MEASUREMENT OF DIELECTRIC CONSTANT
AND DIPOLE MOMENT OF LIQUIDS

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MEASUREMENT OF DIELECTRIC CONSTANT
AND DIPOLE MOMENT OF LIQUIDS

THESIS

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by

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CHAPTER I

THEORETICAL DISCUSSION

Dipole Moment and the Debye Equation

A dipole consists of two electric charges very close together and opposite in sign. The moment of such a dipole is measured by the product of either charge by the distance between the two charges. As the moment acts in the direction of the line joining the two charges it is a vector quantity. The moment of a molecule is the vector sum of all the individual moments in its structure. In some molecules one or two dipoles are so much larger than the others that only the moments of the larger dipoles are considered in the complete moment of the molecule. ¹

Some molecules exhibit a permanent dipole moment, while other molecules have a dipole moment only in the presence of an electric field. The latter molecules form non-polar substances, while molecules with permanent dipole moments form polar substances. Thus, non-polar molecules have a center of symmetry, i.e., the center of all the positive and the center of all the negative charges in the molecule coincide. The shape of polar molecules may be determined by observing

the value of the permanent dipole moment and constructing a molecular model whose calculated dipole moment is nearest that observed.

To arrive at an expression for molar polarization and molecular polarizability in terms of the dielectric constant, consider two parallel plates which are large in comparison with their separation. The medium between the plates may be any homogeneous dielectric material. Let a homogeneous field be created by uniform distribution of charges over the two plates. The actual force \( F \) acting on a particle in the medium carrying a unit positive charge may be thought of as consisting of three components

\[ F = F_1 + F_2 + F_3. \]  

(1)

\( F_1 \), the force due to the charges distributed uniformly on the surface of the plates, is

\[ F_1 = 4\pi \sigma \]  

(2)

where \( \sigma \) is the surface density of charge on the plate. Now let a small sphere enclose the particle. The component of force \( F_2 \) is then due to the polarization of the medium exterior to the small sphere when the medium inside the sphere is removed. \( F_2 \) is made up of two parts, first the force due to the layers of induced charge on the dielectric facing the conducting plates, and second the layer of charge on the small spherical cavity. The force \( F_2 \) is then

\[ F_2 = -4\pi I + 4\pi I/3 \]  

(3)

where \( I \) is the polarization of the medium, or the electric
moment per unit volume set up in the dielectric. The component $F_3$ is the force on the particle due to the medium inside the small sphere. If the dielectric is assumed to be a liquid whose molecules move totally independently of each other, then $F_3 = 0$. The total force then becomes

$$F = 4\pi \sigma - 4\pi I + \frac{4}{3}\pi I$$  \hspace{1cm} (4)

A fundamental law connecting electric displacement $D$ with the charges states

$$D = 4\pi \sigma$$  \hspace{1cm} (5)

Now making use of the equation for $D$, which is a general relation independent of the form of the law connecting polarization and electric intensity, namely

$$D = E + 4\pi I,$$  \hspace{1cm} (6)

the equation for the total force becomes

$$F = E + 4\pi I/3.$$  \hspace{1cm} (7)

This relation between the actual force $F$ per unit charge, the electric intensity $E$, and the polarization $I$, exists providing $F_3$ is assumed to be zero. This relation will hold only in the case of gases and very dilute solutions. If the average moment of one molecule is

$$m = dF,$$  \hspace{1cm} (8)

where $d$ is called the polarizability, and if $n$ is the number of molecules contained in one cc., then by the definition of the polarization $I$ as the electric moment per unit volume, $I$ is given by

$$I = nm = n dF = n (E + 4\pi I/3).$$  \hspace{1cm} (9)
Since the general relation for $D$ is given in equation (6), by eliminating $I$ between equations (6) and (9) the relationship connecting $D$ and $E$ can be found; i.e., the dielectric constant $\epsilon$ expressed in terms of the molecular polarizability $\alpha$ can be found. By making use of the relationship

$$D = \epsilon E$$

the results can be put in the form

$$\frac{\epsilon - \frac{1}{2}}{\epsilon + \frac{1}{2}} = \frac{4\pi n \alpha}{3}. \quad (10)$$

By multiplying both sides of equation (10) by the quotient of the molecular weight $M$ over the density $d$ of the dielectric, the left hand side of the equation becomes

$$\frac{\epsilon - \frac{1}{2}}{\epsilon + \frac{1}{2}} \cdot \frac{M}{d} \quad (11)$$

while the right hand side of equation (10) becomes the molar polarization $P$. It is given by

$$P = 4\pi N \alpha/3 \quad (12)$$

where $N$ is Avogadro's constant and is equal to $nM/d$. From its definition $P$ may then be determined from the equation

$$P = \frac{4\pi \epsilon_0 \epsilon - \frac{1}{2}}{\epsilon + \frac{1}{2}} \cdot \frac{M}{d}. \quad (13)$$

If now the molecule is considered as a rigid system of charges with an electric moment $\vec{m}$ (the arrow denotes a vector) and a field intensity $\vec{F}$, the potential energy $u$ of the molecule is given by

---

where the dot indicates the scalar product of the two vectors. If there are no forces acting, the moments of a number of molecules will, on the average, be distributed with the same probability over all directions in space. Then the number of molecules pointing in the directions confined in a solid angle $d\Omega$, shown in Figure 1, is

$$A d\Omega$$

where $A$ is a constant depending on the total number of molecules considered. In a field of intensity $F$ the number of molecules confined in $d\Omega$, according to Boltzmann's law, is

$$A e^{-(\gamma/kT)} d\Omega$$

where $k$ is equal to the gas constant per molecule and equal to $1.37 \times 10^{-16}$ e.s.u.

**Fig. 1**--Diagram for space orientation of dipoles.
If $\theta$ is the angle between the directions of $m$ and $F$, then

$$u = -\mu F \cos \theta$$

(16)

where $\mu$ is the absolute value of the electric moment. A specific molecule pointing in the direction of $d\Omega$ has a component $\mu \cos \theta$ in the direction of the field. The average moment $\bar{m}$ in the direction of the field of one molecule is found in calculating the expression

$$\bar{m} = \frac{\int A e^{(\mu F/kt) \cos \theta} \mu \cos \theta \ d\Omega}{\int A e^{(\mu F/kt) \cos \theta} \ d\Omega}$$

(17)

where the integration is taken over all possible directions.

If

$$\frac{\mu F}{kt} = x$$

(18)

the result can be expressed by the equation

$$\frac{\bar{m}}{\mu} = \coth x - \frac{1}{x} = L(x)$$

(19)

where $L(x)$ is called Langevin’s function. In dealing with electric moments conditions are such that very often $x = \mu F / kt$ is a small number. In this case $L(x)$ can be replaced by its first approximation

$$L(x) \approx x/3,$$

such that

$$\bar{m} = \frac{\mu^2}{3kt} F$$

(20)

For small field intensities the apparent average moment of one molecule is proportional to the field intensity, although the molecular system is not distorted. Equation (20) was obtained by considering a rigid system where no change was
induced, so it does not account for induced polarization. Therefore, the mean electric moment \( \bar{m} \) is expressed by

\[
\bar{m} = (\alpha_o + \frac{\alpha^2}{3K_T})F.
\]  
(21)

The general expression for \( \alpha \) is given by

\[
\alpha = \alpha_o + \frac{\alpha^2}{3K_T}.
\]  
(22)

The expression for the molar polarization \( P \) then becomes

\[
P = 4\pi N/3 (\alpha_o + \alpha^2/3K_T)
\]  
(23)

or, \( P = (4/3)\pi N\alpha_o + (4/3)\pi N\alpha^2/3K_T. \)

If \((4/3)\pi N\alpha_o\) is set equal to \(a\), and \((4/3)\pi N\alpha^2/3K\) is set equal to \(b\), equation (23) may be written as

\[
P = a + \frac{b}{T}.
\]  
(24)

Substituting the values for \( N \) \((N = 6.06 \times 10^{23} \text{ per mole})\) and \( K \) \((K = 1.37 \times 10^{-16} \text{ ergs per degree})\) in the equation for \( b\), the value for \( \alpha \) becomes

\[
\alpha = 0.0127 \sqrt{b} \times 10^{-18} \text{ e.s.u.}
\]  
(25)

In a plot of \( P \) against \(1/T\) the slope of the line determines the value for \( b. \)

**Dielectric Constant and Its Significance**

The dielectric constant of a substance may be defined as the ratio of the capacitance of a condenser filled with the dielectric in question to the capacitance of the condenser.

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with air (or a vacuum) between the plates. Materials which fall in the conductor classification are not usually thought of as dielectrics. Thus, a material with a dielectric constant of 80 or more is considered a conductor. Materials which have a resistivity in ohm centimeters of $10^5$ to $10^{10}$ may have values of dielectric constant from 20 to 6. Materials in the insulator class have a resistivity in ohm-centimeters from $10^{15}$ to $10^{20}$ and greater. These materials may have dielectric constants from 5 to 1. Good dielectrics are those which have very low dielectric constants (below 3) and corresponding high resistances. Although the relation between the dielectric constant and resistivity is not strictly a functional one, a material with a dielectric constant of 2 can be assumed to have a very high resistivity and can be placed in the insulator classification.

Methods For Determining Dielectric Constant

Three methods in use at the present for determining dielectric constant are the bridge method, the resonance method, and the heterodyne-beat method. The heterodyne-beat method was used in the present investigation and will be discussed in detail later.

In all three methods, the capacitance of a test cell is measured without and with the dielectric between the electrodes. Essentially, the dielectric constant is the ratio

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of the capacitance of the test cell with the dielectric to that without the dielectric.

Minor corrections for the capacitance of the leads to the test cell and certain other factors can be made when precision results are desired. The three methods differ only in the manner in which the capacitances are measured.

The bridge method for measuring capacitances is one in which the capacitances are balanced one against the other. Since the material to be measured may have appreciable conductance, adjustable resistances are connected in parallel with the capacitances in the bridge arms. The resistances are balanced against each other and then the capacitances are balanced. From the resistance readings the conductivity of the dielectric may be found, while the dielectric constant is found by means of a precision condenser in parallel with the test cell. A balance is obtained with no dielectric in the test cell by adjusting the precision condenser. The dielectric is added and the precision condenser readjustment is made. The difference between the two readings of the precision condenser gives the added capacitance due to the dielectric. Balancing the bridge with the precision condenser before the test cell is connected makes possible the calculation of the capacitance of the cell when empty. As in the other methods the dielectric constant is the ratio of the
capacitance of the cell containing the dielectric to the capacitance of the empty cell. 6

Briefly, the principle of the resonance method is to attain a maximum current in a secondary circuit, which contains an inductance and capacitance in series, coupled loosely to the primary high frequency circuit. The capacitance of the secondary circuit consists of a test cell in parallel with a precision condenser. When the dielectric changes the capacitance of the test cell, and consequently the current in the secondary circuit, the current is returned to maximum by adjusting the precision condenser. This gives the change in capacitance caused by the addition of the dielectric. The dielectric constant is then calculated as before. 7

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7Ibid., p. 1000.
CHAPTER II

DESCRIPTION OF THE HETERODYNE-BEAT APPARATUS

The heterodyne-beat apparatus consists of a power supply, a Hartley oscillator, an antenna, a radio-frequency amplifier, a detector-mixer stage, and a two-stage audio amplifier. Other apparatus used consists of a constant-temperature bath made by Precision Scientific Company, an audio oscillator, a cathode-ray oscilloscope, and the dielectric constant test cell.

The power supply, as shown in the upper section of Figure 2, is mounted on an aluminum chassis, 12" x 7" x 3", separated from the oscillator-amplifier sections for shielding purposes and to prevent overheating of the oscillator section. The rectifier is a 5U4G tube feeding into a condenser input filter. Direct current voltages are tapped from a bleeder resistor. Two filament voltages, a 6.3-volt and a 2.5-volt filament supply, are necessary. The 6.3-volt supply is a winding of the power transformer (see Y of Figure 3), while a small filament transformer supplies 2.5 volts (see X of Figure 3). Explanation of symbols in the power supply is as follows: $S_1$ is a single-pole-single-throw switch; $T_1$ is a 375-0-375 volt power transformer with a 6.3 volt filament winding and a 5 volt rectifier filament winding;
$T_4$ is a 2.5 volt filament transformer; $C_1$ is an 8-microfarad, 600-volt electrolytic can condenser; $L_1$ is an 8-henry filter choke with an 85-milliampere rating; $D$ is a 10,000-ohm, 100-watt Ohmite adjustable resistor with a current rating of 0.100 ampere.

![Image of electronic equipment](image)

**Fig. 2**—Rear view of Heterodyne-beat apparatus with power supply on top panel.

The oscillator-mixer-amplifier section is mounted on an aluminum chassis 12" x 10" x 3". In Figure 2, nearest the
camera, on the left is the coil $L_3$ and the 24-A tetrode tube and shield. Beyond the coil and the 24-A is the variable condenser $C_V$. On the right are the 6J5 detector, the 6SJ7 audio amplifier, and the 6J5 audio amplifier tubes. Behind these tubes nearest the panel are the tuning condenser, $C_{10}$, and the R. F. amplifier tube, 6SJ7. The choke, $L_1$, and the audio transformer, $T_2$, are also mounted on top of the chassis. A metal shield is mounted between the variable condenser, $C_V$, and the R. F. amplifier tube, 6SJ7. The radio frequency signal from a broadcast station is picked up by the antenna and mixed with the signal from the Hartley oscillator in the grid circuit of the 6J5 amplifier-detector tube. This stage is coupled by an audio transformer to the next audio-frequency amplification stage, containing the 6SJ7 tube, which is resistance-capacitance coupled to the final audio amplification stage. The beat-frequency signal is then fed through a choke and, at B, connected to the vertical sweep of a cathode-ray oscilloscope. The leads at A are connected to the test cell which is in parallel with the precision condenser, $C_p$.

Explanation of symbols for Figure 3 is as follows: $T_3$ is a radio-frequency transformer; $T_2$ is a Halldorson inter-stage audio transformer, single plate to single grid, 1:3 ratio; $R_1$ is 1 megohm; $R_2$ is 1500 ohms; $R_3$ is 2000 ohms; $R_4$ is 100,000 ohms; $R_5$ is 25,000 ohms; $R_6$ is 100,000 ohms; $R_7$ is 500 ohms; $R_8$ is 1,000 ohms; $C_2$ is a 4 microfarad, 450-volt dry electrolytic condenser; $C_3$ is 0.0025 Mfd.; $C_4$ is
Fig. 3--Schematic Diagram of Heterodyne-beat Apparatus
.005 Mfd.; $C_5$ is .001 Mfd.; $C_7$ is 150 MMfd.; $C_8$ is .01 Mfd.; $C_9$ is .01 Mfd.; $C_{10}$ is 260 MMfd. variable; $C_{11}$ is 6 MMfd.; $C_{12}$ is .1 Mfd., 600 volts; $P_2$ is a 500,000-ohm potentiometer; $P_3$ is a 25,000-ohm potentiometer; $L_2$ is a radio-frequency choke; $L_3$ is 51 turns of number 26 wire wound on an octahedral form 3.6 in diameter, with 20 turns in the grid circuit; $C_v$ is a 1,000 MMfd. variable condenser; $C_p$ is a 1,100 MMfd. precision condenser (Type 722-D, General Radio Company).\(^1\)

The leads from $C_v$, leaving the rear of the chassis by means of small plugs and jacks, are mechanically fixed to the connections on the precision condenser as shown by Figure 4. Stand-off insulators mounted on the chassis and the cabinet keep these leads in a fixed position. Leads from $C_p$ are connected to a socket at the side of the cabinet. Parallel line leads (Amphenol 300-ohm "Twin Lead") connect the socket to the test cell to keep lead capacitance constant for all measurements.

The switch and a.c. lead are shown on the top panel of Figure 4. Below, on the left, is the tuning dial for $C_{10}$, while on the right is the tuning dial for $C_v$. To the left of the indicator light is the control knob for $P_2$, and on the right is the control knob for $P_3$.

\(^1\)Ibid., pp. 1000-1005. This description varies slightly from that given by Smyth.
Fig. 4—Front view of apparatus showing the precision condenser below the other sections.

The construction of the dielectric constant cell is shown in Figures 5 and 6. Except for the three concentric cylinders, leads and spacers, the cell is made of Pyrex glass. Corning 707 glass is preferable to Pyrex because of the relatively low dielectric losses in 707 glass, but Pyrex

Fig. 5--Cross-section of Test Cell
Fig. 6--Detail cross-section of mounting of concentric cylinders. (Legend also applies to Figure 5.)
(1)--Copper leads
(2)--Nickel strips
(3)--Mica spacers
(4)--Standard ground glass joint

is adequate for this investigation. The outer glass tube (see D, Figure 5) has a length of 8 inches. The inside diameter of the lower part is one inch, and the inside diameter of the opening is 1 3/8 inches. The glass tube supporting the mercury cups and concentric cylinders (see E, Figure 5) is constructed to fit in the outside tube, leaving room for leads and cylinders. The mercury cups are 5 inches apart. Nickel strips are soldered to the copper lead wire on each
end to connect the cylinders to the mercury cups. The cylinders were machined from bar monel metal to the following dimensions:

Cylinder A, O. D. \(\frac{54}{64}\)", I. D. \(\frac{51}{64}\)", length 2 \(\frac{3}{8}\)"

Cylinder B, O. D. \(\frac{48}{64}\)", I. D. \(\frac{45}{64}\)", length 2.0"

Cylinder C, O. D. \(\frac{42}{64}\)", I. D. \(\frac{39}{64}\)", length 2 \(\frac{3}{8}\)"

Mica spacers, two or three millimeters square and thick enough to hold the cells rigidly when in place, are placed between each cylinder. Mica was also used to insulate the nickel strip connected to cylinder B from the other two cylinders. The inner and outer cylinders are connected together and grounded. The middle cylinder (b) is connected to the high potential lead.

Fig. 7--Test Cell
In cleaning the cell the following procedure was followed: 3

(1) Fill cell with benzene or like solvent while the cell is hot (say, 60° C.) and let soak for fifteen minutes.
(2) Remove benzene and rinse cell with fresh benzene.
(3) Repeat (1) and (2).
(4) Repeat (1) and (2) using acetone.
(5) Let dry in 100° C. oven until all traces of solvent are gone, or dry with ether.

3Ibid., p. 584.
CHAPTER III

PROCEDURE AND TECHNIQUE FOR MEASURING THE
DIELECTRIC CONSTANT OF LIQUIDS

The heterodyne-beat method for measuring the dielectric constant of liquids is based on the same principle as the other two methods already discussed, that of finding the ratio of the capacitance of the test cell filled with the liquid to the capacitance of the empty cell. To do this the heterodyne-beat method used in this investigation utilized a carrier frequency of 820 kilocycles (station WFRA/WBAP) as received on the antenna and amplified. This frequency was combined with the Hartley oscillator frequency of the apparatus to produce a beat-frequency of approximately one kilocycle which was amplified through the two-stage audio amplifier. The beat-frequency was then applied to the vertical plates of a cathode-ray oscilloscope, and a 1000-cycle voltage from a supplementary audio oscillator was applied to the horizontal plates. When the beat frequency and the supplementary audio frequency were the same, an ellipse, depending on their respective amplitudes, appeared on the screen of the oscilloscope. From this point, the null point, the capacitance and change of capacitance of the test cell on addition of the liquid were measured.
To arrive at the true capacitance of the test cell, a null point was attained by adjusting \( C_v \) to minimum capacitance and adjusting \( C_p \) to the maximum capacitance giving a null point with the test cell disconnected. At this point the setting of the precision condenser in micromicrofarads was recorded. The empty test cell was then placed in a 20\(^\circ\)C. constant temperature bath and the precision condenser adjusted until the null point was again attained. At this point the direct reading of the precision condenser was again recorded. This procedure was repeated for the two other temperatures used in this investigation, 40\(^\circ\)C. and 60\(^\circ\)C. Enough thiophene-free benzene was added to the test cell to cover the concentric cylinders, approximately 25 cc., and the precision condenser was again adjusted to the null point and the direct readings recorded for the three temperatures. Since the dielectric constant of benzene was known, the capacitance of the test cell was calculated by two equations\(^1\)

\[
C_1 = C_a + C_g
\]

\[
C_2 = \varepsilon C_a + C_g
\]

where \( C_1 \) is the measured capacitance of the empty cell, \( C_a \) is the true air capacitance, \( C_g \) is the capacitance due to the spacers and leads, and \( C_2 \) is the capacitance of the cell filled with the benzene of known dielectric constant, \( \varepsilon \).

Since a beat frequency, and thus a null point, could be

\(^1\)Ibid.
reached by tuning the Hartley oscillator one kilocycle above or below the standard 620 kilocycle frequency, care was taken in finding the null point by consistently approaching that point from a high capacitance reading on the precision condenser.

A light oil, S. A. E. No. 10, was used in the constant temperature bath. After the bath medium reached the desired temperature a period of at least twenty minutes was allowed to elapse before null point readings of the precision condenser were recorded.

To attain the desired range of capacitance readings on the precision condenser, only one section of the three-sectioned condenser, $C_v$, was used. Three turns of wire also were taken from the grid circuit of the coil, $L_2$.

The wave form of the beat frequency was found to be distorted when the circuit was connected as shown in the schematic diagram, Figure 3. This effect was caused by the overloading of the 6J5 detector. To prevent the distortion, the condenser, $C_{ll}$, was removed from the circuit leaving an open circuit at that point. Coupling of the oscillator to the detector stage was accomplished by means of stray capacitances.

Solutions of stilbene, Eastman Kodak Company, in benzene were investigated. Dilutions of five grams of stilbene in a 50 cc. solution of benzene and of 5/10 gram of stilbene in a 50 cc. solution of benzene were used. The direct capacitance reading of the precision condenser was found by
adjusting the precision condenser to a null point at the temperatures 20° C., 40° C., and 60° C. for each of the dilutions. At each temperature and each dilution five readings of the null point were taken. Density measurements on a Westphal balance were taken at each of the dilutions and temperatures.

The dilution of 5 gram of stilbene in a 50 cc. solution of benzene was then subjected to ultra-violet radiation for thirteen hours. The direct capacitance reading of the irradiated sample was recorded at each of the three temperatures and the density measurements taken. The density values are needed in the computations.

During the course of the investigation, it was necessary to dismantle the test cell and replace the mica insulating strips. After this adjustment the cell was again calibrated by the use of pure benzene.
CHAPTER IV

EXPERIMENTAL DATA AND CALCULATED RESULTS

In this chapter the experimental data and the results derived from this data will be presented. Four different liquids were investigated as described in the previous section. The error made in adjusting the precision condenser to obtain a null point was measured by making nine consecutive readings before the test cell was in place. The maximum deviation found by this method was five parts in forty thousand. The probable error was less than one part in forty thousand. During the investigation the frequency drift of the instrument relative to the audio oscillator was found to be of the order of one cycle per second after the dielectric in the test cell had reached a constant temperature.

In all data tables the liquids investigated are referred to as solution No. 1, pure benzene; solution No. 2, 5 grams of stilbene in a 50 cc solution of benzene; solution No. 3, 6.5 gram of stilbene in a 50 cc solution of benzene; solution No. 4, irradiated sample of 0.5 gram of stilbene in a 50 cc solution of benzene.

Table 1 shows experimental and calculated results from investigation of the solutions at $20^\circ$ C. The column headings are as follows: $d$ is density; $C_o$ is the true air capacitance.
TABLE 1
DIELECTRIC CONSTANT MEASUREMENT AT 20° C.

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>d g/cc</th>
<th>C_o MMfd</th>
<th>C_x MMfd</th>
<th>ε</th>
<th>P cc</th>
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<tr>
<td>1</td>
<td>.8786</td>
<td>94.757</td>
<td>216.777</td>
<td>2.2877</td>
<td>26.6709</td>
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<td>2</td>
<td>.8779</td>
<td>94.757</td>
<td>221.117</td>
<td>2.3335</td>
<td>30.95</td>
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<td>94.757</td>
<td>217.157</td>
<td>2.2917</td>
<td>27.25</td>
</tr>
<tr>
<td>4</td>
<td>.8755</td>
<td>97.077</td>
<td>215.577</td>
<td>2.2207</td>
<td>26.15</td>
</tr>
</tbody>
</table>

of the test cell; C_x is the capacitance of the test cell filled with the dielectric solution; ε is the dielectric constant; and P is the molar polarization of the solution. Tables 2 and 3 show the same type of experimental results, but at temperatures of 40° and 60° C. respectively.

TABLE 2
DIELECTRIC CONSTANT MEASUREMENT AT 40° C.

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>d g/cc</th>
<th>C_o MMfd</th>
<th>C_x MMfd</th>
<th>ε</th>
<th>P cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.8662</td>
<td>94.465</td>
<td>212.307</td>
<td>2.2405</td>
<td>26.3513</td>
</tr>
<tr>
<td>2</td>
<td>.8751</td>
<td>94.465</td>
<td>216.727</td>
<td>2.2872</td>
<td>30.42</td>
</tr>
<tr>
<td>3</td>
<td>.8615</td>
<td>94.465</td>
<td>213.037</td>
<td>2.2482</td>
<td>26.95</td>
</tr>
<tr>
<td>4</td>
<td>.8622</td>
<td>96.723</td>
<td>211.777</td>
<td>2.1895</td>
<td>26.08</td>
</tr>
</tbody>
</table>

The calculated results for ε were obtained with the formula $\varepsilon = \frac{C_x}{C_o}$ as explained in the preceding sections. The calculated results for P were obtained by the use of the
formula

\[ P = \frac{e^{-1}}{e+2} \frac{M_1 c_1 + M_2 c_2}{d} \]

where \( M_1 \) and \( M_2 \) are the molecular weights of the solvent and solute, \( c_1 \) and \( c_2 \) the mole fractions of the solvent and solute respectively. The letter \( d \) refers to the density.

**TABLE 3**

DIELECTRIC CONSTANT MEASUREMENT AT 60° C.

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>( d ) g/cc</th>
<th>( C_e ) MMfd</th>
<th>( C_x ) MMfd</th>
<th>( \varepsilon )</th>
<th>( P ) cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.8523</td>
<td>94.450</td>
<td>206.610</td>
<td>2.1805</td>
<td>25.6592</td>
</tr>
<tr>
<td>2</td>
<td>.8724</td>
<td>94.450</td>
<td>208.827</td>
<td>2.2038</td>
<td>29.02</td>
</tr>
<tr>
<td>3</td>
<td>.8483</td>
<td>94.450</td>
<td>204.607</td>
<td>2.1663</td>
<td>26.45</td>
</tr>
<tr>
<td>4</td>
<td>.8487</td>
<td>96.711</td>
<td>207.377</td>
<td>2.1443</td>
<td>25.85</td>
</tr>
</tbody>
</table>

Table 4 shows only calculated results of the investigation. The column heading \( c_1 M_1 + c_2 M_2 \) was explained previously in this chapter. The values of \( b \) were computed by determining the slope of the line formed in a plot of the molar polarization \( P \) against the reciprocal of the absolute temperature.\(^2\) The dipole moment, \( \mu \), was then computed from the equation of Debye

\[ \mu = 0.01281 \sqrt{b} \times 10^{-18} \text{ c.s.u.} \]

---


where the quantity $10^{-18}$ e.s.u. is sometimes called the Debye unit of electric dipole moment.

**TABLE 4**

**CALCULATED DIPOLE MOMENT**

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>$c_1M_1 + c_2M_2$</th>
<th>$b$</th>
<th>$b$ (cck^0)</th>
<th>(b) ((cck^0)^{1/2})</th>
<th>$\mu \times 10^{-18}$ e.s.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>78.11</td>
<td>2422</td>
<td>49.3</td>
<td>.555</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>88.5</td>
<td>4235</td>
<td>65.1</td>
<td>.84</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>79.15</td>
<td>1985</td>
<td>44.45</td>
<td>.568</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>79.15</td>
<td>605</td>
<td>24.6</td>
<td>.315</td>
<td></td>
</tr>
</tbody>
</table>

The plots of $P$ against $1/T$ are shown in Figure 8. The graph exhibits some non-linearity which could have been caused by the change of the effect of the solvent with temperature. While equation (2) is strictly true only in the case of gases, it can be applied with good approximation to very dilute solutions of a polar solute in a non-polar solvent.³

³Ibid.
Fig. 8--Variation of $P$ with $1/T$
CHAPTER V

SIGNIFICANCE OF RESULTS OBTAINED AND
SUGGESTIONS FOR FURTHER WORK

All of the results of the investigation of the four
liquids were based on the accepted value of the dielectric
constant of pure benzene at 25\textdegree C. The true air capacitance
of the test cell, \(C_0\), was measured from this standard. The
true air capacitance of the test cell varied only slightly
from 20\textdegree C. to 60\textdegree C. temperature change. The \(C_0\) value for
solution No. 4 was computed after the test cell had been
altered slightly.

The values of \(C_x\) for all solutions were found to vary
in a similar manner with temperature. The change in capac-
itance between 40\textdegree C. and 60\textdegree C. was greater than the change
in capacitance measured between 20\textdegree C. and 40\textdegree C. Thus, the
change in capacitance of these liquid dielectrics for a
given change in temperature is not constant. The change in
the dielectric constant for the four solutions over the given
temperature range was proportional to the change in capac-
itance of the test cell. The molar polarization change for a
given temperature change was very similar to the change of
the dielectric constant.
The change in density of the four liquids had an inverse relationship to the temperature change, as was expected.

In computing \( b \), the points in the \( P \) versus \( 1/T \) graph did not lie on straight lines as should be the case theoretically, assuming no interaction between the molecules of the solute and assuming no temperature-dependent effect of the solvent. Apparently these assumptions are not strictly valid in the present cases. Although a straight line is drawn as near the points as possible, the value obtained for the slope of the straight line was not as good an approximation as was desired. An error of ten per cent is sometimes encountered when computing the value of \( b \) with the most nearly ideal data for liquids. Non-linearity of the slope produces an error above that which is normally expected. The results obtained for the dipole moment of benzene were very much higher than the accepted value for benzene \( (0.08 \times 10^{-18} \text{ e.s.u.}) \). The benzene used, while thiophene-free and pure enough for most chemical uses, could have had small amounts of polar impurities which would render it unsuitable for use as a solvent in electric moment measurements. Experimental data by other investigators for the other solutions tested could not be found, thus the error encountered could not be computed.

Future measurements made with this apparatus should be preceded by a careful determination of the dielectric constant of a known liquid and recomputation of the true air capacitance of the cell. The dielectric constant of still
another known liquid should then be measured, as a check.
In the present investigation, time did not permit this pro-
cedure. Enough data were taken, however, to show that the
apparatus is very stable and the method reliable.

The dipole moment of the irradiated stilbene sample was
found to be unexpectedly low, lower than the dipole moment of
the benzene used here or of the same sample before irradia-
tion. Expected results were that the irradiated sample would
exhibit a greater dipole moment than the non-irradiated sam-
ple, because the normal form of stilbene in the trans config-
uration and irradiation with ultra-violet light causes partial
conversion to the cis configuration. The latter configuration
would be expected to exhibit polar characteristics more
strongly than the former. The anomalous results obtained here
might be explained by the presence of polar impurities in the
benzene which were affected by the radiation to a greater ex-
tent than was the stilbene.

Subsequent investigators will have less difficulty in
adjusting the precision condenser to a null point on the osc-
cilloscope if a crystal oscillator is used instead of the
modulated signal of a commercial station mixed with the
Hartley oscillator frequency to produce a beat-frequency.

By using a solvent of greater purity the investigator
should have little difficulty in obtaining results within the
range of unavoidable error. Dielectric constant measurements
good to four or five significant figures should be attainable. Values of dipole moment good to possibly ten per cent should be realizable.

The writer suggests the following lines of investigation which are of possible interest to future investigators in the field of dielectric constant measurements on solutions. Stilbene is one of a series of chemical compounds known as diphenylpolyenes. It would be interesting to investigate the dipole moment of other compounds in this series to determine any possible dependence of the moment on the length of the molecular chain.

The anomalous results obtained in the present investigation upon irradiation of a stilbene solution in benzene with ultra-violet light have yet to be explained. Further investigation is indicated. It would be interesting to irradiate a sample of pure benzene as a control and to repeat the experiment with stilbene. Similar tests with other members of the diphenylpolyene family of compounds could be made.
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