relation.

$$\frac{\tanh \gamma_2 d}{\gamma_2 d} = \frac{1}{\gamma_1 d}\left[\frac{(E_{min}/E_{max}) - j\tan\beta_1 x_0}{1 - j(E_{min}/E_{max})\tan\beta_1 x_0}\right] \qquad (1)$$

The notation used here and throughout this paper is: β, the phase factor; x_0, the magnitude of the distance from the interface to the first mimimum of the electric field in the air filled quide; d, the thickness of the dielectric; γ, the propagation factor; and E_{min}/E_{max}, the inverse voltage standing wave ratio in the air filled quide. The subscripts refer to the medium. The phase factor, in terms of the wave length, is given by $\beta = 2\pi/\lambda$. The propagation factor is expressed in terms of the attenuation factor, α, and the phase factor by the relation $\gamma = \alpha + j\beta$. It may be assumed that no loss occurs in the air filled wave guide. Thus $\alpha_1 = 0$ and $\gamma_1 = j\beta_1$.

Major (12) showed that the inverse standing wave ratio may be expressed as

$$\frac{E_{min}}{E_{max}} = \frac{\sin \pi \Delta x/\lambda_1}{[(E(x_1)/E_{min})^2 - \cos^2 \pi \Delta x/\lambda_1]^{\frac{1}{2}}} \qquad (2)$$

where $x_1 = x_{min} \pm \Delta x/2$, x_{min} being the position of E_{min}. The ratio of the power at x_1 to that at x_{min} is $P_1/P_{min} = (E(x_1)/E_{min})^2$. If $P_1/P_{min} = 2$, the denominator of equation (2) becomes $[1 + \sin^2 \pi \Delta x/\lambda_1]^{\frac{1}{2}}$.

Suppose the field is being sampled by a detector of response law n. If the ratio of the voltage signal from the detector at x_1 to that at x_{min} is K, it can be shown that the power ratio is given by $P_1/P_{min} = K^{2/n}$. If, for convenience, one chooses $K = 2$, then $P_1/P_{min} = 4^{1/n}$. Equation (2) then becomes

$$\frac{E_{min}}{E_{max}} = \frac{\sin \pi \Delta x/\ _1}{[(4^{1/n} - 1) + \sin^2 \pi \Delta x/\lambda_1]^{\frac{1}{2}}} \qquad (3)$$

From the analysis of the propagation of a wave in a dielectric medium, one can determine the complex dielectric constant, k*, in terms of the propagation factor, the cutoff wave length, λ_c, and the free space wavelength, λ_f. Assuming a non-magnetic medium, Crawford (3) expressed the following relation.

$$k^* = k' - jk'' = \frac{(1/\lambda_c)^2 - (\gamma_2/2\pi)^2}{(1/\lambda_f)^2} = \frac{(1/\lambda_c)^2 - (\gamma_2/2\pi)^2}{(1/\lambda_c)^2 + (1/\lambda_1)^2}$$

Solving this equation for the real and imaginary parts of the dielectric constant, k' and k'' respectively, one obtains:

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

Thus, both the real and imaginary parts of the dielectric constant can readily be obtained if one knows the attenuation factor and the phase factor, λ_c and λ_f being readily determined quantities.[1]

The generalization of the Debye theory (5) for the mean molecular moment due to permanent dipoles to include high frequency effects gives

$$\frac{k^* - 1}{k^* + 2} = \frac{k_\infty - 1}{k_\infty + 2} - \frac{4\pi\mu^2 n}{9KT(1 + j\omega\tau)}.$$

The complex dielectric constant at very high frequencies, k_∞ is assumed to be given by $k_\infty = N^2$, where N is the index of refraction at optical frequencies. The average dipole moment is μ, the number of molecules per ml is n, K is the Boltzman constant, T the absolute temperature, ω the angular frequency and τ the relaxation time.

Crawford (3) solved this equation and obtained

$$\left.\begin{array}{l} \mu^2 = \dfrac{9KT(R - P)\{1 + [I/(R - P)]^2\}}{4\pi n} \\ \text{and} \qquad \tau = \dfrac{I}{\omega(R-P)} \\ \text{where} \qquad R = \dfrac{k'^2 + k' + k''^2 - 2}{(k' + 2)^2 + k''^2}, \\ I = \dfrac{3k''}{(k' + 2)^2 + k''}, \qquad P = \dfrac{N^2 - 1}{N^2 + 2}. \end{array}\right\} \quad (5)$$

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[1] In a rectangular wave guide of width a, $\lambda_c = 2.000$ a (16). $\lambda_f = C/f$, C being the velocity of light and f the frequency used.

From these relationships the magnitude of the average electric dipole moment of a material may be determined if k*, N, T, and n are known. k* can of course be determined from α_2 and β_2.

SOLUTION OF EQUATIONS

The solution of equation (1) is needed to give γ_2 in terms of readily measured quantities. Though graphical solutions of the equation were used in some of the original works, the accuracy of this method is not too great and the range of values of γ_2 and d are limited unless one has access to a great supply of graphs. Crawford (3) and Hering (7) simplified the solution by setting d equal to a multiple of $\lambda_2/4$. At these positions $\tanh\gamma_2 d$ reduces to a real quantity and a relatively simple equation results.

There are two principal objections to the latter method. It greatly limits the thickness of the dielectric that can be used. The method requires a very accurate determination of λ_2 and the accurate setting of d to a multiple of $\lambda_2/4$. This accurate fixing of d is very difficult to do physically.

If d is equal to an odd multiple of $\lambda_2/4$, $\tan\beta_1 x_0$ becomes infinite. This property can be used to help in the solution only if d is accurately set to $n\lambda_2/4$, n odd. If d is equal to an even multiple of $\lambda_2/4$, $\tan\beta_1 x_0 = 0$, but again if this is not very accurately determined, $\tan\beta_1 x_0$ may be either positive or negative. A slight error in one direction will give data for which no solution exists. For these reasons multiples of $n\lambda_2/4$, especially for n even, should be avoided if possible.

It is apparent that the best method of solving the equation is a method of successive approximation or iteration. This, however, would be prohibitive with hand computation. This then suggests the use of an electronic computer for the solution.

The exact method of solution used is as follows. To simplify the right side of equation (1) let

$$\frac{-j}{\beta_1 d}\left[\frac{(E_{min}/E_{max}) - j\tan\beta_1 x_0}{1 - j(E_{min}/E_{max})\tan\beta_1 x_0}\right] = A + jB.$$

Solving this equation for A and B, one obtains

$$A = \frac{1}{2}\,\frac{[(E_{min}/E_{max})^2 - 1]\sin 2\beta_1 x_0}{\beta_1 d\{[(E_{min}/E_{max})^2 - 1]\sin^2\beta_1 x_0 + 1\}}$$

$$B = -\frac{E_{min}/E_{max}}{\beta_1 d\{[(E_{min}/E_{max})^2 - 1]\sin^2\beta_1 x_0 + 1\}} \qquad (6)$$

Expressing $\tanh\gamma_2 d$ in terms of trigonometric functions and making the change in variables $X = \alpha_2 d$, $Y = \beta_2 d$ gives, from equation (1)

$$\frac{\cos Y\sinh Y + j\sin Y\cosh X}{(\cos Y\cosh X + j\sin Y\sinh X)(X + jY)} = A + jB.$$

Now rationalizing and separating the real and imaginary parts

$$\begin{aligned}
&\text{Real:}\quad f(X,Y) = \cos Y\sinh X - (AX - BY)\cos Y\cosh X + (AY + BX)\sin Y\sinh X = 0\\
&\text{Imag:}\quad g(X,Y) = \sin Y\cosh X - (AY + BX)\cos Y\cosh X - (AX - BY)\sin Y\sinh X = 0
\end{aligned} \qquad (7)$$

This gives two equations in two variables to solve. From the first order Taylor expansion in two variables,

$$F(x_1,y_1) \cong F(x_0,y_0) + (x_1 - x_0)F_x + (y_1 - y_0)F_y$$

where F_x and F_y denote the partial derivatives of $F(x,y)$ with respect to x and y respectively, evaluated at (x_0,y_0), equation 7 may be expanded as

$$\begin{aligned}
f(X_1,Y_1) &\cong f(X_0,Y_0) + hf_x + kf_y\\
g(X_1,Y_1) &\cong g(X_0,Y_0) + hg_x + kg_y
\end{aligned} \qquad (8)$$

where $h = X_1 - X_0$, $k = Y_1 - Y_0$. Now for a solution, (X_1,Y_1) must be found such that $f(X_1,Y_1) = g(X_1,Y_1) = 0$. If these are set equal to zero and equation (8) solved for h and k,

$$\begin{aligned} h &= \frac{-f(X_0,Y_0)gy + g(X_0,Y_0)f_y}{f_x g_y - f_y g_x} \\ k &= \frac{-g(X_0,Y_0)f_x + f(X_0,Y_0)g_x}{f_x g_y - f_y g_x} \end{aligned} \qquad (9)$$

Thus with an original guess (X_0, Y_0), one can use equation (9) to find an h and k. Adding these to X_0 and Y_0 respectively gives a better solution (X_1,Y_1). By iteration, a solution can be obtained to the accuracy desired.

Taking the partial derivatives of equation (7) gives

$$\begin{aligned} f_x = g_y = {} & (1 - A)\cos Y\cosh X - (AX - BY)\cos Y\sinh X \\ & + (AX + BY)\sin Y\cosh X + B\sin Y\sinh X \\ f_y = g_x = {} & -(1 - A)\sin Y\sinh X + (AX - BY)\sin Y\cosh X \\ & + (AY + BX)\cos Y\sinh X + B\cos Y\cosh X \end{aligned} \qquad (10)$$

The flow chart for the computer program using this method to solve the impedance equation and then to calculate k', k", μ, and τ as well as to average the results in sets of five is given in plate I. The numbers in parentheses indicate the particular equations used in each calculation.

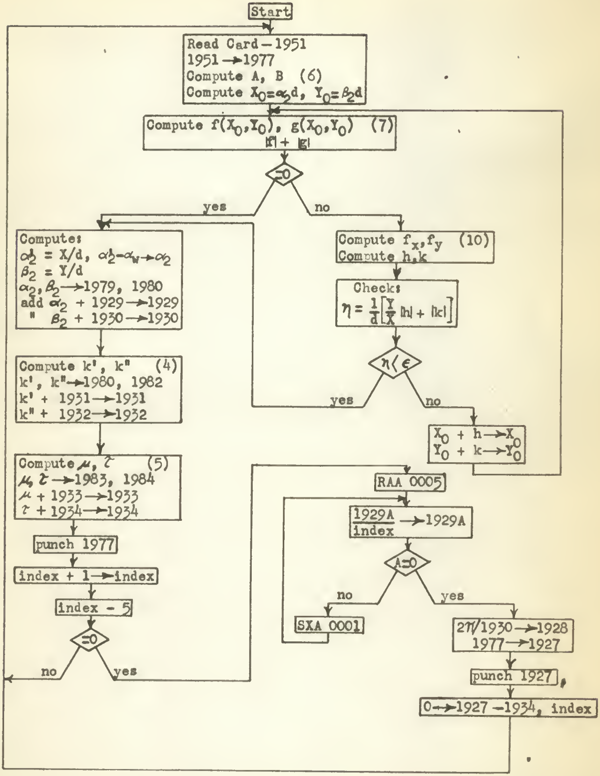
EXPLANATION OF PLATE I

Flow Chart for the Computer Program

The numbers in parentheses indicate the equations used in particular calculation. The quantities in each of the input and output locations are given below. The # refers to a data identification number. Except for the first two locations, the output in the 1927 band consists of averages for the corresponding quantities in the 1977 band for the previous five sets of data. 1927 contains the number of the last set of data calculated. 1928 contains λ_2 calculated from the average β_2 found in 1930.

INPUT	OUTPUT	
		(Averages)
1951 #	1977 #	1927 #
1952 d	1978 E_{min}/E_{max}	1928 λ_2
1953 T	1979 α_2	1929 α_2
1954 Δx	1980 β_2	1930 β_2
1955 x_0	1981 k'	1931 k'
1956 N	1982 k''	1932 k''
1957 n	1983 μ	1933 μ
1958 O	1984 τ	1934 τ

PLATE I


Start
Read Card — 1951
1951 → 1977
Compute A, B (6)
Compute $X_0 = \alpha_2 d$, $Y_0 = \beta_2 d$
Compute $f(X_0, Y_0)$, $g(X_0, Y_0)$ (7)
$|f| + |g|$
=0
yes
no
Compute:
$\alpha_2^1 = X/d$, $\alpha_2^1 - \alpha_W \rightarrow \alpha_2$
$\beta_2 = Y/d$
$\alpha_2, \beta_2 \rightarrow$ 1979, 1980
add α_2 + 1929 → 1929
" β_2 + 1930 → 1930
Compute f_x, f_y (10)
Compute h, k
Checks:
$\eta = \frac{1}{d}\left[\frac{Y}{X}|h| + |k|\right]$
$\eta < \epsilon$
yes
no
$X_0 + h \rightarrow X_0$
$Y_0 + k \rightarrow Y_0$
Compute k', k" (4)
k', k" → 1980, 1982
k' + 1931 → 1931
k" + 1932 → 1932
Compute μ, τ (5)
μ, τ → 1983, 1984
μ + 1933 → 1933
τ + 1934 → 1934
punch 1977
index + 1 → index
index - 5
=0
no
yes
RAA 0005
1929A / index → 1929A
A=0
no
yes
SXA 0001
2π/1930 → 1928
1977 → 1927
punch 1927
0 → 1927 – 1934, index

APPARATUS

The general microwave circuit consisted of a klystron oscillator, a variable attenuator, a wave meter, an isolator, a standing wave detector and a cell with a variable short (see Plate II).

The type 2K25 klystron was mounted in a section of X-band wave guide[1] with energy fed into the circuit by its antenna stub. The klystron was frequency modulated by the sawtooth sweep voltage from a type 545 Tektronix Oscilloscope. This positive sawtooth voltage was fed through a d-c restorer circuit which gave the sawtooth a negative d-c baseline level of approximately 210 volts.

The variable attenuator was a Hewlett-Packard model X375A which could reduce the signal to the rest of the microwave circuit by as much as 20 db.

The wave meter was a cylindrical transmission resonance cavity with one movable wall. As the cavity had been calibrated by the National Bureau of Standards, it was used as an accurate frequency meter.

The isolator, a Uniline model 88-96B, was a unidirectional transmission line which transmitted the signal away from the klystron but blocked any reflected energy.

The principal measuring device was the Hewlett-Packard standing wave detector assembly which consisted of a model 809B carriage assembly, a model 810 wave guide slotted section, a model 440A detector mount, and a model 442A broadband probe. The probe was inserted into the wave guide about one millimeter or less in order to keep any interference with the field at a minimum.

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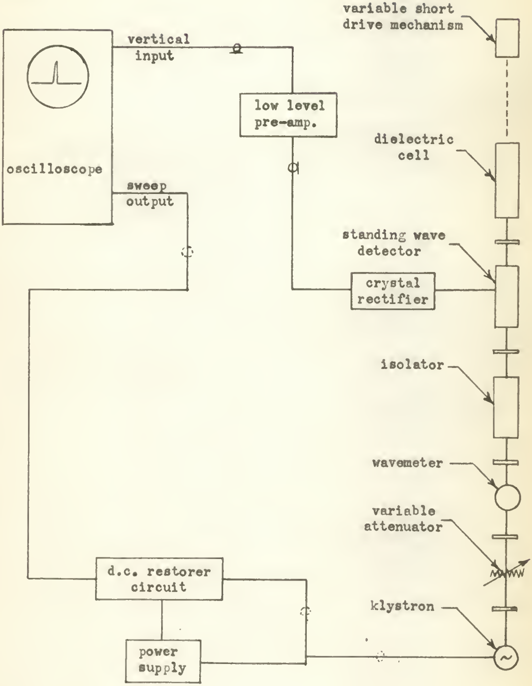
[1] X-band wave guide is manufactured with inside dimensions of .900±.003 by .400±.003 inches and is recommended for operation with frequencies from 8.2 12.4 kMc.

EXPLANATION OF PLATE II

General Circuit Diagram of
the Microwave Measuring Apparatus.

PLATE II


variable short
drive mechanism
vertical
input
low level
pre-amp.
dielectric
cell
oscilloscope
sweep
output
standing wave
detector
crystal
rectifier
isolator
wavemeter
variable
attenuator
d.c. restorer
circuit
klystron
power
supply

Here some compromise had to be reached. If the probe was not inserted a certain amount, the signal picked up was too small for measurement, but if inserted too far, the probe would cause interference problems. Therefore the probe was inserted just far enough to pick up the minimum required signal.

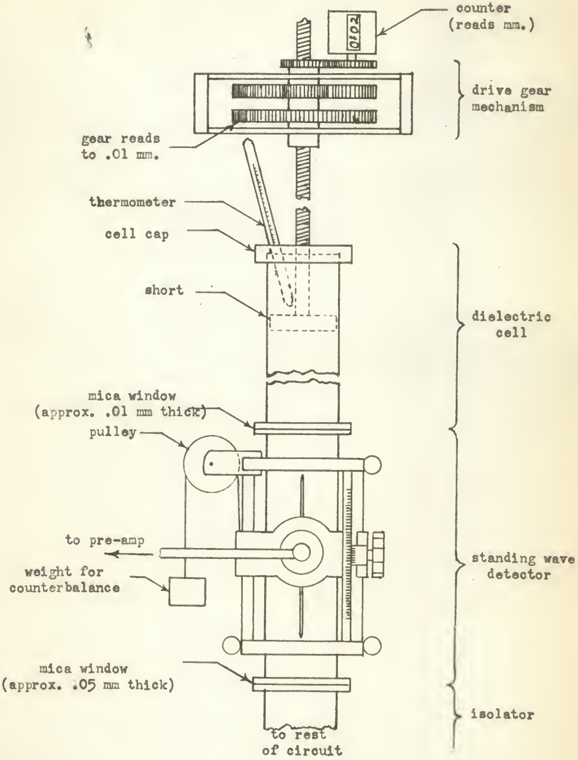
The signal from the probe was fed to a crystal diode which was used as a detector. Different types of diodes were tried and the response law of each was determined as indicated in the following section. The signal from the detector was fed through coaxial cable to a type 122 Tektronix low level pre-amplifier which was set for band pass from 0.2 cps to 10 kc and a gain of one thousand. The input of the pre-amplifier was shunted by a 2400 ohm resistance. This was necessary because the 10 megohm input resistance of the pre-amplifier was much too large a load resistance for optimum crystal response. The shunting resistance slightly increased the noise level and slightly decreased the gain of the pre-amplifier but neither effect caused any difficulties. The signal from the pre-amplifier was fed to the vertical input of the oscilloscope, set with sweep speed of 500 microseconds per cm, where the pulse was observed for the measurements.

As the materials on which data were to be taken were liquid, it was necessary to devise some method of containing the liquid in a section of wave guide. This consideration determined the physical arrangement of the microwave circuit. The microwave circuit was arranged vertically with the dielectric cell on the top. Plate III shows the details of the arrangement of the standing wave detector, dielectric cell, and variable short mechanism.

EXPLANATION OF PLATE III

Details of the dielectric cell, variable short mechanism, and standing wave detector arrangement.

PLATE III


counter
(reads mm.)
0402
drive gear
mechanism
gear reads
to .01 mm.
thermometer
cell cap
short
dielectric
cell
mica window
(approx. .01 mm thick)
pulley
to pre-amp
weight for
counterbalance
standing wave
detector
mica window
(approx. .05 mm thick)
isolator
to rest
of circuit

As the standing wave detector was designed for use in the horizontal position, it was necessary to modify it by means of a counterbalance so it could function properly in the vertical position.

The dielectric cell consisted of a section of X-band wave guide 15 cm. long with a thin mica window (about 10 to 15 microns thick) on the lower end. Crawford (3) showed that no appreciable effects were caused by mica windows of this thickness used on the cell. The window was made from a thin piece of mica cut about 2.5 cm by 3.5 cm in cross section. A small amount of Fuller's adhesive was then spread on the cell flange. After the window was placed on this, a metal plate was clamped tightly over it to hold it securely in place for several hours until the adhesive was well set. This adhesive served very well. With the window secured in this manner there were no difficulties with the adhesive being dissolved by the benzene solutions as reported by some workers. The window was occasionally replaced when it was removed so as to facilate cleaning and polishing the cell. As a precautionary measure to keep the sample out of the remainder of the microwave circuit if the cell window should be accidentally broken, a second mica window (about 50 microns thick) was placed between the isolator and the standing wave detector.

An aluminum cap, drilled to admit the mount for the shorting plunger and a thermometer, was set on top of the cell to keep evaporation to a minimum.

Some characteristics of various types of shorts are discussed in the next section. The short was attached to the end of a long rod threaded with one thread per millimeter. The threaded rod passed through a permanently mounted gear mechanism. A counter coupled to the gear mechanism gave the position of the short. In addition the drive gear was marked so as to divide its circumference into one hundred equal intervals. This, with the counter, enabled the relative position of the short to be read to the nearest .01 mm. However, play in the gear mounting decreased the accuracy of the readings to about .02 mm. To facilitate rapid motion of the short through several centimeters the gear mechanism was coupled to a hand crank.

The dielectric cell and short arrangement has several advantages. The simple cell is very easy to clean and polish. The vertical position allows filling by merely pouring the dielectric in the top and eliminates problems of trapping air in the cell. It is relatively easy to empty the cell by removing the cell and pouring the dielectric out the top. The independent mounting of the short allows more accurate determination of its physical position than if it were mounted on the cell. Though it was hoped that this independent mounting would also eliminate recalibration of the short position each time the cell was filled, it was found that the effective electric short is not in general at the surface of the physical short and furthermore, that its position depends upon the dielectric. Therefore recalibration is still required. The vertical arrangement also allows a thermometer to be placed directly in the dielectric above the short, thus allowing the accurate determination of the temperature of the dielectric.

An Abbe refractometer was used to determine the refractive index of the solutions at optical frequencies.

CALIBRATION AND CORRECTION FACTORS.

In order to obtain meaningful results, all the apparatus used for making measurements must be accurately calibrated. It is also necessary to use correction factors in the calculations where the physical properties do not closely follow the theory.

If a metal short is placed at the end of the slotted wave guide section, nulls of the standing wave must occur at the surface of the short and at multiples of a half wave length from the short. Thus if the wave length is known, the probe position scale on the standing wave detector can easily be calibrated. The scale was adjusted to read directly by moving the vernier scale to the correct position. This calibration was checked each time after the probe had been removed or repositioned in the carriage.

It was found that many crystal diodes varied considerably from a square law response. (see plate IV, figure 2) The response laws of all crystals used were determined by half maximum method described by Ginzton(6). In this method a metal short is placed at the end of the slotted wave guide section, then the distance , L, between the two points where the voltage signal from the detector is one half the maximum of the standing wave is determined. Since the standing wave is sinusoidal, the response law can then be determined. Ginzton gives a plot of the response law, n, verses $2L/\lambda_1$, from which the response law can be obtained. By varying the maximum of the standing wave with the variable attenuator, the response law was determined as a function of the voltage signal from the crystal. Though the response law was also dependent upon the load resistance (see plate IV, figure 1) it was found that with a 24K load resistance all crystals used showed a constant response law over a wide range of signals. As the 1N1611 crystal gave the largest magnitude of response,

EXPLANATION OF PLATE IV

Fig. 1. Dependence of 1N22 crystal diode upon load resistance and signal

Fig. 2. Response laws of some crystal diodes

PLATE IV

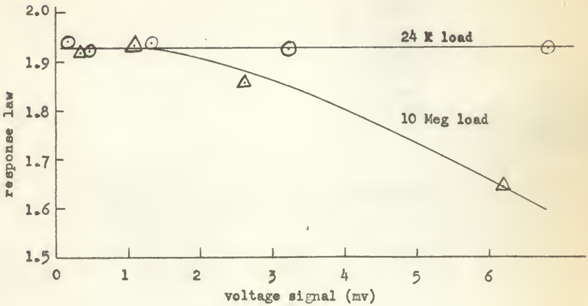


Figure 1.

Response Laws of Crystals

Type	Law
1N22 #1	1.93
1N22 #2	1.31
1N23C	1.62
1N1611	1.82

Figure 2.

it was used for the majority of the measurements.

As mentioned before, the effective electrical short is not in general at the surface of the variable short, but is dependent upon both the type of short and the medium in which the wave is propagated. Sketches of various shorts tried and the position of the effective electrical short for air are given in plate V. Most of the data were taken using short E.

No precise method for calibration of the short has been found, but the standing wave properties can be used to give very accurate calibration for low and medium loss materials. Plate VI, figure 1, gives curves A, B, C, and D for different loss tangents of x_0/λ_1 verses d/λ_2. Each group of curves, corresponding to a specific value of n, appears to pass through the points $(n/4, 0.5)$, $((n+1)/4, 0.25)$ and $((n+2)/4, 0)$ respectively, n even, for all values of $\tan\delta$. Whether they actually pass through these points can be checked by looking at equation (1).

By expressing $\tan {}_2d$ in terms of trigonometric functions, one may obtain from equation (1)

$$\frac{\cos\beta_2 d \sinh\alpha_2 d + j\sin\beta_2 d \cosh\alpha_2 d}{\cos\beta_2 d \cosh\alpha_2 d + j\sin\beta_2 d \sinh\alpha_2 d} =$$

$$\frac{\beta_2(E_{min}/E_{max})(1 + \tan^2\beta_1 x_0) + \alpha_2 \tan\beta_1 x_0[(E_{min}/E_{max})^2 - 1]}{\beta_1[1 + (E_{min}/E_{max})^2 \tan^2\beta_1 x_0]}$$

$$+ \frac{j\{\beta_2 \tan\beta_1 x_0[(E_{min}/E_{max})^2 - 1] - \alpha_2(E_{min}/E_{max})(1 - \tan^2\beta_1 x_0)\}}{\beta_1[1 + (E_{min}/E_{max})^2 \tan^2\beta_1 x_0]}.$$

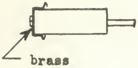
If $\beta_2 d = n\pi/2$, the left side of the equation becomes $\tanh\alpha_2 d$ or $\coth\alpha_2 d$ for n even or odd respectively. In either case, the left side is real so the right side must also be real. Setting the imaginary part equal to zero gives

$$\tan\beta_1 x_0/(1 - \tan^2\beta_1 x_0) = \alpha_2(E_{min}/E_{max})/\beta_2.$$

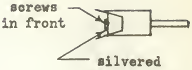
EXPLANATION OF PLATE V

Types of shorts and positions of effective electrical shorts.

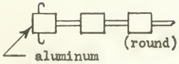
PLATE V



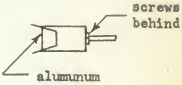
A.



B.



C. (brass contacts) D. (nichrome contacts)



E .

Position of effective electrical short in air.

Short	Distance in front of surface
A	0.037 cm
B	0.125 cm
C	0.034 cm
D	-0.059 cm
E	0.115 cm

EXPLANATION OF PLATE VI

Fig. 1. Variation of x_0/λ_1 with d/λ_2.

Fig. 2. Variation of E_{min}/E_{max} with d/λ_2.

The curves were obtained from data on nitrobenzene with loss tangents as follows: B-$\tan\delta$ = .028, A-$\tan\delta$ = .044, D-theoretical curve for $\tan\delta$ = 0.

PLATE VI

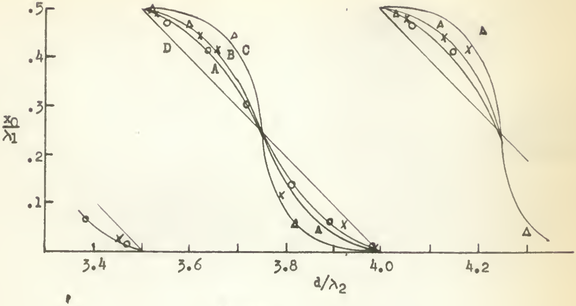


Figure 1.

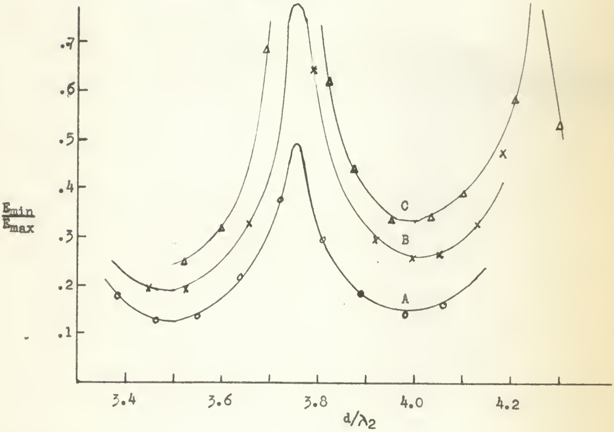


Figure 2.

Therefore the curves pass through the above mentioned points only if $\alpha_2 = 0$. However, as both α_2 and E_{min}/E_{max} are always less than one and, for low loss materials, are less than 0.1, the curves pass extremely close to the points, for low and medium loss materials. Further it is seen from the graph that in the neighborhood of $d/\lambda_2 = m/4$, m odd, the slope has a large negative value for high loss materials. Therefore, although the curve passes through $d/\lambda_2 = m/4$, m odd, a small distance above $x_0/\lambda_1 = 0.25$, the curve still passes very close to the point $(m/4, 0.25)$, m odd.

This property was used to calibrate the variable shorts. The probe was set at an odd multiple of $\lambda_1/4$ from the interface and the short then moved until a minimum of the standing wave occured at the probe, that is until $x_0 = \lambda_1/4$. This was done until several positions of the short had been determined for which $x_0 = \lambda_1/4$. The distance between these positions was $\lambda_2/2$, and as shown above each position was a distance $m\lambda_2/4$, m odd, from the surface of the dielectric. Thus the short could be calibrated to read the correct positions.

As previously stated, this method is not exact. The distance thus obtained will be slightly short, but will be well within the uncertainties of the measurements.

A similar method could be used for calibration of the probe position if necessary, but the method used is more accurate and more convenient.

Some loss may be caused by some factors other than the dielectric, such as the walls of the wave guide not being perfect conductors, the guide junctions not being perfect, the solvent not being completely non-polar, etc. In this case the attenuation factor, α_2', obtained from the calculation is not the attenuation factor, α_2, of the dielectric. Von Hippel (16) shows that $\alpha_2' = \alpha_2 + \alpha_w$, where α_w is the attenuation factor due to all the side effects.

Accordingly a correction is provided for in the computer program, but as α_w is quite small, it is very difficult to determine accurately. Yet this correction must be made if one goes to extremely dilute solutions.

As the index of refraction, N, varies with temperature, and the temperature of the solution being measured in the dielectric cell could not be controlled, it was necessary to find N as a function of temperature. This was done by determining N at two different temperatures using the Abbe refractometer. The index of refraction at the temperature of the solution in the cell was found by interpolation. According to the measurements N varies with temperature at a rate of -.0005 per °C for most of the samples.

Several workers have found that solvent effects occur when the dipole moment of liquids are determined. Smyth (14) compares several of the empirical corrections for the solvent effects that have been tried by various workers. Most have been quite satisfactory in many cases, but all have proven unsatisfactory in some instances. Efforts to determine empirical correction factors to correlate the measured values of some common materials with published values for infinite dilution were not sufficiently extensive to determine positive results.

PROCEDURE

Two methods were used in preparing the solutions. In the first method, the desired amount of solute was weighed, then placed in a given volume of benzene solution. When this method was used, the number of molecules per unit volume, n, was found from the equation, $n = N_0D/M$, where N_0 is Avagadro's number, M is the molecular weight of the solute and D is the density of grams of solute per unit volume of solution.

The second method, though not as accurate as the first, was found to be much more satisfactory when solutions of several concentrations of the same solute were desired. In this method a given volume of solute, say 4 ml, was placed in a 100 ml volumetric flask, which was then filled with benzene. After thoroughly mixing, 50 ml of the solution was drawn off and saved for measurement. The flask was again filled with benzene, the solution mixed and 50 ml drawn off. By repeating this procedure solutions were obtained in which the concentration of the solute was decreased by a factor of two each time until the minimum concentration desired was obtained. When this method was used, n was found from the equation, $n = N_0Cd/M$, where d is the density of the pure solute and C is the concentration of the solute expressed as the volume of solute per unit volume of solution.

After the dielectric cell had been fastened to the standing wave detector and the variable short inserted, about 35 ml of the solution was poured into the cell and the short set at some convenient position. The wave meter was set for the desired frequency[1] and the variable attenuator adjusted so as to give a signal large enough that noise did not interfere with the measurement,

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[1] All data were taken using a frequency of 9.349 kMc.

yet small enough to prevent overdriving the pre-amplifier. Δx was then determined at each of four successive minima in the slotted wave guide section and the average of these taken. As x_0 could not be determined directly, it was determined indirectly as follows. The distance of four successive minima from the dielectric surface was determined, then x_0 was obtained from the average of the four values obtained from the equation $X_0 = X - n\lambda_1/2$, where X is the distance of the $(n + 1)$ minimum from the interface. The temperature of the solution was then read and recorded.

The above procedure was usually repeated to obtain data for either five or ten different thicknesses of dielectric, usually at either one or two millimeter intervals.

The variable short was calibrated for each solution as indicated in the previous section.

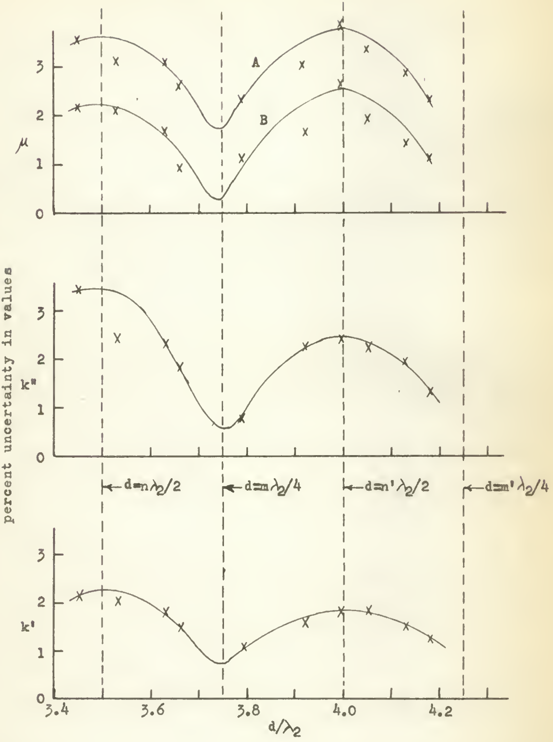
The data were then punched on cards to be used by the computer for the calculations.

EXPLANATION OF PLATE VII

Uncertainties in k', k", and μ

These curves give the uncertainties in the quantities due to uncertainties in measurements. The uncertainties are those determined for a nitrobenzene solution of density .01092 gm/ml. Uncertainties in the measured values were taken as ±.005 cm for d, Δx, and x_0 and ±.003 (curve A) and ±.001 (curve B) for N.

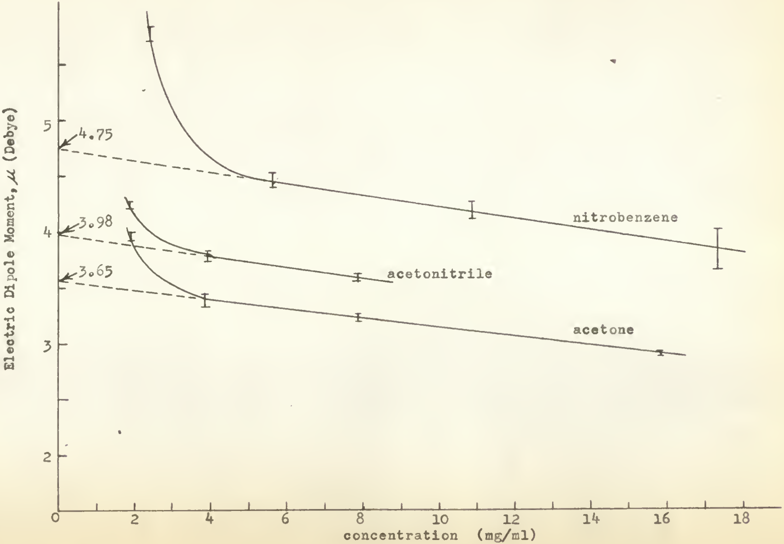
PLATE VII


percent uncertainty in values
μ
A
B
k"
k'
0
1
2
3
d=nλ₂/2
d=mλ₂/4
d=n'λ₂/2
d=m'λ₂/4
3.4
3.6
3.8
4.0
4.2
d/λ₂

EXPLANATION OF PLATE VIII

Variation of measured dipole moment with concentration of solution.

PLATE VIII


Electric Dipole Moment, μ (Debye)
5
4
3
2
4.75
3.98
3.65
nitrobenzene
acetonitrile
acetone
0
2
4
6
8
10
12
14
16
18
concentration (mg/ml)

EXPLANATION OF PLATE IX

Comparison of values of μ obtained by extrapolation to infinite dilution with those given in the literature.

PLATE IX

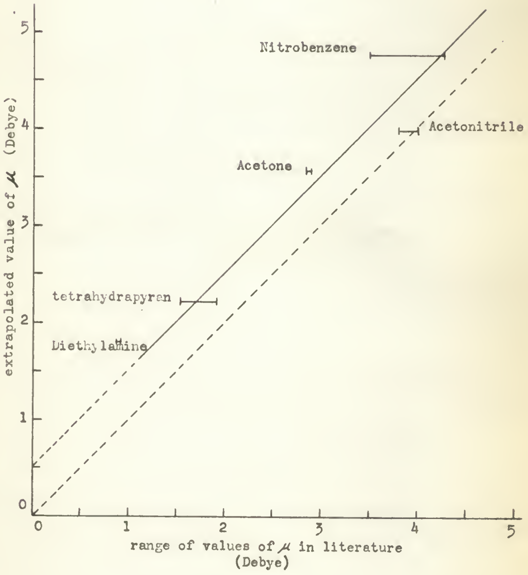

Nitrobenzene
Acetonitrile
Acetone
tetrahydrapyran
Diethylamine
extrapolated value of μ (Debye)
0
1
2
3
4
5
0
1
2
3
4
5
range of values of μ in literature
(Debye)

Table 1. Results obtained for various materials and concentrations*

Molecule	Density (mg/ml)	k'	tan δ	τ ($\mu\mu$ sec)	μ & av. dev. (Debye)	values in literature
Acetone	15.84	2.512	.0143	2.01	2.90 ±.01	2.85[1], 2.75[2] (14)
	7.92	2.407	.0099	1.84	3.24 ±.02	2.87-2.89[1] (11)
	3.86	3.330	.0052	2.12	3.37 ±.05	3.04[3] (3)
	1.98	3.331	.0030	1.89	3.97 ±.03	2.72-2.78 (17)
	0				3.56[4]	
Acetonitrile	7.83	2.531	.2300	2.60	3.59 ±.02	3.94[1], 3.4-3.5[2] (14)
	3.92	2.401	.0110	2.58	3.80 ±.04	3.8-4.0[1] (11)
	1.96	2.341	.0063	2.35	4.23 ±.02	3.2-3.6[3] (7)
	0				3.98[4]	3.11-3.51 (17)
Diethylamine	14.22	2.307	.0057	2.91	1.81 ±.04	.9[1], 1.13[2] (14)(17)
	7.11[5]	2.367	.0032	.97	2.68	.89-.95[1] (11)
Nitrobenzene	17.41	2.465	.0415	7.56	3.78 ±.10	3.5[1], 3.2[2] (14)
	"	2.464	.0457	8.45	3.85 ±.16	4.17-4.27[1] (11)
	10.92	2.393	.0291	6.78	4.20 ±.05	3.92 (19)
	"	2.392	.0276	6.50	4.17 ±.04	4.3[3] (3)
	5.68	2.332	.0164	6.25	4.49 ±.05	3.90-4.05 (17)
	"	2.331	.0161	6.23	4.45 ±.03	
	2.42	2.295	.0069	4.22	5.74 ±.05	
	"	2.295	.0064	3.93	5.70 ±.02	
	0				4.75[4]	
Tetrahydrapyran	40.19	2.448	.0154	3.10	1.66 ±.01	1.55 (2)
	"	2.447	.0186	3.12	1.66 ±.01	1.87 (1)(17)
	"	2.447	.0185	3.15	1.65 ±.01	2.14-2.30 (7)
	16.73	2.338	.0075	3.01	2.00 ±.02	
	"	2.337	.0072	2.96	1.98 ±.02	
	"	2.343	.0077	2.97	2.05 ±.02	
	0				2.24[4]	

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*The values given are the averages of results obtained at five different dielectric thicknesses.

[1] Values obtained in vapor state.

[2] Values obtained in solution.

[3] Obtained using apparatus and method similar to that used in this work.

[4] Obtained from extrapolation of plots in Plate VIII.

[5] Only one set of data.

DISCUSSION OF RESULTS

It has been found that the uncertainty in the calculated values of k', k", and μ due to uncertainties in the measurements of x_0, Δx, d and N depends greatly upon the thickness of the dielectric (see plate VIII). In addition to these uncertainties, there would be some caused by measurements of $_1$, T and the number of molecules per ml. However the accuracy of these measurements is such that the combined uncertainty caused by these would be less than one half per cent. The uncertainties in these results were least when the value of d was close to an odd multiple of $\lambda_2/4$ and greatest when d was near an even multiple. Therefore, the most dependable results can be obtained in those using dielectric thicknesses near an odd multiple of $\lambda_2/4$. These are also the most convenient thicknesses to use. As indicated in plate VI, figure 2, E_{min}/E_{max} reaches maxima in these regions, therefore Δx is more easily determined as the signal from the probe in the neighborhood of the minimum of the standing wave will be large enough for good observation.

The percent uncertainty in μ indicated by plate VII for this particular material and thickness, if N is accurate to $\pm .001$, is less than 2.5. This should be the maximum uncertainty expected as the uncertainties in the measurements used to obtain this value were definably as large as and probably slightly greater than the actual uncertainty in the measured quantities. This is also borne out by the average deviations for μ shown in Table 1.

The results obtained for the electric dipole moments of the materials used are given in Table 1 and Plate VIII. These results are compared with the values given in the literature in Table 1 and Plate IX.

It was found that for all materials used, the calculated dipole moment increased as the concentration of the solution decreased. As shown in

Plate VIII, the values for Acetone, Acetonitrile and Nitrobenzene (the only solutions with sufficient data) fell on a straight line for the high concentrations, but increased considerably above this when the concentration was decreased below about 3 mg/ml.

The graph on Plate IX compares the values for μ obtained by extrapolating the straight line portion to infinite dilution with the values given in the literature. If a straight line is drawn through these values, it is seen that the values obtained for μ are too large by about .5 Debye.

The average deviations shown in Table 1 as well as the curves in Plate VII show that this method of determination of the dipole moment of materials gives quite consistant results with a high degree of reproducability. This degree of reproducability indicates that the apparent poor results are probably due to either wall losses or solvent effects.

An attempt to correct for wall losses was made by direct determination but the loss was so small that this was impossible. A correction was tried by setting the attenuation factor due to wall losses equal to .004 which is probably too large by a factor of two at least. With this large value used, the values of μ were decreased by less than 2 per cent, so it was decided that wall losses could be neglected without appreciable error.

The disagreement between the calculated value for μ and those found in the literature, therefore, is apparently due principally to solvent effects and an emperical correction factor can possibly be found. However, as indicated by Smyth (14) no foolproof method for making this correction has been found.

As indicated by Plate IX, one might try correcting the calculated values by subtracting .5 D from them. If this is done, all the values would fall within 8 per cent of the values in the literature and most would be closer than that. However, with the limited data taken, one cannot say if this correction is correct. This method of correction would probably not work in general for all materials. However it would probably be quite satisfactory if one was confined to a given chemical series.

Whiffen (18) has made measurements which indicate that one may obtain small dielectric losses in normally non-polar materials such as benzene. For benzene, at about 9 kMC, he obtains a value of about, $\tan\delta = 5 \times 10^{-4}$. Whiffen explains this as being due to an average dipole moment of about .1 D, which is produced by molecular distortion.

Such dielectric loss in benzene was also observed in this work and in that of Crawford (3). However, if this is due to an induced dipole moment, one would expect it to be dependent upon the intensity of the applied electric field. Whiffen makes no mention of the magnitudes of fields he used; therefore, the magnitude of the field in his results may not be applicable to other cases. If the values Whiffen gives are correct, this would explain one fifth of the .5 D disagreement mentioned above, however the accuracy of his results is questioned.

Some workers have shown that the simple Debye equation used in this work does not take into account all the necessary effects. Several variations have been tried successfully, but the results obtained from them differ little from those obtained with the Debye equation. For example Hill (8) shows that Onsager's theory applied to this case gives results that vary from those obtained from Debye equation by less than one per cent. Therefore, although other relations may be more exact, the Debye equation should give results within the accuracy of the measurements of this work.

The results indicate that the method of measurement and calculation used will give quite consistant results. It appears from the comparisons made on Plate IX that by taking sufficient data, one can obtain an emperical correction factor which can be used to obtain reliable results. This should be especially true within a given series of compounds.

As the arrangement of the experimental apparatus and the use of the electronic computer has made it possible to obtain results in sufficient quantities to observe definite tendencies in the results, the feasibility of determining reliable emperical correction factors for given chemical series should be explored more fully.

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LITERATURE CITED

1. Allen, J. Stanley and Harold Hibbert. Studies on reactions relating to carbohydrates and polysouhaids. XLVII. The Oxygen Valence Angle and Structure of Glucose and Related Compounds. Jour. Amer. Chem. Soc. 56:1398. 1934.

2. Cumpu, C.W.N. and A.I. Vogel. Physical properties and chemical constitution. Part XXVII. Dipole Moments of Some Cyclic Ethers, Sulphids, Sulphoxides and Sulphone. Jour. Chem. Soc. (London) 3521. 1959

3. Crawford, J. C. Microwave measurements of dielectric properties of some polar liquids. Unpublished M.S. thesis, Kansas State University, Manhattan, Kansas. 1959.

4. Chipwell, F. T. and G.B.B.M. Sutherland. Some measurements of the absorption of centimetric waves by liquid dielectrics. Trans. Far. Soc. 42A:149-162. 1946.

5. Debye, P. Polar Molecules. Chemical Catalog Co. 1929, p. 90.

6. Ginzton, Edward L. Microwave measurements. New York:McGraw-Hill, 1957.

7. Hering, Karl Herman. Investigation of the dipole moment and relaxation time of organic molecules. Unpublished M.S. Thesis, Kansas State University, Manhattan, Kansas. 1960.

8. Hill, N. E. The application of Onsager's theory to dielectric dispersion. Proc. Phys. Soc. (London) 72:532-537. 1958.

9. Krishna, K. V. Gopala. A method for determining the dipole moment and relaxation time from microwave measurements. Trans. Far. Soc. 53:767-770. 1957.

10. Krishna, K. V. Gopala. A new method for computing the compound dielectric constant from ultra-high frequency impedence measurements. Trans. Far. Soc. 52:1110-1111. 1956.

11. Maryott, A. A. and F. Buckley. Table of dielectric constants and electric dipole moments of substances in the gaseous state. N. B. S. Cir. 537, June 25, 1953.

12. Major, S.S. A method for measuring the dielectric constant at microwave frequencies using a standing wave detector. Unpublished M. S. thesis, Kansas State College, Manhattan, Kansas. 1952.

13. Roberts, S. and A. von Hippel. A new method for measuring dielectric constant and loss in the range of centimeter wave. Jour. Appl. Phys. 17:610-616. 1946.

14. Smyth, Charles P. Dielectric behavior and structure. New York: McGraw-Hill, 1955.

15. Surber, W. H. Jr. and G. E. Crouch, Jr. Dielectric measurements methods for solids at microwave frequencies. Jour. Appl. Phys. 19:1130-1139. 1948.

16. von Hippel, Arthur R. Dielectric materials and applications. New York, John Wiley & Son, 1954.

17. Wesson, L. G. Tables of electric dipole moments. Chambridge, Mass. Technology Press, 1948.

18. Whiffen, D. H. Measurements on the absorption of microwaves. Part IV Non-polar liquids. Trans. Far. Soc. 46:124-130. 1950.

19. Whiffen, D. H. Measurements on the absorption of microwaves. Part V. The variation of Relaxation Time with Solvent. Trans. Far. Soc. 46:1930-1932. 1950.

MICROWAVE MEASUREMENTS OF THE ELECTRIC DIPOLE MOMENT AND OTHER DIELECTRIC PROPERTIES OF SOME ORGANIC COMPOUNDS

BY

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B. S. Fort Hays Kansas State College, 1959

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If the propagation factor for microwaves in a dielectric medium is known the complex dielectric constant of the medium can be determined. The propagation factor of liquid dielectric are determined using x-band wave guide terminated by a metal short. The short, which was a movable plunger so the thickness of the dielectric could be varied, was calibrated by using the wave properties.

The Debye equation is used to determine the average electric dipole moment from the complex dielectric constant.

The microwave circuit was arranged vertically with the dielectric cell on top. This simplified filling the cell, eliminated the necessity of the plunger end of the cell having a liquid tight cell, and allowed the independent mounting of the short. The dielectric was contained in the cell by a thin mica window.

Due to the difficulty of solving the impedance equations for general dielectric thicknesses by hand calculations, an electronic computer was used for their solution. Since it was necessary to use the computer for the solution of the impedance equation, all the calculations to arrive at the value for the dipole moment were carried out on the computer.

The microwave energy was supplied by a frequency modulated Klystron. The properties of the standing wave set up by the reflection from the detector surface were measured with a standing wave detector.

Measurements for acetone, acetonitrile, diethylamine, nitrobenzene, and tetrahydrapyran in dilute solutions of benzene were taken for various concentrations.

It was found that the dipole moment varies linearily with the concentration at higher concentrations used. However, at very low concentrations the values obtained were considerably higher. Although the values obtained were all higher then those given in the literature, a very high degree of reproducibility was obtained.

From the limited date obtained, it appears that one could obtain an emperical correction factor which would be valid, at least within a given chemical series.