The Dielectric Loss Characteristics of a Chlorinated Diphenyl

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INTRODUCTION

Considerable attention has been devoted of recent years to the development of synthetic insulating materials devoid of the uncertainties and limitations of naturally occurring dielectrics and their modifications (such as cellulose, rubber, oil, and wax compounds). Into this category falls a range of non-inflammable chlorinated diphenyl compounds known in this country as Permitol. The members of this range consist of a double benzene ring as basis with which chlorine atoms have been combined. By controlling the degree of chlorination, it is possible to produce compounds ranging at room temperatures from crystalline solids to liquids of relatively low viscosity. The present paper deals with a study of the dielectric behaviour over the frequency range 50 to 10^7 cycles per second and at temperatures extending from −20 to +80° C of a sample of chlorinated diphenyl classed as suitable for condenser impregnation. Its viscosity at 60° C is that of a light transformer oil, but with temperature decrease the viscosity increases very rapidly until the material becomes a glassy solid about −10° C.

One of the most desirable characteristics of a material to be used for this purpose is a high dielectric constant (permittivity) allied to freedom from dielectric loss. A high permittivity is usually associated, however, with the presence of polar molecules in the material, and these, according to the Debye theory of dielectric absorption, must be responsible for dielectric loss in alternating electric fields under suitable conditions of temperature and frequency. For a dilute solution of polar molecules in a non-polar solvent, the power factor passes through a maximum at a frequency given by

\[ f = \frac{kT}{8\pi^2a^3\eta}, \]

where \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( a \) is the radius of an equivalent sphere representing the dipole molecule or group, and \( \eta \) is the viscosity opposing molecular orientation. The power factor becomes zero at both zero and infinite frequency. At sufficiently low frequency the polar molecules orient freely in sympathy with the electric
field variations; the power factor is therefore low and the dielectric constant high; but at high frequencies the sympathetic orientation of the polar molecules is prevented by their viscous environment, their contribution to the total dielectric polarization becomes negligible, and the power factor and dielectric constant are together low. Similar power factor and permittivity changes result on variation of the temperature, and with it the viscosity at constant frequency. It is evident that maximum dielectric constant and low dielectric loss for a given polar material can exist simultaneously by a suitable choice of the operating conditions of temperature and frequency.

The partially chlorinated diphenyl molecule is a permanent electric dipole, and while it is not to be expected that the Debye theory of dilute solutions can be accurately applied to its behaviour in bulk, the above type of loss characteristic is to be expected, and is, in fact, demonstrated very emphatically by the experimental work recorded in the paper. It is found that the power factor-temperature curve for the material is extremely sensitive to temperature variation, so much so that a 20° C change is sufficient to convert it from a good to a quite useless dielectric medium.

It has frequently been doubted whether the necessary physical conditions for the appearance of a Debye power factor maximum at frequencies as low as 50 cycles per second can arise at normal temperatures. Since it has been possible in the present work to follow this maximum throughout the frequency range from 10⁷ to 50 cycles per second within the temperature span from + 40 to — 5° C, this doubt can no longer be maintained.

**THE METHODS ADOPTED FOR POWER FACTOR MEASUREMENT**

The frequency range mentioned was covered in steps and a power factor-temperature curve for the dielectric obtained at each of the chosen frequency values. Over the range 10⁵ — 10⁷ cycles per second, the method employed was a resonance substitution one, the circuit diagram of which is shown diagrammatically in fig. 1. In order to avoid any assumptions regarding zero loss in the comparison air condenser, and at the same time to allow for any residual loss in the test condenser not arising from the inserted dielectric, use was made of two condensers C and Cₓ, identical in construction. A description of these condensers and of the arrangements for their temperature variation has been given elsewhere.* The dielectric to be investigated was poured into Cₓ and the capacitance of C, having air dielectric, was then adjusted until it equalled that of Cₓ. When this adjustment had been made the circuit remained in tune to the chosen frequency

when the condenser was changed from \( C_x \) to \( C \) at the switch \( S \). The power factor of the dielectric of \( C_x \) was derived from the difference between the total circuit power factor when the capacitance was formed by \( C_x \) and by \( C \). In the higher part of this frequency range the power factor was deduced from the width of the resonance curve delineated on the thermionic voltmeter \( V \) by suitable incremental changes in the oscillator frequency, but in the lower part it was more convenient to employ resistance insertion at the resonant adjustment.

In the audio frequency range the dielectric power factor was determined by arranging the test and air condensers to form in turn one arm of a low-voltage Schering bridge. The 50-cycle measurements included in the paper are due to the British Thomson Houston Company and were also obtained on a Schering bridge, but at much higher voltage gradients.

**Fig. 1—**

- \( C_x \), test condenser; 
- \( C \), identical air condenser; 
- \( S \), change-over switch; 
- \( V \), thermionic voltmeter; 
- \( E \), earthpoint.

**STATEMENT AND DISCUSSION OF THE RESULTS**

The combined results of the power factor measurements are shown in fig. 2. It is seen somewhat surprisingly that in a frequency change from 50 to \( 10^7 \) cycles per second the position of the power factor maximum is shifted upwards in the temperature range by only about \( 45^\circ \) C, and also, but quite analogously, that the power factor-temperature curves are exceedingly sharp. With the exception of the 50-cycle curve \( A \), the curves at the several frequencies are of closely the same height. The maximum power factor, \( 21.5\% \), is so large as to render the material valueless for dielectric purposes in the immediate vicinity. Only a \( 20^\circ \) C temperature displacement from this point is necessary, however, to improve the power factor to a desirable value of less than \( 1\% \). The discrepancy in the height of the 50-cycle curve can probably be accounted for in the fact that this curve relates to a different sample of the same material, and the author is in-
formed that such differences are to be expected from sample to sample. This observed independence of the power factor maximum of frequency and temperature is in agreement with the existing Debye theory. The theory would lead to the expectancy of an increase in height of the curve with decrease in temperature; but for the 10% change in absolute temperature from the peak of curve H to that of B this effect would not be very important.

The expression (1) giving the condition for the appearance of the power factor maximum as a function of the frequency, the temperature and the physical constants of the dielectric medium, and also the corresponding expressions for the variation of the power factor with frequency and temperature separately have been derived by Debye for the case of dilute solutions of polar molecules in non-polar solvents. The treatment for a polar material in bulk has not yet been developed, and this fact should be borne in mind during the subsequent discussion of the results.

The Debye theory gives the power factor as a function of frequency in the form

\[ \tan \delta = \frac{\varepsilon_0 - \varepsilon_\infty}{\sqrt{\varepsilon_0 \varepsilon_\infty}} \frac{A \omega \tau}{A^2 + \omega^2 \tau^2} \]  

where \( \tau = \frac{4 \pi \alpha^2 \gamma}{kT} \) is the relaxation time of the polar molecules in the viscous.

Fig. 2—Frequency values in cycles per second—A, 50; B, \( 10^3 \); C, \( 6 \times 10^3 \); D, \( 10^5 \); E, \( 2.95 \times 10^5 \); F, \( 9.5 \times 10^5 \); G, \( 2.75 \times 10^6 \); H, \( 1.09 \times 10^7 \).
environment concerned; \( A = \sqrt{\frac{\varepsilon_0}{\varepsilon_\infty}, \left(\frac{\varepsilon_\infty + 2}{\varepsilon_0 + 2}\right)} \) and \( \varepsilon_0, \varepsilon_\infty \) are the dielectric constant values at zero and infinite frequency \((\omega/2\pi)\) respectively. The power factor has its maximum value

\[
\tan \delta_m = \frac{\varepsilon_0 - \varepsilon_\infty}{2\sqrt{\varepsilon_0\varepsilon_\infty}},
\]

at the frequency for which

\[
\omega = 2\pi f = \frac{A}{\tau} = \frac{kT}{4\pi a^3 \eta} \cdot \sqrt{\frac{\varepsilon_0}{\varepsilon_\infty}, \left(\frac{\varepsilon_\infty + 2}{\varepsilon_0 + 2}\right)}.
\]

The important criterion governing the magnitude of the power factor maximum is the factor \((\varepsilon_0 - \varepsilon_\infty)\), and this may be estimated from a curve such as that of fig. 3, in which the dielectric constant is plotted as a function of the temperature at a constant frequency of \(0.95 \times 10^6\) cycles per second. This curve corresponds to the power factor-temperature curve \( F \) of fig. 2 and demonstrates that the region of dielectric constant change coincides with that of appreciable power factor. As previously implied, \( \varepsilon_\infty \) corresponds to a state where, at a given frequency, the temperature is so low that the movement of the dipole molecules is completely restricted and they are unable to make any resultant contribution to the total polarization; this may be said to occur in the portion \( AB \) of the curve of fig. 3, so that \( \varepsilon_\infty \) may be taken as \( 2.80 \). Similarly, it may be inferred that the polar molecules are able to orient in perfect sympathy with the alternating electric field in the portion \( CD \) of the curve. The maximum value of the dielectric constant may be taken, therefore, as a measure of \( \varepsilon_0 \), although this is likely to be an underestimate. If these values for \( \varepsilon_0 \) and \( \varepsilon_\infty \) are substituted in equation (3), the maximum power factor \( \tan \delta_m \) is given as \( 0.233 \), which is in fair agreement with the experimental value \( 0.216 \).
Consideration of equation (4) permits an examination of the physical factors controlling the position of the power factor maximum in the spectrum of frequency and temperature. As mentioned previously, the equation as it stands cannot be expected to apply rigorously to a perfectly concentrated polar material, but in general form it should be correct. Thus the frequency of maximum power factor can reasonably be written as a function of the absolute temperature $T$, the viscosity opposing dipole orientation $\eta$ and the volume of the orienting dipole $V$, in the form

$$f = K \cdot \frac{T}{V\eta}.$$  

The volume $V$ being a characteristic of the material may be expected to be a constant, and since several corresponding values of $f$ and $T$ are given by the power factor-temperature curves of fig. 2, a quantity proportional to $\eta$ can be calculated and its variation with temperature studied. This quantity has been calculated from the position of each of the peaks of the curves, and its logarithm plotted against the temperature in curve B, fig. 4.
Each of the points on this curve corresponds to a different frequency, and a certain amount of evidence is available to suggest that the viscosity decreases with rise in frequency. The possibility of a frequency dependence may be investigated by comparing the viscosity-temperature variation derived as above with an independent determination of this variation by viscometric measurements. These latter measurements were carried out over the temperature range 13–55°C in an equipment, of which a description will be published later, developed by Professor R. V. Southwell and Dr. A. Gemant. The logarithm of the measured viscosity values is plotted as a function of the temperature in curve A, fig. 4. The derivations from equation (5) give only a quantity proportional to the viscosity, but for the purpose of comparing the temperature variation, curve B has been made coincident with curve A at the point $a$. It is seen that the two curves are very similar in shape, with the calculated curve of somewhat smaller slope. If the viscosity were dependent on frequency in the manner suggested, the calculated curve B would be expected to have a greater slope than that of curve A, and it seems, therefore, that there is no such frequency dependence for this material.

### Table I

<table>
<thead>
<tr>
<th>Frequency c.p.s.</th>
<th>Temperature of power factor maximum</th>
<th>Viscosity poise</th>
<th>Apparent volume V in cu A</th>
<th>Apparent equivalent radius $a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 x $10^3$</td>
<td>9.5 282.5 1.45 x $10^4$</td>
<td>22.0</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>10$^3$</td>
<td>17.5 290.5 9 x $10^4$</td>
<td>22.0</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>2.95 x $10^3$</td>
<td>21.8 294.5 2.55 x $10^4$</td>
<td>26.5</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>9.5 x $10^3$</td>
<td>26.0 299.0 83.2</td>
<td>26.0</td>
<td>1.84</td>
<td></td>
</tr>
<tr>
<td>2.75 x $10^3$</td>
<td>31.7 304.7 24.5</td>
<td>30.5</td>
<td>1.94</td>
<td></td>
</tr>
<tr>
<td>1.09 x $10^3$</td>
<td>39.0 312.0 6.20</td>
<td>31.5</td>
<td>1.96</td>
<td></td>
</tr>
</tbody>
</table>

If the experimentally determined viscosity value at the position of the peak of a power factor-temperature curve be substituted in equation 4, along with other known data, an apparent value can be obtained for the dimension $a$, or the volume $V = 4/3 \cdot \pi a^3$, of the orienting portion of the chlorinated diphenyl molecule. This process has been carried out for each of the curves of fig. 2, and the results of the calculations are given in Table I.

The variation observed in the computed value of $V$ is consistent with the disagreement between the two curves of fig. 4. The mean value of $V$ is about 26.5 cu A, and the corresponding apparent value of the equivalent radius for the orienting portion of the molecule is 1.85 x $10^{-8}$ cm.
The apparent molecular volume found here is of the right order of magnitude, but somewhat too small. The volume of the molecule may be estimated by use of Sugden's parachor values; thus taking \( V = 2 \cdot 0 \times 10^{-25} \text{ P cc} \), the volume of a monochlorodiphenyl molecule \( \text{C}_{12}\text{H}_9\text{Cl} \) is \( 83 \cdot 4 \text{ cu A} \). This is to be increased by \( 7 \cdot 4 \text{ cu A} \) for each extra chlorine atom substituted in the molecule. An analysis of the permitol by sodium peroxide fusion in a Parr bomb gave the chlorine content of the material as \( 56 \cdot 3\% \) by weight. This suggests an average of about 4 chlorine atoms per molecule. (The Carius method of determining the chlorine content gave a very low figure—36\%).

The smallest possible polar group in the molecule capable of independent orientation is monochlorophenyl with a volume of \( 45 \cdot 4 \text{ cu A} \). The substitution would have to be ortho- or meta- for this independent rotation, and even then the independence would only apply for rotation of the group about one axis, and still but partially. The actual mixture presumably contains substituents mainly in ortho- and para-positions. The latter require the full volume, or something even larger, since the dipole is parallel to the long axis of the molecule. It follows that the mean value to be taken for the volume of the molecule cannot be much less than 80 cu A, as compared with the mean value of 26 \cdot 5 \text{ cu A} \) derived from the experimental results.

It is observed from the preceding table that the apparent volume rises somewhat with increasing temperature (and frequency) from 23 cu A at \( 10^\circ \text{ C} (10^4 \text{ cycles}) \) to about 33 cu A at \( 40^\circ \text{ C} (10^7 \text{ cycles}) \). This sort of behaviour is fairly characteristic. The outstanding example is, of course, glycerol with an apparent molecular volume of \( 0 \cdot 18 \text{ cu A} \). Debye is now studying the possibility of attributing such results to the "quasicrystalline" structure of liquids. It is in agreement with this theory that the apparent molecular volume approaches the true value as the temperature is raised, since rise of temperature tends to destroy any quasicrystalline structure present.

The experimental work recorded was carried out in the Engineering Laboratory, Oxford. The author is indebted to the British Thomson Houston Company for supplying the chlorinated diphenyl sample, to Mr. F. C. Frank for undertaking the chemical analysis, and to the Department of Scientific and Industrial Research for a grant which enabled the research to be performed under the direction of Mr. E. B. Moullin.
The paper describes a series of power factor measurements on a chlorinated diphenyl over the frequency range 50 to $10^7$ cycles per second and at temperatures from $-15$ to $+80\,^\circ C$. The results are discussed in terms of the Debye theory and related to the chemical constitution of the material. It has frequently been doubted whether the necessary physical conditions for the appearance of a Debye power factor maximum at frequencies as low as 50 cycles can arise at normal temperatures. Since it has been possible with this material to follow the maximum through the above frequency range within the temperature span $-5$ to $+40\,^\circ C$, and relate this behaviour to the variation of the measured viscosity coefficient, this doubt can no longer be maintained.

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The Crystal Structure of Ice at Low Temperatures

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[Plate 2]

1—Introduction

The use of X-rays in the study of the mechanism of crystal growth showed that if the vapour of a substance came in contact with a cold surface, it condensed to form a solid, the structure of which depended on the temperature of the condensing surface.*† The authors announced recently‡ that ice formed by condensation at low temperatures and pressures also changed form with temperature. Details of the apparatus and the results follow in this paper.

2—Method and Preliminary Work

Analysis was carried out by the Hull-Debye-Scherrer method, using the $K_a$ doublet of copper. With a camera of 5 cm radius, photographs

† See reference in Clarke's paper, "Symposia on Quantitative Biology," vol. 11, p. 6 (1934).