MICROWAVE MEASUREMENTS OF DIELECTRIC PROPERTIES OF SOME POLAR LIQUIDS

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INTRODUCTION

In the past 15 years, the properties of dielectrics in the microwave band of frequencies have been increasingly explored. The property most often studied is the complex dielectric constant of the particular material.

The methods used to determine the complex dielectric constant may be broadly divided into two categories:

(a) The reflection from a surface of the dielectric enclosed in a section of wave guide.

(b) The change in Q and resonant frequency of a resonant cavity resulting from the introduction of a dielectric sample into the cavity.

Some of the original work in this field was done by Roberts and von Hippel (1) who adapted a cylindrical wave guide for their measurements. These experiments were successful in obtaining the complex dielectric constant by examining the reflection from a liquid dielectric in the wave guide.

Although Roberts and von Hippel presented the original formulation, there have been many subsequent variations and refinements. Most of the later works were aimed at either simplifying the mathematical calculations or improving the experimental procedure (2), (3), (4), (5). A method utilizing the resonant cavity with procedures for a wide range of frequencies has been published by Jackson and Powles (6).

When these dielectrics are subjected to high-frequency electromagnetic radiation, the polarization process may exhibit a
definite tendency to lag the applied field due to the extreme rapidity of the applied oscillation. This difference in phase is generally referred to as relaxation.

The complete polarization effect is a composite of four distinct processes:

(a) Electronic polarization consists of the small displacement of the electrons with respect to the nucleus. This is an extremely fast process, requiring on the order to $10^{-15}$ seconds to reach equilibrium.

(b) Entire atoms may each experience a small displacement with respect to each other, known as atomic polarization. This is only a very small effect and has an equilibrium time of approximately $10^{-12}$ to $10^{-14}$ seconds.

(c) Ionic crystals may exhibit a small amount of polarization, due to displacement of the lattice ions, with a time of about $10^{-12}$ seconds.

(d) The polarization resulting from the orientation of permanent dipoles may have various equilibrium times depending on the state of the material. For a gas, this time is approximately $10^{-12}$ seconds, for small molecules of low viscosity the time is from $10^{-10}$ to $10^{-11}$ seconds, for heavy viscous liquids it increases to about $10^{-6}$ seconds, and on the order of minutes for some solids.

Since the period of a microwave oscillator is on the order of $10^{-10}$ seconds, a liquid dielectric, under the influence of microwave radiation, will show an appreciable effect resulting
from permanent dipole polarization. Debye (6) developed the original theory showing the functional relationship for the complex dielectric constant, permanent dipole moment, and relaxation time.

The method described in this paper is essentially a variation of the theory of Roberts and von Hippel in an effort to minimize the assumptions necessary for a numerical solution of the problem and to keep the theory as general as possible. Using computed values of the complex dielectric constant, the dipole moment and relaxation time may be computed for a liquid, polar dielectric.

**THEORY**

**Complex Dielectric Constant**

In general the dielectric constant of a material medium is defined by the ratio of the capacitances of a capacitor with the plates separated by vacuum to the capacitance with some dielectric medium separating the plates.

$$K = \frac{C_{\text{vac}}}{C_{\text{dielectric}}} = \frac{\varepsilon}{\varepsilon_0}$$

This results in the dielectric constant being equal to the relative permittivity of the medium (where $\varepsilon$ is the permittivity of the medium and $\varepsilon_0$ is the permittivity of vacuum). The above definition holds for a constant electric field in the medium or
for a time varying electric field with a low frequency\(^1\) of oscillation if \(\varepsilon\) is corrected for the possibility of ohmic conduction through the dielectric.

If an oscillating electric field is applied to the dielectric with a frequency in the megacycle range, the molecular orientation may begin to lag the applied field, thus acquiring an electric field component which is out of phase with the applied signal. This is known as relaxation and will appear as energy dissipation within the dielectric.

In terms of current through the capacitor, the regular capacitive current will lag by 90 degrees the applied voltage. Representing this in the complex plane,

\[
I = i\omega \varepsilon' C_0 V
\]

where \(C_0\) is the capacitance assuming no loss, \(V\) is the applied voltage of angular frequency \(\omega\), and \(\varepsilon'\) the ideal permittivity (no loss). The dissipative term due to relaxation and any actual conduction through the dielectric will be in phase with the voltage and can be represented as

\[
I' = G V
\]

The total current can then be written as

\[
I_T = I + I' = (i\omega \varepsilon' + \frac{G}{C_0}) C_0 V
\]

By defining a complex permittivity \(\varepsilon'' = \varepsilon' - i\varepsilon''\), the total current may be represented in terms of this complex quantity by

\[
I_T = (i\omega \varepsilon' + \omega \varepsilon'') C_0 V = i\omega \varepsilon'' C_0 V
\]

\(^1\)Frequencies on the order of kilocycles per second.
Thus $\varepsilon'$ is a measure of the normal capacitive current and $\varepsilon''$ the dissipation, or ohmic current. This definition of the complex permittivity permits the use of the normal form of the equations with the replacement of $\varepsilon$ by $\varepsilon''$ to recognize the possibility of dissipation within the dielectric. The dissipation is usually designated by the loss tangent, $\tan \delta$, defined by

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (5)$$

Following the above reasoning, one defines the complex dielectric constant as

$$k'' = k' - i k'' \quad (6)$$

Propagation in a Dielectric-filled Wave Guide

Assuming that the $x$ direction is the direction of propagation of electromagnetic radiation, the electric and magnetic field vectors must satisfy the wave equations

$$\nabla^2 E = \varepsilon'' \mu' \frac{\partial^2 E}{\partial t^2} \quad (7)$$

$$\nabla^2 H = \varepsilon'' \mu'' \frac{\partial^2 H}{\partial t^2} \quad (7a)$$

where the complex permittivity and permeability have been used to account for high-frequency radiation. These equations have well known solutions for $E$ and $H$ in free space:

$$E = E_0 e^{i\omega t - k x} \quad H = H_0 e^{i\omega t - k x} \quad (8)$$

with $E_0$ and $H_0$ being the amplitude factors.

To apply these results to the radiation in a rectangular
wave guide, the solutions to the wave equations are assumed to be

\[ E = E_0(y, z)e^{i\omega t - \gamma_1'y} \quad H = H_0(y, z)e^{i\omega t - \gamma_1'y} \quad (9) \]

The quantity \( \gamma_1' \) is the propagation factor for the electromagnetic waves in an air-filled wave guide as contrasted to \( \gamma_1 \), the propagation factor in free space. In solving the free space radiation problem, the propagation factor is found to be

\[ \gamma_1 = i \omega \sqrt{\varepsilon \mu} \quad (10) \]

which may be introduced into the wave guide equations such that \( E \) and \( H \) may be functions of \( \gamma_1' \) and \( \gamma'_e \).

The assumed solutions must not only satisfy the wave equations but also the boundary conditions imposed by the conducting walls of the wave guide. The electric field must have no tangential component at the walls and the magnetic field should be parallel to the walls at the boundaries. Subjected to these conditions, the expressions for all the components of \( E \) and \( H \) may be obtained.

The quantity of major interest, however, is the propagation factor which determines the characteristics of propagation in the wave guide. Carrying out the solution of the wave equations, one is led to an expression

\[ \gamma_1' = \sqrt{(\gamma_1)^2 + \left(\frac{mn}{a}\right)^2 + \left(\frac{mn}{b}\right)^2} \quad (11) \]

where \( a \) and \( b \) are the cross-sectional dimensions of the wave guide, and \( m \) and \( n \) are integers arising from the application of the boundary conditions. Recalling the value of \( \gamma_1 \)
\[ \delta_1' = \sqrt{\frac{1}{\varepsilon^\ast \mu^\ast}} \omega^2 - \left[ \left( \frac{m \pi}{a} \right)^2 + \left( \frac{n \pi}{b} \right)^2 \right] \] (12)

If \( \delta_1' \) were real, the term \( e^{-\delta_1' x} \) would be only an exponential increase or decrease and would not correspond to a propagation term. Therefore \( \delta_1' \) must be either complex or imaginary, which imposes the condition on \( \omega \) that

\[ \omega \leq \sqrt{\frac{1}{\varepsilon^\ast \mu^\ast}} \left[ \left( \frac{m \pi}{a} \right)^2 + \left( \frac{n \pi}{b} \right)^2 \right] \] (13)

Thus there is a minimum frequency allowed for propagation in any particular wave guide and it is called the "cut-off frequency" denoted by \( f_c \).

\[ f_c = \frac{\omega_c}{2\pi} = \sqrt{\frac{1}{\varepsilon^\ast \mu^\ast}} \left[ \left( \frac{m}{2a} \right)^2 + \left( \frac{n}{2b} \right)^2 \right] \] (14)

The above equations have all been derived for the case of an air-filled rectangular wave guide, but they may be generalized to include a dielectric-filled wave guide by merely using the values for \( \varepsilon^\ast \) and \( \mu^\ast \) appropriate to the dielectric. With this in mind, the above equations are true for any medium in a rectangular wave guide.

Since \( \frac{1}{\sqrt{\varepsilon^\ast \mu^\ast}} \) is the phase velocity of the wave in the medium described by \( \varepsilon^\ast \) and \( \mu^\ast \),

\[ f_c \sqrt{\varepsilon^\ast \mu^\ast} = \frac{f_c}{v} = \frac{1}{\lambda_c} = \sqrt{\frac{m}{2a}^2 + \frac{n}{2b}^2} \] (15)

where \( \lambda_c \) is the cut-off wavelength. It will be noticed that although the cut-off frequency is a function of the medium through which the wave is traveling, the cut-off wavelength is
a function of the waveguide dimensions only.

When \( \varepsilon_2^*, \mu_2^* \), and \( \gamma_2' \) represent the parameters of a dielectric-filled waveguide, equation (11) may be solved for \( \varepsilon_2^* \mu_2^* \).

\[
\varepsilon_2^* \mu_2^* = \frac{\left[ \left( \frac{mn}{a} \right)^2 + \left( \frac{nn}{b} \right)^2 \right]}{\left[ \frac{2\pi}{\lambda_f} \right]^2} - \gamma_2' \omega^2
\]

(16)

where \( v \) = velocity in free space and \( \lambda_f \) is the free space wavelength. Assuming a non-magnetic medium,

\[
\frac{\varepsilon_2^*}{\varepsilon_0} = \frac{\left( \frac{1}{\lambda_c} \right)^2 - \gamma_2' \omega^2}{\left( \frac{1}{\lambda_f} \right)^2} = \frac{\left( \frac{1}{\lambda_c} \right)^2}{\left( \frac{1}{\lambda_f} \right)^2 + \left( \frac{1}{\lambda_1'} \right)^2} \]

(17)

where \( \lambda_1' \) is the wavelength in an air-filled waveguide.

The notation that has been introduced here will be carried throughout the paper:

Subscript 1 indicates a quantity in air (or vacuum).

Subscript 2 indicates a quantity in the dielectric.

The primes on the quantities \( \lambda' \) and \( \gamma' \) indicate they are describing conditions inside the waveguide in contrast to their free space counterparts \( \lambda \) and \( \gamma \).

It can be seen from the above equation that one may calculate the real and imaginary parts of the dielectric constant once the complete propagation factor is known, since the cut-off wavelength (\( \lambda_c \)) and the air-filled guide wavelength are easily measured quantities. It will be shown in the next section that
$(\phi_2')$ is a complex quantity, as indeed it must be to give a complete solution to the problem.

It should be noted here that the integers $m$ and $n$, which result from the introduction of boundary conditions, actually denote the mode of propagation in the wave guide. The integer $m$ specifies the number of half-wave forms on side $a$, of the wave guide, and $n$ the number of half-wave forms on the side $b$. The most common mode is one in which the electric field is perpendicular to the direction of propagation and is called transverse electric wave (abbreviated $\text{TE}_{mn}$). This development uses the lowest order wave in which $m = 1$ and $n = 0$ and is denoted $\text{TE}_{10}$.

**Impedance Equations**

Referring to Plate I, it will be seen that because of reflections at the interface and the short circuit, there will be standing waves in media 1 and 2. The electric and magnetic vectors of the standing waves in medium 1 may be represented as

$$E_1 = E_{01} \left( e^{i\omega t} - \frac{\phi_1'}{r_0} e^{i\omega t} + \frac{\phi_1'}{r_0} \right)$$  \hspace{1cm} (18)

$$H_1 = H_{01} \left( e^{i\omega t} - \frac{\phi_1'}{r_0} e^{i\omega t} + \frac{\phi_1'}{r_0} \right)$$  \hspace{1cm} (18a)

where $r_0$ denotes the reflection coefficient at the dielectric interface. The intrinsic impedance of the wave guide ($Z_1$) is defined as

$$Z_1 = \frac{E_{01}}{H_{01}}$$  \hspace{1cm} (19)

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EXPLANATION OF PLATE I

Illustrating relative placement of dielectric sample, mica window, and wave guide; also giving diagram representation to the notation introduced.
The impedance $Z$ at any point in the guide is $E_1/H_1$. $Z(0)$ is known as the terminating impedance of medium 1 and is given by

$$Z(0) = \frac{E_1(0)}{H_1(0)} = Z_1 \left( \frac{1 + r_0}{1 - r_0} \right) \quad (20)$$

The reflection coefficient $r_0$ is, in general, complex and may be written as

$$r_0 = e^{-2\psi} = e^{-(2\rho + i2\psi)} \quad (21)$$

Combining these two equations,

$$Z(0) = Z_1 \frac{e^{\psi} + e^{-\psi}}{e^{\psi} - e^{-\psi}} = Z_1 \frac{\tanh \rho - i \cot \psi}{1 - i \tanh \rho \cot \psi} \quad (22)$$

Referring again to the propagation factor $\delta_1'$, it can be written as a complex number $(\alpha_1 + i \beta_1)$ where it can be seen from the wave function that $\alpha_1$ represents the attenuation factor and $\beta_1$ the phase factor. The quantity $\beta_1$ is defined in the usual way,

$$\beta_1 = \frac{2\pi}{\lambda_1'} \quad (23)$$

For an air-filled wave guide there is negligible attenuation. Thus the maximum and minimum values of $E$ may be determined.

$$E_{\text{max}} = E_0(1 + |r_0|)$$
$$E_{\text{min}} = E_0(1 - |r_0|)$$

$$\frac{E_{\text{min}}}{E_{\text{max}}} = \frac{(1 - |r_0|)}{(1 + |r_0|)} = \frac{1 - e^{-2\rho}}{1 + e^{-2\rho}} = \tanh \rho \quad (24a)$$

It can also be shown that

$$\cot \psi = \tan(\beta_1 x_0) \quad (24b)$$

where $x_0$ is the distance from the interface to the first minimum of $E$ in the air-filled guide.
Using these results, equation (22) may be re-expressed as:

\[
Z(0) = Z_1 \left[ \frac{E_{\text{min}} - i \tan \beta_1 x_0}{E_{\text{max}}} \right]
\]

(25)

The terminating impedance, \(Z(0)\), may also be evaluated in terms of the parameters of medium 2. Considering the wave in medium 2,

\[
E_2 = E_{\text{02}}(e^{i\omega t} - j_2'(x-d)) + r_2 e^{i\omega t} + j_2'(x-d)
\]

(25)

\[
H_2 = H_{\text{02}}(e^{i\omega t} - j_2'(x-d)) - r_2 e^{i\omega t} + j_2'(x-d)
\]

(26a)

Since the termination of medium 2 is a metal short, the value of \(r_2\) is -1 and the impedance may again be evaluated at \(x = 0\) in terms of the intrinsic impedance \(Z_2\) of the dielectric-filled wave guide, where

\[
Z_2 = \frac{E_{\text{02}}}{H_{\text{02}}}
\]

\[
Z(0) = Z_2 \frac{e^{+j_2d} - e^{-j_2d}}{e^{+j_2d} + e^{-j_2d}} = Z_2 \tanh j_2d
\]

(27)

It can be shown that

\[
Z_1 \gamma_1' = Z_2 \gamma_2'
\]

(28)

Therefore by combining equations (25), (27), and (28), the following equation may be obtained.

\[
\tanh (\gamma_2'd) = \frac{1}{\gamma_1'} \left[ \frac{E_{\text{min}} - i \tan \beta_1 x_0}{E_{\text{max}}} \right]
\]

(29)

It will be assumed that negligible attenuation occurs in the
air-filled wave guide. Thus $\alpha_1 = 0$ and $\beta'_1 = j\beta_1$.

Solutions to the Impedance Equations

Essentially, equation (29) represents a solution to the problem, that is, it gives $\beta'_2$ in terms of $\frac{E_{\min}}{E_{\max}}$, $\beta_1$, and $x_0$, which can all be measured. Practically, however, this expression presents difficulties in obtaining a numerical solution since there is no straightforward manner in which this type of equation may be solved. Graphical solutions to the problem were used in the early development of this work and are still used in some instances.

The method presented in this paper for the solution of the above equation will alter the number of unknowns by measuring $\beta_2$ experimentally and using this along with the other measured quantities to determine $\alpha_2$.

If $\beta_2$ is measured, the value of the radiation wavelength in the dielectric-filled wave guide ($\lambda'_2$) is determined. The thickness, $d$, may then be chosen experimentally as any desired function of wavelength to simplify the solution of equation (29) for $\beta'_2$.

If $d$ is chosen as some integral multiple of a half wavelength, $d = \frac{n\lambda'_2}{2} = \frac{n\pi}{\beta_2}$, then equation (29) takes the form

$$\frac{\tanh (\alpha_2 d + in\pi)}{(\alpha_2 + i\beta_2)} = \frac{1}{i\beta_1} \left[ \frac{E_{\min} - i \tan \beta_1 x_0}{E_{\max}} \right] \left[ 1 - i \frac{E_{\min}}{E_{\max}} \tan \beta_1 x_0 \right]$$

(30)
For convenience, let
\[
\frac{E_{\text{min}} - i \tan \beta_1 x_0}{E_{\text{max}}} = A + iB \tag{31}
\]
\[
1 - i \frac{E_{\text{min}}}{E_{\text{max}}} \tan \beta_1 x_0
\]

The hyperbolic function may be expanded in terms of its real and imaginary parts as
\[
\tanh(\alpha_2 d + i\pi) = \frac{\sinh(\alpha_2 d) \cos \pi + i \cosh(\alpha_2 d) \sin \pi}{\cosh(\alpha_2 d) \cos \pi + i \sinh(\alpha_2 d) \sin \pi} \tag{32}
\]
\[
\tanh(\alpha_2 d + i\pi) = \tanh\alpha_2 d \tag{32a}
\]

Normally, the quantities that were measured were very low loss materials which permits the simplifying of the equations by neglecting \(\alpha_2\) in the term \((\alpha_2 + i\beta_2)\), since \(\alpha_2\) is much smaller than \(\beta_2\). Using these simplifications,
\[
\tanh \alpha_2 d = \frac{\beta_2}{\beta_1} (A + iB) \tag{33}
\]
which may be solved directly for \(\alpha_2\). It should be noted, however, that this approximation is valid only for low loss substances.

An alternate procedure would be to choose the sample thickness such that
\[
d = (2n + 1) \frac{\lambda_2'}{4} \tag{34}
\]
where \(n\) is any integer. The hyperbolic tangent then becomes
\[
\tanh \left[ \alpha_2 d + i(2n + 1) \frac{\pi}{2} \right] = \coth \alpha_2 d \tag{35}
\]
Using this result in equation (29), the general equation for
\( \alpha_2 \) becomes

\[
(\alpha_2 + i\beta_2) \tanh \alpha_2 \, d = i \beta_1 \left[ \frac{1}{A + i\, B} \right]
\]  
(36)

This equation may be expressed in terms of a power series by using the power series for \( \tanh (\alpha_2 \, d) \) which leads to the equation (for the case when \( n = 0 \))

\[
\alpha_2^2 \frac{\lambda_2'}{4} - \frac{\alpha_2}{3} \left( \frac{\lambda_2'}{4} \right)^3 + ... + i \beta_2 \alpha_2 \frac{\beta_2'}{4} - 1 \frac{\alpha_2}{3} \left( \frac{\alpha_2 \lambda_2'}{4} \right)^3
\]

\[
+ ... = i \beta_1 \frac{1}{A + i\, B}
\]  
(37)

This complex equation may be separated by equating its real and imaginary parts, thus leading to two equations involving \( \alpha_2 \) in terms of experimentally measured quantities.

\[
\alpha_2^2 \frac{\lambda_2'}{4} - \frac{\alpha_2}{3} \left( \frac{\lambda_2'}{4} \right)^3 + ... = \beta_1 \left( \frac{B}{A^2 + B^2} \right)
\]  
(38)

\[
\alpha_2 \frac{\lambda_2'}{4} - 1 \left( \frac{\alpha_2 \lambda_2'}{4} \right)^3 + ... = \frac{\beta_1}{\beta_2} \left( \frac{A}{A^2 + B^2} \right)
\]  
(38a)

Again, however, the above pair of equations represents useful solutions to the problem only when a certain low loss condition is satisfied, that being the quantity \( \frac{\alpha_2 \lambda_2'}{4} \) (or in general \( \left[ (2n + 1) \frac{\alpha_2 \lambda_2'}{4} \right] \)) must be less than unity. If the material being measured is such that \( \left( \frac{\alpha_2 \lambda_2'}{4} \right)^5 \) is negligible, then either of the above equations should give a correct result for \( \alpha_2 \) by merely solving a quadratic or cubic equation.

Although this solution to the problem remains a low loss
approximation, it could conceivably solve some problems in which equation (33) would be useless. For instance, if $\alpha_2$ were on the order of 0.1 and $\lambda_2 = 4$ cm, then $\beta_2$ would have a value of 1.57 and one would not be justified in neglecting $\alpha_2$ in favor of $\beta_2$. Equations (38) or (38a) would, however, be permissible since $\left(\frac{\alpha_2 \lambda_2}{4}\right)^5$ would be on the order of $10^{-5}$ and could be omitted without introducing appreciable error. These two methods of solution should cover a wide range of samples that are in the low loss category.

The Complex Debye Equation

In any material in which there are permanent molecular dipoles it is assumed that the directions of these dipoles are arranged according to a Boltzmann distribution. With this distribution it can be shown\(^1\) that under the influence of an applied static electric field, the material will exhibit an average dipole moment per molecule of

$$\bar{m} = \frac{\mu^2 E}{3 k T} = \alpha_1 E$$

(39)

where $\mu$ is the dipole moment of each molecule, $K$ is Boltzman's constant, and $T$ is the temperature, in degrees Kelvin, of the dielectric. The constant $\alpha_1$ is then the polarizability of each molecule due to the permanent dipoles.

\(^1\)Page, Leigh. Introduction to Theoretical Physics, D. Van Nostrand Company, 1955, page 393.
In addition to the polarization of the permanent dipoles, there is also an effect due to the dipole moments induced by the applied electric field. The average moment per molecule for the induced dipoles is directly proportional to the applied field

$$\bar{m'} = \alpha_0 E$$

(40)

where $\alpha_0$ is the polarizability for induced dipoles.

The relationship for the total polarizability ($\alpha$) of a material is given in terms of its dielectric constant by the well known Mossetti equation,

$$\frac{k - 1}{k + 2} = \frac{4 \pi n \alpha}{3}$$

(41)

where $n$ is the number of molecules per unit volume, and the total polarizability ($\alpha$) is given by the sum of $\alpha_1$ and $\alpha_2$.

The result is the Debye equation for static fields

$$\frac{k - 1}{k + 2} = \frac{4 \pi n \alpha_0}{3} + \frac{4 \pi n \mu^2}{9 K T}$$

(42)

As was mentioned earlier, the effects of a static or low-frequency field are quite different from those produced by a high-frequency field. The one change that has been presented is the replacement of $k$ by $k^*$. Debye showed that the mean molecular moment $m$, due to permanent dipoles, also became frequency dependent and expressed the complex molecular moment as

$$\bar{m}^* = \frac{\mu^2 E}{3 K T(1 + i \omega r)}$$

(43)

where $r$ is the relaxation time. The relaxation time is defined

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as the time required for the molecule to return to normal of its \( t_{\text{max}} \) displacement when acted upon by an electric field.

Generalization of equation (42) to include the high-frequency effects gives

\[
\frac{k^* - 1}{k^* + 2} = \frac{4 \pi n \alpha_0}{3} + \frac{4 \pi n \mu^2}{9 \, k T (1 + i\omega)}
\]

As \( \omega \) approaches infinity, the second term on the right approaches zero and \( \alpha_0 \) is given by

\[
\frac{4 \pi n \alpha_0}{3} = \frac{k_\infty - 1}{k_\infty + 2}
\]

where \( k_\infty \) is the dielectric constant at extremely high frequencies. The final form of the complex Debye equation is

\[
\frac{k^* - 1}{k^* + 2} = \frac{k_\infty - 1}{k_\infty + 2} + \frac{4 \pi n \mu^2}{9 \, k T (1 + i\omega)}
\]

where \( k_\infty \) is equal to the square of the index of refraction \( N \), measured at optical frequencies.

It should be noted here that, most generally, equation (46) is written in the literature with \( \epsilon^* \) in place of \( k^* \), and \( \epsilon_\infty \) in place of \( k_\infty \), but in either notation the quantities represent the dielectric constant and not the permittivity.

It can be seen, then, from the Debye equation that if one has calculated the real and imaginary parts of the dielectric constant, a good deal of information may be obtained about the dielectric solution. A separation of real and imaginary parts of this complex equation yields

\[
\frac{(k' + 2 + k'' - 2)}{(k' + 2)^2 + k''^2} = \frac{N^2 - 1}{N^2 + 2} + \frac{4 \pi n \mu^2}{9 \, k T (1 + \omega^2 \tau^2)}
\]
and \[ \frac{3 k''}{(k' + 2)^2 + k''^2} = \frac{4 m \mu^2 \omega r}{9 KT(1 + \omega^2 P^2)} \] \[(48)\]

For simplification let \[ R = \frac{(k'^2 + k' + k''^2 - 2)}{(k' + 2)^2 + k''^2} \] \[ I = \frac{3 k''}{(k' + 2)^2 + k''^2} \] \[ P = \frac{N^2 - 1}{N^2 + 2} \] \[(49)\]

Then dividing equation (48) by (47), the result is \[ \frac{I}{R - P} = \omega r \] \[(50)\]

Substitution of the value for \( \omega r \) into equation (47) yields the value for \( \mu^2 \).

\[ \mu^2 = \frac{9 KT(R - P) \left[ 1 + \left( \frac{1}{R - P} \right)^2 \right]}{4 \pi n} \] \[(51)\]

Nodal Shift Determination of Residual VSWR

When two sections of wave guide are joined together by some mechanical means, it is quite possible that there is not a perfect match between the two sections either electrically or mechanically. This mismatch may cause spurious reflections of the electromagnetic wave which would cause a small value of the voltage standing wave ratio (abbreviated VSWR) due to the junction alone in addition to the VSWR of the particular load being measured. It would be desirable to be able to isolate this residual VSWR from the junction so it could be measured and used to correct the desired measurements. For this experiment, the situation was aggravated somewhat by the necessity of having a
liquid-tight seal at the junction between the standing wave detector and dielectric cell which might cause even greater residual reflections.

A method which has been devised\(^1\) for measuring the residual VSWR is called the nodal shift method. If a movable shorting plunger is placed at the left of the coupling network and a movable probe at the right of the network, with the wave incident from the right, then the movable probe will determine the position of any chosen electric field minimum. When the plunger is moved to the left, the particular minimum measured by the probe will also move to the left. However, the minimum position will not always move the same distance as the plunger if there are reflections from the coupling network as well as those from the shorting plunger. Let the distance moved by the plunger be \(x_2\) and the distance moved by the minimum position be \(x_1\). If the quantity \((\beta_1 x_1 - \beta_2 x_2)\) is plotted against \(x_2\), a sinusoidal curve will be produced. \(\beta_1\) is the phase factor of the wave guide in which the probe moves, and \(\beta_2\) is the phase factor of the wave guide in which the plunger moves. When this curve has been drawn, let \(D\) be twice the amplitude of the curve and the residual VSWR (denoted by \(r\)) is given by

\[
r = \frac{1 + \sin D/2}{1 - \sin D/2}
\]

Calculation Outline

There are eight quantities that must be measured experimentally. They are:

1. Inverse standing wave ratio, \( \frac{E_{\text{min}}}{E_{\text{max}}} \).
2. Wavelength in dielectric-filled guide, \( \lambda' \).
3. Wavelength in air-filled guide, \( \lambda_1' \).
4. Distance from interface to first minimum, \( x_0 \).
5. Index of refraction of liquid dielectric, \( N \).
6. Temperature, \( T \).
7. Number of polar molecules per unit volume, \( n \).
8. Thickness of dielectric sample, \( d \).

The quantity \( \alpha_2 \) may be calculated from equation (33),

\[
\tanh \alpha_2 d = \frac{\beta_2}{\beta_1} (A + iB)
\]
or equation (38a). With the value of \( \alpha_2 \), then \( \varepsilon_2' \) and \( \varepsilon_2'' \) may be calculated from the separation of equation (17) into its real and imaginary parts.

\[
\frac{\varepsilon_2'}{\varepsilon_0} = \frac{\left( \frac{1}{\lambda_c} \right)^2 - \alpha_2^2 - \beta_2^2}{\left( \frac{1}{\lambda_c} \right)^2 + \left( \frac{1}{\lambda_1} \right)^2} = k_2'
\]

\[
\frac{\varepsilon_2''}{\varepsilon_0} = \frac{2\alpha_2 \beta_2}{\left( \frac{1}{\lambda_c} \right)^2 + \left( \frac{1}{\lambda_1} \right)^2} = k_2''
\]

Knowing the values of \( k_2' \) and \( k_2'' \), the Debye equation may be used to calculate the dipole moment,

\[
\mu^2 = \frac{9 K T(R - P)}{4 \pi n} \left[ 1 + \left( \frac{I}{R - P} \right)^2 \right]
\]
and the relaxation time,

\[ r = \frac{I}{\omega(R - P)} \]

APPARATUS AND MEASUREMENTS

General Microwave Circuit

The general microwave circuit consisted of a klystron oscillator, cylindrical transmission cavity isolator, directional coupler, standing wave detector, and the dielectric cell (see Plate II).

A type 2K25 klystron was mounted in a short section of x-band,\(^1\) wave guide with its energy fed into the circuit by a vertical stub antenna. The antenna was an integral part of the klystron tube. The klystron was frequency modulated by a sawtooth wave form from the sweep voltage of a type 551 Tektronix dual-beam oscilloscope which was externally triggered by a 10,000-cycle sine wave. The approximate form of this modulator wave form is shown in Plate II. The klystron was modulated about a central frequency of 9.349 kilomegacycles through a band width of 26 megacycles. Therefore the frequencies present at the output of the klystron varied approximately from 9.336 to 9.362 kilomegacycles. Since the repeller of the klystron required a

\(^1\)X-band wave guide has inside dimensions of approximately 7/8 inch by 3/8 inch and is normally used for transmitting frequencies from 8.2 kilomegacycles to 12.4 kilomegacycles.
EXPLANATION OF PLATE II

General circuit diagram for entire microwave measuring apparatus.
negative bias, the sawtooth voltage from the oscilloscope was fed through a d-c restorer circuit which gave the sawtooth a negative d-c level of approximately 210 volts. Adjacent to the klystron mount was a variable attenuator by which the signal in the rest of the circuit may be reduced as much as 20 dB.

Coupled directly to the attenuator mount was a cylindrical, resonant, transmission cavity with one movable wall. The movable wall was attached to a micrometer screw and could be varied so as to change the resonant frequency. The cavity, arranged in this manner, acted as a very narrow band-pass filter. Thus the signal out of the cavity was essentially monochromatic and appeared as one pulse for each complete sweep cycle. This cavity was calibrated by the National Bureau of Standards so it also functioned as a frequency meter.

The next circuit element was a microwave isolator. This is merely a unidirectional transmission line which transmits the signal easily away from the klystron but blocks any reflected energy from returning to the source and causing trouble by coupling with the klystron.

Fastened to the isolator was a two-way directional coupler which was used to monitor the reflected wave. Since it measures directly only one component of a standing wave, it disregards any phase relationship of the two waves and deals only with their magnitudes. This device does not appreciably alter the field since the output of the coupler is 20 dB below the actual field intensity. The particular directional coupler used was constructed of slightly larger wave guide (H-band) than the rest of
the circuit but the connection from this size to x-band was not difficult.

The major measuring device of the circuit was the Hewlett-Packard Model 809B standing wave detector. This piece of apparatus consisted of a slotted section of wave guide with a movable probe designed to move along the slot and sample the electric field in the wave guide. The probe was inserted into the wave guide a distance of approximately one millimeter such that it did not appreciably distort the field pattern. The high-frequency signal from the field was fed through a 1N21 diode acting as a square-law detector to produce an output in the form of a pulse whose amplitude was proportional to the square of the electric field intensity or the power of the wave. This pulse was fed into a pre-amplifier and a high-gain linear pulse amplifier (a modified A-1 amplifier) and then directly to the oscilloscope. Since the oscilloscope was the source of the sweep modulation signal on the klystron, there was one pulse per sweep of the electron beam which produced a very good display of the energy received from the field.

Because the amplifier had a gain on the order of $10^5$ with poor overload characteristics, it had a definite tendency to be easily overdriven. This was an easily recognizable phenomenon since the oscilloscope trace became highly distorted when this occurred. The equipment was checked for the region in which the amplifier was not overdriven and found to be linear for this range. Thus as long as the trace was not distorted, it was assured that the equipment was operating within its range of
linearity.

Two different dielectric cells were used during the experiment, each being a section of wave guide fitted with a movable, short-circuiting plunger. The short-circuiting elements were those removed from Hewlett-Packard X920-A adjustable shorts. The first cell used was approximately 8 cm long with a plunger travel of 5 cm. The second cell was approximately 20 cm in length, with 13 cm of plunger travel. After a short time the small cell was abandoned completely because it was desirable to have a long dielectric sample for measuring samples of low loss.

Because all the measurements were to be made with liquid materials and because the standing wave detector was designed for horizontal operation, there were only two choices as to the mounting position of the cell. One possibility was to mount the cell vertically by placing a 90-degree wave guide section between the standing wave detector and the cell. By positioning the cell in this manner, the liquid would be contained by the action of gravity and the cell could remain open to the surface of the liquid. This method met with two difficulties. First, the interface was not a plane because of the meniscus, and, second, the interface was found to change its position due to evaporation. The second possibility was adopted, that of mounting the dielectric cell approximately horizontal and containing the liquid at the interface by some sort of window which would not affect the measurements appreciably. The choice of this window material will be discussed in detail in the next section.

The mechanism for the movable plunger was placed in the end
of the cell opposite the window. It was necessary, if mounted exactly horizontally, to maintain a liquid-tight seal around the turning shaft and the other parts making up the adjusting mechanism. For ordinary liquids (such as water, or alcohol), a seal was obtained by merely packing the moving parts with a very stiff vacuum grease. This permitted a liquid-tight cell along with easily operated moving parts. However, most materials that were measured in this experiment were in a benzene solution which was a very good solvent for this particular grease and for other sealing substances as well, so the entire microwave assembly was mounted at an angle of approximately 15 degrees above the horizontal. Then by filling the cell until the liquid level was just under the moving mechanism, the turning shaft was enabled to operate above the surface of the liquid, thereby eliminating the need for sealing the end of the cell.

Operational Procedure

As stated earlier, it was decided shortly after the experiment was begun that a window to contain the dielectric would be most desirable.

In deciding on the general design for the window, there were two choices available: either a window of an extremely low-loss material which could be made a half wavelength thick, or a window that could be made very thin. The choice of the thick window would require a very low-loss material but mechanical stability would not be a problem. Some work has been done in this area
with a teflon window cut to exactly one-half wavelength thickness (9). The thin window idea has the advantage of much less rigid requirements for the loss of the material but when materials are made so thin, the mechanical stability becomes a problem.

For this experiment several window materials were considered. Some of these were cellophane, thin plastic film, polyethylene, and mica. The first two were quickly discarded. The most desirable form of polyethylene was a very thin tape. This was tried and found to stretch completely out of shape when in contact with a benzene solution, so if a polyethylene window were to be used it would have to be on the order of a millimeter thick to have any rigidity at all. By contrast, a sheet of mica could be split to a very small thickness and still be rigid enough to contain the liquid in a flat plane but mica is a very lossy material.

The nodal shift method was used to measure the residual VSWR due to the introduction of each of these materials between the flanges of the wave guide junction. The evaluation of these two window materials consisted of comparing the residual VSWR of the open wave guide junction to their residual VSWR's. The resulting graphs are shown by Plate III. The residual VSWR of the open junction and that of the mica window can be seen to be approximately equal, while that for the polyethylene window is considerably larger. The actual calculated values for the residual VSWR from the three curves are:

1. Open junction VSWR = 1.030 ± 0.008
2. Mica window VSWR = 1.024 ± 0.008
EXPLANATION OF PLATE III

Curves obtained for calculating the residual VSWR of the mica window.

From these figures it can be seen that within the range of experimental error, the mica window introduced negligible reflection but the polyethelene very definitely produced spurious reflections. On the basis of these findings the remainder of the experiment was carried out using a thin mica window to contain the liquid.

Even though the mica was extremely thin (on the order of 15 microns), a measurement was taken to determine whether or not the added thickness of the mica could be detected by the apparatus. This was done by placing a polished brass shorting plate flat against the flange of the standing wave detector and finding the minima positions in the slotted section. The same measurement was taken with the piece of mica inserted between the flange and the shorting plate. There was no shift in the standing wave pattern, which would indicate that the added thickness of the mica was negligible for this particular apparatus. With the above information it was decided that there would be no factor necessary to correct for the use of the thin mica window.

All measurements were taken with benzene solutions which are excellent solvents for almost any material. The mica windows were sealed to the wave guide flange by heating the flange, applying an ether resin, and pressing the window onto the hot resin. After several days this resin would be dissolved and the window would have to be replaced. Along with the ether resin, a pressure sensitive teflon adhesive was used from time to time. Although this adhesive was also soluble in benzene, it was much
easier to apply since it did not require heating the wave guide.

In addition to numerous window replacements, it was necessary to periodically disassemble the dielectric cell, clean, and polish it. The walls were silver-plated and had to be kept clean to prevent excessive wall loss.

All measurements were carried out with the particular dielectric dissolved in benzene. One reason for the choice of benzene was, of course, its extreme solvent action on a wide range of materials. More important, however, was the fact that it is a non-polar compound and has extremely low loss factor.

In the formulation of the Debye theory, it was assumed that the individual permanent dipoles experienced negligible interaction with their neighboring dipoles. This assumption is valid only in a gas or a dilute solution of the dipoles in a non-polar solvent. Essentially the dilute solutions produce the gaseous condition with respect to the permanent dipoles.

It will be noticed that equation (46) requires the number of dipoles per unit volume. This was calculated from the expression

\[ n = N_0 \cdot \frac{1}{M} \cdot d \]

where \( N_0 \) is Avagadro's number, \( M \) is the molecular weight of the solute, and \( d \) is the density, in grams of solute per unit volume of solution.

Preliminary to the actual experimental work on the sample, the standing wave detector required a calibration check. The scale on the carriage of the detector was supposedly calibrated to read the distance from the probe to the face of the flange.
(which would be the distance from probe to dielectric interface). A quick check showed this to be an error. By measuring the wavelength in the guide, the exact location of the standing wave pattern could be calculated for the short circuit placed at the end of the standing wave detector. This is possible since a minimum electric field will be located at the position of the short and at intervals of $\lambda_1/2$ back along the slotted line. The scale readings on the standing wave detector were found to be .030 cm less than the actual distance from probe to interface. In subsequent data this correction was made in all readings.

Because the scale on the dielectric cell could only determine position relative to an arbitrary zero, it also required calibration. This scale was constantly being assembled and disassembled. Therefore this particular calibration was made preliminary to each sample measurement. The scale was calibrated by setting it at some arbitrary point and noting the shift in the standing wave pattern from its position with the shorting plate at the end of the slotted line. This shift in the pattern was the actual distance from the window to the shorting plunger. Comparison of this thickness with the scale reading gave a correction figure for any scale reading. This entire procedure was carried out with the dielectric cell empty.

The cell was filled from the rear with the front of the cell slanting down. To eliminate air bubbles in the sample, the entire cell and standing wave detector had to be turned vertically momentarily after filling. It was quite apparent on the oscilloscope when air bubbles were present as a small tap on the
cell would cause sizable variations in the amplitude of the output signal, but the signal was quite steady when the cell was filled beyond the plunger.

The first measurement to be made after the cell had been filled with dielectric was the determination of the wavelength in the dielectric-filled wave guide, \( \lambda' \). This was done by connecting a crystal detector to the reflected signal output of the directional coupler and feeding this signal through the amplifier to the oscilloscope. The output of the directional coupler was essentially a measure of the absolute value of the reflection coefficient. By moving the plunger, a point of minimum reflection could be determined. The distance from that point to the next point of minimum reflection represented one-half of a wavelength in the dielectric-filled guide. By noting the positions of successive minimum reflection points, a reliable value of \( \lambda' \) could be determined. Knowing the value of the wavelength, the appropriate thickness of the dielectric sample [either \( \frac{\lambda'}{2} \) or \( (2n + 1) \frac{\lambda'}{4} \)] may be fixed for the subsequent measurements of \( x_0 \), and the inverse standing wave ratio. Normally, approximately 30 successive positions were determined so as to get an average value for wavelength.

After the thickness of the sample had been set, the position of the first measurable electric field minimum was determined with the traveling probe. Since the slot in the standing wave detector did not extend over the full length of the detector, it was impossible to measure directly the position of the first minimum. The distance \( x_0 \) from the interface to the first
minimum was extrapolated from the position of the first measurable minimum by the following relation:

\[ x_0 = x - \frac{n \lambda_1'}{2} \]

where \( x \) is the distance from the \((n + 1)\) minimum to the interface and \( \lambda_1' \) is the air-filled guide wavelength. The value of \( x \) is read directly from the slotted line (taking into account the previously mentioned correction factor).

Because of the relative ease with which the amplifier could be overdriven, it was desirable that any measurements should be made in the vicinity of the electric field minima. It was necessary to use an indirect method of evaluating the inverse standing wave ratio \( \left( \frac{E_{\text{min}}}{E_{\text{max}}} \right) \). It can be shown\(^1\) that this ratio may be determined from the following relation.

\[ \frac{E_{\text{min}}}{E_{\text{max}}} = \frac{\sin \left( \beta_1 \frac{\Delta x}{2} \right)}{\left[ 2 - \cos^2 \beta_1 \frac{\Delta x}{2} \right]^{\frac{1}{2}}} \]

The quantity \( \Delta x \) is the distance between points on either side of the minimum where the output power is twice that of the minimum power. Thus \( \frac{E_{\text{min}}}{E_{\text{max}}} \) may be determined without any danger of

overdriving the amplifier. This method also minimizes the distortion of the standing wave pattern resulting from the insertion of the probe into the wave guide.

At the frequencies used in this experiment, which were approximately 4.5 cm, there were usually four distinct, measurable minimum positions in the standing wave detector. Therefore the above procedure was carried out at each of the four minimum positions giving four values for $x_0$ and $\frac{E_{\text{min}}}{E_{\text{max}}}$. A typical set of values for $x_0$ and $\Delta x$ is:

<table>
<thead>
<tr>
<th>$x_0$</th>
<th>$\Delta x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.216 cm</td>
<td>.064 cm</td>
</tr>
<tr>
<td>2.218</td>
<td>.065</td>
</tr>
<tr>
<td>2.219</td>
<td>.065</td>
</tr>
<tr>
<td>2.215</td>
<td>.066</td>
</tr>
</tbody>
</table>

**DISCUSSION OF RESULTS**

In Table 1 it will be noticed that for each measurement recorded the corresponding sample thickness is indicated. This is done because, as shown by the theory, the method of calculation depends upon the choice of the dielectric thickness. For a thickness of $(2n + 1) \lambda_2'/4$ equation (38) is used, and for thicknesses of $n \lambda_2'/2$ equation (33) is used to calculate $\alpha_2$.

The densities recorded are obtained by dividing the mass of the material by the total volume of the solution.

A preliminary set of data was taken for pure benzene. As mentioned before, benzene is a non-polar compound, and thus
Table 1. Results of measurements on various liquids.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (gm/cc)</th>
<th>k'</th>
<th>k''</th>
<th>tan δ</th>
<th>μ (Debye cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.8790</td>
<td>2.285</td>
<td>0.0202</td>
<td>0.0087</td>
<td>1/4</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.8790</td>
<td>2.285</td>
<td>0.0082</td>
<td>0.0036</td>
<td>2</td>
</tr>
<tr>
<td>Dimethylamino azobenzene</td>
<td>0.49 x 10⁻⁴</td>
<td>2.285</td>
<td>0.0203</td>
<td>0.0091</td>
<td>1/4</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.38 x 10⁻⁴</td>
<td>2.281</td>
<td>0.0033</td>
<td>0.0014</td>
<td>9/4</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.64 x 10⁻⁴</td>
<td>2.285</td>
<td>0.0040</td>
<td>0.0018</td>
<td>9/4</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.64 x 10⁻⁴</td>
<td>2.285</td>
<td>0.0092</td>
<td>0.0039</td>
<td>2</td>
</tr>
<tr>
<td>&quot;</td>
<td>91.0 x 10⁻⁴</td>
<td>2.301</td>
<td>0.015</td>
<td>0.0065</td>
<td>3.05</td>
</tr>
<tr>
<td>&quot;</td>
<td>91.0 x 10⁻⁴</td>
<td>2.297</td>
<td>0.017</td>
<td>0.0074</td>
<td>3.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>91.0 x 10⁻⁴</td>
<td>2.297</td>
<td>0.010</td>
<td>0.0044</td>
<td>3.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>99.0 x 10⁻⁴</td>
<td>2.301</td>
<td>0.0154</td>
<td>0.0067</td>
<td>3.06</td>
</tr>
<tr>
<td>&quot;</td>
<td>182 x 10⁻⁴</td>
<td>2.311</td>
<td>0.025</td>
<td>0.0108</td>
<td>2.38</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>101 x 10⁻⁴</td>
<td>2.413</td>
<td>0.0874</td>
<td>0.0362</td>
<td>4.25</td>
</tr>
<tr>
<td>&quot;</td>
<td>118 x 10⁻⁴</td>
<td>2.440</td>
<td>0.1033</td>
<td>0.0424</td>
<td>4.38</td>
</tr>
<tr>
<td>&quot;</td>
<td>117 x 10⁻⁴</td>
<td>2.481</td>
<td>0.0420</td>
<td>0.0169</td>
<td>3.04</td>
</tr>
<tr>
<td>Acetone</td>
<td>117 x 10⁻⁴</td>
<td>2.481</td>
<td>0.0420</td>
<td>0.0169</td>
<td>3.04</td>
</tr>
<tr>
<td>P-Aminoazo benzene</td>
<td>125 x 10⁻⁴</td>
<td>2.306</td>
<td>0.0166</td>
<td>0.0072</td>
<td>2.64</td>
</tr>
<tr>
<td>&quot;</td>
<td>235 x 10⁻⁴</td>
<td>2.334</td>
<td>0.0249</td>
<td>0.0107</td>
<td>2.40</td>
</tr>
</tbody>
</table>

#1 Debye = 10⁻¹⁸ e.s.u. charges x cm.

should have a value of zero for its dipole moment. By equation (46), it can been seen that a non-polar substance should have zero value for k'' and k' = k_∞ = N². In other words, benzene should be completely lossless. From the data it can be seen that benzene exhibits a finite loss although it is very small. The
major part of this loss is probably due to ohmic dissipation in the benzene. The value for the real dielectric constant agreed very well with that recorded in the literature (from 2.275 to 2.285). The loss tangent has been measured by other observers as less than .007, which is somewhat lower than the results in line 1.

The data for line 1 was taken for a one-quarter wavelength sample which makes the thickness approximately .6 cm. When the thickness was increased (line 2), the calculated loss decreased, which would indicate that measurements for the thin sample were beyond the sensitivity of the apparatus.

One of the materials investigated was dimethylaminoazobenzene. Its dielectric properties have been measured before (8) but only in the low-frequency region. Measurements were taken on solutions of varying densities, beginning with extremely dilute samples. From the table it will be noticed that the real part of the dielectric constant did not change from that for pure benzene until the density was increased to .0091 gm per cc. For these solutions in which \( k' \) did not change, it would have been meaningless to calculate the dipole moment. However, some inconsistencies may be seen by comparing the values of \( k'' \) for these solutions.

The first two samples were measured with a sample thickness of one-quarter wavelength. Due to the low loss of these samples, as with pure benzene, the accuracy of the results was severely limited by the sensitivity of the apparatus. In an effort to correct this, the sample length was increased to nine one-quarter
wavelengths. The results show these samples to give a much lower value for $k''$. Although there is nothing published with which to compare these values, the results with the longer sample should give a more reliable property of the dielectric.

For the sake of comparison, the same sample was measured by each of the two methods presented in the theory section (see lines 5 and 6 in Table 1). It can be seen from the table that there was an appreciable difference in the values obtained from the two methods. When the sample thickness is set at some odd multiple of a quarter wavelength, the value of $x_0$ is such that the term $\tan \beta_1 x_0$, is dominant in the calculation of $k''$. This means that the value of the standing wave ratio is rather unimportant in the calculation. However, the calculation for a sample whose thickness is some multiple of a half wavelength exhibits approximately equal sensitivity to both the standing wave ratio and the value of $x_0$. Another difference in the two methods is that in the first method, the mica window and wave guide junction are in the vicinity of an electric field maximum, whereas in the second method they are in the vicinity of an electric field minimum. It was decided that most of the subsequent measurements would be made by setting the sample thickness at some multiple of a half wavelength.

Not until the density of the solute was increased to $91 \times 10^{-4}$ gm per cc did the real part of the dielectric constant show an appreciable change in value. This indicated that the

\[ 1 \text{This corresponds to } 2.436 \times 10^{19} \text{ polar molecules per cubic centimeter of the solution.} \]
dipoles were beginning to have some effect and that it might be feasible to calculate the dipole moment. The value given by Campbell (8) for the dipole moment was 3.22 Debye. In the literature giving the calculated values of dipole moments, there is often a range of .2 or .3 Debye over which these values have varied. This would indicate that 3.00 Debye would not be an unreasonable value for the dipole moment.

The most prominent discrepancy of the entire experiment arose when the density of the sample was increased to 182 x 10^-4 gm per cc. The values of the real and imaginary parts of the dielectric constant increased over the previous sample which is consistent with what one would expect, but the calculated value of the dipole moment dropped drastically from the other values.

There are three logical places where an error of this size might be introduced: in the value of k', in the value of the index of refraction N, and in the number of dipoles per unit volume n. Because of the very good consistency displayed by all values k', there is no reason to doubt the validity of this particular value. The index of refraction of the solution was measured on an Abbe refractometer which is accurate to four decimal places. The most likely place for this error, then, is in the number of dipoles per unit volume, but no error has as yet been found in that calculation. The substances were carefully weighed on an analytic balance so it should be correct. As one might conclude from the previous statements, this deviation cannot yet be explained.

Because of this unexplained variation from the expected
results, two other materials were measured. Each of these materials has been measured previously and the results have been published (2). The range of values given for the dipole moment of nitrobenzene is from 3.90 to 4.3 Debye, and for acetone from 2.6 to 2.78 Debye. The densities for the acetone and nitrobenzene samples, in lines 13 and 14, were calculated on the basis of volume measurement instead of mass measurements which introduced some inaccuracy in the determination of $n$ for these two samples. The samples should have been weighed on an accurate balance since the value of $n$ is quite critical. The density in line 12 was calculated from mass measurements but showed no outstanding variation. The values of $k'$ and $k''$ for both samples did agree quite well with the published values for this approximate concentration. The calculations for acetone and nitrobenzene did show that the experiment was at least approaching correct operation.

Many more measurements and calculations are advisable and necessary to establish the complete reliability of the experimental procedure. Measurements for various densities of acetone and nitrobenzene would be desirable. Also a measurement on a different sample of dimethylamino azobenzene which has a density of approximately $1.32 \times 10^{-3}$ would be desirable.

There is one other possible explanation of the deviation exhibited by line 10. If the concentration has been increased so much that the assumption of no dipole interdependence is no longer valid, then the value of the dipole moment would be expected to go down. Considering only the number of molecules per
unit volume, the solution is well within the range of published results. However, the dimethylaminoazobenzene molecules are quite heavy and complex, which might possibly increase the molecular interaction.

Within the knowledge of the author, dipole moment values have not been published for P-aminoazobenzene. From lines 15 and 16 of Table 1, it can be seen that the more concentrated solution gave a lower dipole moment. This decrease might again be the result of increasing dipole interaction of the sample.

These measurements would indicate that it might be advisable to carry out this experiment for increasingly dense samples. If there were a consistent decrease of dipole moment with increasing density, one might gain insight as to ways to account for the dipole interaction.

A theoretical discrepancy which arose during the course of the experiment was found in the calculation of $\alpha_2$. For a sample length of $(2n + 1)\lambda_2'/4$, two equations, (38) and (38a), resulted from the solution of equation (29). Each of the two equations should have given equally valid results. It was found, however, that equation (38a) gave acceptable results, while equation (38) gave an imaginary value for $\alpha_2$. No explanation for this has been resolved as yet.

The methods presented in this paper are an attempt to solve the equations for the complex dielectric constant with as few assumptions as possible. The direct measurement of $\beta_2$ and the choice of the dielectric sample thickness make the solution of
the problem somewhat more straight-forward. These additional experimental measurements only minimize the assumptions and are not used with the idea of attempting to simplify the calculations.
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MICROWAVE MEASUREMENTS OF DIELECTRIC PROPERTIES OF SOME POLAR LIQUIDS

by

JOHN CLARK CRAWFORD

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The real and imaginary parts of the complex dielectric constant may be determined by measuring the propagation factor of microwaves through the dielectric. This propagation constant is measured using liquid dielectric in rectangular wave guide terminated by a metallic short. To facilitate the solution of the problem, the terminating short was in the form of a movable plunger which made possible the direct measurement of the radiation wavelength in the dielectric sample. The thickness of the sample can then be made a suitable function of the wavelength. Two possible solutions to the problem are presented, one corresponding to a sample thickness of a multiple of a half wavelength and the other to an odd multiple of a quarter wavelength. Both of these solutions are restricted to low-loss samples.

The value of the complex dielectric constant is used in the complex Debye equation to determine the permanent dipole moment of a polar dielectric.

The dielectric solution was contained in the wave guide by means of a thin sheet of mica. The effect of the mica was evaluated by measuring the residual standing wave ratio.

The general experimental procedure utilized a frequency-modulated klystron operating in x-band. The wavelength was measured by using the movable short in conjunction with a directional coupler, and a standing wave detector was used to measure the reflection from the dielectric interface.

Measurements were conducted with samples of benzene, nitrobenzene, acetone, dimethylaminoazobenzene, and P-aminoazobenzene, with the last four being dilute solutions in benzene.
Samples of various concentrations of the solutions were measured.

Although the values for the dielectric constants were reliable, the dipole moment seemed to be extremely sensitive to concentration.