CHAPTER VII

DIELECTRIC CONSTANT

7.1 INTRODUCTION

Study of the variation of permittivity and loss angle tangent (tanδ) of electret forming materials on polarization is still in infancy. Wiseman et al. reported that the dielectric constant of electrified wax was not significantly different. In the present investigation no effect of polarization on the dielectric constant of acenaphthene has been found. The measurement of dielectric constant is important as a number of empirical connections between dielectric constants and other properties of chemical compounds were claimed in the earlier literature. Obach (1891) had noted a relationship between the dielectric constant and the latent heat of vaporisation.

Other relationship are discussed in Kauffmann's Beziehungen Zwischen Physikalischen Eigenschaften and Chemischer Konstitution (Stuttgart 1920) and Walden's Elektrochemie Nichtwasseriger Losungen (Leipzig 1924).

Dubey et al. have correlated the dielectric constant of powder and bulk material in the form

\[ \varepsilon_s = \frac{1}{S^2} \left( \varepsilon_p - \varepsilon \right) \left( \frac{1}{2} - S \right) \left( \frac{1}{2} - S \right)^2 + \varepsilon \]

where \( \varepsilon_p \) - dielectric constant of powder material
\( \varepsilon_s \) - dielectric constant of bulk material
\( S \) - packing fraction and \( A \) - constant(=0.5).
The formula gives accurate results both at radio and microwave frequencies. Recently Seitz-Sokoly\textsuperscript{326} and Seitz-Holliday\textsuperscript{327} reported high temperature dielectric behaviour of doped and undoped inorganic substances as a function of frequency. They have concluded that barrier layer polarization was responsible for the observed dielectric behaviour and have shown that the effective dielectric constant increases exponentially with temperature.

7.2 \hspace{1cm} \textbf{PARAMETERS INFLUENCING DIELECTRIC CONSTANT}

\hspace{1cm} (i) \hspace{1cm} \textbf{TEMPERATURE DEPENDENCE}

The temperature dependence of dielectric constant is generally towards its increase at higher temperature, which is brought about by expansion of lattices. Measurable changes in the dielectric constant are obtained at higher temperature in the case of ionic dielectric because of the loosening of the bonds which are responsible to hold the ions in place\textsuperscript{328}. An increment in temperature when the dielectric is a semiconductor, may give rise to free charge carrier density to introduce conduction losses. The temperature dependence of the dielectric constant is the resultant of three factors\textsuperscript{329}.

\hspace{1cm} (1) Increase of polarizability of the particles as a result of expansion of the lattice.
(2) Decrease in the number of polarizations per unit volume because of thermal expansion.

(3) Dependence of microscopic polarizability on temperature at constant volume.

Having\(^{330}\) has shown that the contribution from the second factor is the greatest. Recently it has been shown that the contribution from (1) and (2) factor is positive in many cubic ionic compounds and that the contribution from (3) may be both either positive or negative.\(^{331}\)

(ii) FREQUENCY DEPENDENCE

By the application of an ac field in the dielectric, the polarization varies periodically with the time as does the dielectric displacement. The dielectric constant when absorption occurs, is treated as a complex quantity.

\[
\varepsilon^* = \varepsilon' - j \varepsilon'' \quad \ldots \quad (7.1)
\]

where \(\varepsilon'\) is measured dielectric constant and \(\varepsilon''\) is the loss factor.

The phase angle, \(\delta\) known as loss angle, between the displacement and that for applied electric field is given by

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad \ldots \quad (7.2)
\]

and since \(\varepsilon'\) and \(\varepsilon'\) are frequency dependent, \(\delta\) is also frequency dependent.
When the permittivity varies markedly with frequency, the mechanism responsible for the variation can be characterised as a relaxation or as a resonance. The Debye equations for $\varepsilon'$ and $\varepsilon''$ in terms of frequency and relaxation time $\tau$ are

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_c - \varepsilon_\infty}{1 + \omega^2 \tau^2} \quad (7.3)$$

$$\varepsilon'' = \frac{(\varepsilon_c - \varepsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2} \quad (7.4)$$

where $\varepsilon_c$ - the static dielectric constant and $\varepsilon_\infty$ the instantaneous or optical dielectric constant.

These equations give, under certain experimental conditions, at least a satisfactory quantitative representation of the behaviour of dielectric constant and loss, irrespective of mechanism responsible for such behaviour.

Recently Dufour et al.\textsuperscript{332} measured the dielectric constant of PVC at very low frequency. The dielectric constant $\varepsilon'$ increases with the decrease in frequency and increase in temperature. The superposition of a continuous voltage causes a slow decay of $\varepsilon'$. The phenomena observed are attributed to electrochemical reactions of electrodes.

(iii) FIELD DEPENDENCE

When a polar dielectric is subjected to an external field, the permanent dipoles in domain structure tend to orient in the direction of the applied field. The
direction of orientation may be parallel, antiparallel or in some other direction and the direction depends upon the applied field strength. If the field strength is increased continuously the break down is reached much earlier the saturation reaches. The alignment of dipoles parallel to the direction of the field gives a high dielectric loss due to hysteresis in the direction of the field. The dielectric constant at right angles to the direction of the field is diminished.

Robert\textsuperscript{333} and Lal\textsuperscript{334} studied the variation of the dielectric constant with applied static electric field and found that the dielectric constant increases in the direction of the field but decreases at higher fields.

7.3 GENERAL MEASUREMENT TECHNIQUES

A wide variety of experimental techniques are available for the measurement of dielectric constant of materials\textsuperscript{221,335-337}. These techniques depend on the nature of specimen and frequency range in which measurement is to be made. The most general method used for measuring static dielectric constant $\varepsilon'$ and loss $\varepsilon''$ consists of measurement of the capacitance $C_0$ of an empty condenser and the capacitance $C$ and resistance $R$ of the condenser filled with the dielectric material.

Two principle methods of measuring the capacitance of a condenser are the "Capacitance-bridge
method " and " adjusting the capacitance of circuit till the alternating current flowing in the circuit has a certain characteristic frequency ". Cole and Cole\textsuperscript{338} developed a method in which the charging current of the condenser containing the dielectric is observed.

For the accurate measurement of dielectric constant it is necessary to apply some type of thin metallic electrodes to the specimen before it is placed between the rigid electrodes of measuring cell. Any air gap between the rigid electrodes and the specimen's thin metallic electrodes provides a serious air capacitance and the dissipation factor, to avoid this, the electrodes are deposited on the specimen itself.

7.4 PRESENT EXPERIMENTAL TECHNIQUE FOR MEASUREMENT OF DIELECTRIC CONSTANT

The details of experimental technique used in the present investigation are given in the following parts.

(1)(a) Preparation of cell for dielectric constant measurement.

A sandwich type of cell has frequently been used for the measurement of dielectric constant. This cell is prepared in the University workshop and is similar to the one designed and used by Bhatnagar and Srivastava's\textsuperscript{339}. The design of the cell is based on Moon-Sparks primary standards of capacitance with the additional advantage that
electrodes of different metals can be used without changing the capacity.

The cell is prepared by turning a single solid copper rod of 2.25 inches in diameter. The cell consists of an outer casing \( E \), provided with a brass terminal, \( T \), to which the cylinder \( B \) is attached. The guard ring, \( GR \), is screwed to the cylinder \( B \). The central opening of the guard ring is slightly tapered. Theguarded electrode, \( GE \), is situated coaxially with the guard ring, also tapered but in the opposite direction to that of the guard ring, which is held by a circular perspex disc, \( PD \), by means of a fixing nut, \( N \). The disc \( PD \) fits accurately the cylinder \( B \), figure 7.1.

The perspex disc, the guarded electrode, the guard ring and the cylinder \( B \) are turned accurately on the lathe, so that they are coaxial. The locating pins, \( LP \), ensure that the capacitor can be dismantled for cleaning etc. and reassembled without sensible loss of accuracy. The perspex disc carrying the guarded electrode can be kept rigidly in position with the help of the clamping cylinder \( C \).

The guard ring and the guarded electrode are turned accurately on the lathe and the common surfaces of the guard ring, guarded electrode and cylinder \( B \) are cut accurately with a rounded cobalt-steel tool bit. Finally the surface are finished with No. 4/0 silicon
Fig. 7.1 Conductivity cell.
carbide polishing paper.

The high voltage copper electrode, A, is held at a fixed distance from the guard ring by perspex spacers of equal thickness; the ends of the spacers are accurately plane and parallel. The surface of this electrode is prepared with the same manner as the common surfaces of B, GR and GE. The electrode is firmly held in position by means of two brass screw ( diameter 1/16 inches) which pass through spacers and the insulating washers, both made of perspex.

The inner assembly, after cleaning with benzene, can be screwed to the container E. The perspex insulating plug K is screwed in position by means of a pair of compass. The outer crevices are sealed with quickfix. The conductivity cell was calibrated with the help of a thermo-couple.

(b) Constant of the conductivity cell

The inner diameter of the guard ring and the diameter of the guarded electrode were measured by a vernier microscope (P.T.I. Survey, England, Least Count 0.002 cm.). The effective radius r of the guarded electrode is given by Amey-Hamberger Formula.

\[ r = \frac{r_1 + r_2}{2} - \frac{2d}{\pi} \log \left[ \cosh \left( \frac{r_2 - r_1}{4d} \right) \right] \] \hspace{1cm} (7.5)

where \( r_1 \) and \( r_2 \) are the radius of guarded electrode and
guard ring and \( d \) is the thickness of the sample.

The value of \( r \) given by the equation (7.5) is used in computing the vacuum capacitance \( C \) of the cell by the formula.

\[
C = 0.27816 \frac{r^2}{d} \mu \mu F \quad \ldots \quad (7.6)
\]

(ii) PREPARATION OF SAMPLE

The specimen in the form of circular disc is prepared similar to the measurement of electrical conductivity studies. The air layer between the specimen and the electrodes which diversely affects the measurements of \( C \) has been completely avoided by employing the principle of embedded electrodes.

(iii) TEMPERATURE CONTROL

Dielectric constant depends upon the temperature of the specimen hence it is very necessary to obtain the stability of temperature during the course of measurement. This was attained by the use of a thermostat described in section of electrical conductivity.

(iv) DIELECTRIC CONSTANT MEASURING BRIDGE

(a) Capacitance measuring bridge

Marconi T F 2700 Universal Bridge supplied by Associated Instrument M F R S (India) Pvt. Ltd., was used to measure the capacitance of the dielectric. The
T F 2700 Universal bridge is a compact, self contained instrument that brings new versatility to the rapid determination of a wide range of impedance values. Facilities are provided for the application of external ac and dc supplies for the use in a variety of specialized measurements.

Capacitance values of 0.5 PF to 1100μF may be measured at 1 KC/S from the internal oscillator or at frequencies of 20 C/S to 20 KC/S from an external source where an alternative frequency is more appropriate. In addition to an external ac source and external dc supply may also be connected for the polarization of electrolytic capacitors. The internal energizing source for the bridge are 1 KC/S oscillator for ac measurements of capacitance, inductance and resistance, and the 9 volts power supply battery for dc resistance measurements.

The external dc bias may be applied via the bias to the dielectric under test. A suitable limited voltage of up to 500 volt dc may be used for polarizing electrolytic capacitors or for investigating the properties of non linear resistors.

(b) Frequency Generator

Philips Audio frequency generator G M 2308/90 supplied by Philips India Limited was used as external frequency source. This frequency generator provides an ac
voltage with which measurements can be carried out in the audio frequency range i.e. from 30 C/S to 10 KC/S.

The generator comprises of two oscillators, both oscillators work on frequencies around 100 KC/S and thus permit the low pass filter to be of simple design whilst the unwanted harmonics can be readily suppressed. The low pass filter must posses a good transmission characteristic for the beat frequency of 0.16 KC/S and a high attenuation for the fundamental frequency and the sum frequencies of the oscillators. The transmission range can be extended to about 40 l.C/S by connecting a potentiometer across the filter. It is possible to regulate the output voltage continuously with this potentiometer.

An isolating transformer T N 7120 supplied by Marconi Instrument Ltd. England is used as an optional accessory. The T N 7120 transformer has been designed to match an oscillator output impedance of 600 ~ but may be used for other impedances provided that for lower impedance the input power is limited to ½ w.

(v) CIRCUIT ARRANGEMENT AND OPERATIONAL PROCEDURE

The two main electrodes of the cell containing pellet is connected with the terminal marked H I and D E T +ve on the Marconi Universal bridge. The connecting leads should be kept as short as possible in order to avoid the
stray capacitance and mains hum pick up. All the connections are made by grounded and shielded leads. The body of the cell and the grounded terminals of the bridge, generator and isolated transformer are also earthed. The external frequency source is connected to the bridge via a jack plug inserted into the Ext. A C socket; by inserting the plug switches off the internal oscillator. The a.f. supply is connected via an isolating transformer Marconi type TM 7120. The use of the transformer eliminates the possibility of a false balance due to capacitive coupling when measuring low impedences at high frequencies.

Appropriate to the expected value of capacitance, the range full scale is selected with the function and range multiplier switches. The loss balance control is set to about 1 and the sensitivity control is set to give a meter deflection of less than full scale. The bridge is balanced with the main balance and loss balance controls, increasing the sensitivity to keep the meter deflection above zero until the sensitivity control is fully used clockwise. The capacitance of the component under test is given by multiplying the setting of the main balance control with the range of full scale.

The vacuum capacitance $C_0$ of the cell is calculated from its dimensions. The static dielectric
constant is then simply obtained from the formula

$$\varepsilon = \frac{C}{C_0} \quad ... \quad (7.7)$$

7.5 DETAILS OF MEASUREMENTS

In the present investigation the measurements of dielectric constant were carried out in two steps.

(1) The variation of dielectric constant with temperature at various fixed frequencies.

(2) The variation of dielectric constant with frequency at various fixed temperatures.

The value of capacitance is recorded at the different fixed frequency while the temperature increasing and decreasing in steps of $35^\circ C$, $40^\circ C$, $45^\circ C$, $50^\circ C$, $55^\circ C$, $60^\circ C$, $65^\circ C$, $70^\circ C$, $75^\circ C$, $80^\circ C$, $85^\circ C$ and $90^\circ C$.

The value of capacitance is recorded at the different fixed temperature while frequency increasing and decreasing in steps of $1, 3, 5, 7, 9, 11, 13$ and $15$ kC/S.

7.6 RESULTS

(A) Variation of dielectric constant with temperature

The nature of variation of dielectric constant ofacenaphthene with temperature is shown in figure 7.2 to 7.4. The following inferences can be drawn.
Fig. 7.2 Variation of dielectric constant with temperature at various frequency.
Fig. 7.3 Variation of dielectric constant with temperature.
Fig. 7.4 Log of dielectric constant versus inverse of temperature.
(1) The variation of the dielectric constant with temperature varying from $35^\circ\text{C}$ to $89^\circ\text{C}$ at constant frequency of 1 KC/S is from 56.42 to 66.56 and at constant frequency of 15 KC/S is from 49.27 to 58.91.

(2) In general the dielectric constant increases sharply with the increase of temperature from $35^\circ\text{C}$ upto $75^\circ\text{C}$ and then slowly upto $89^\circ\text{C}$ for all frequency figure 7.2.

(3) It is observed that the values of dielectric constant are higher with decreasing temperature than with increasing one figure 7.2.

(4) For complete cycle of heating and cooling the curves show a sort of hysteresis effect.

(5) A plot of log of dielectric constant versus frequency shown in figure 7.4 has been found to be linear.

(B) Figure 7.5 represents the nature of variation of dielectric constant with frequencies at different fixed temperatures. The following results can be observed from the curves.

(1) In general at all temperatures the dielectric constant decreases at a very slow rate with the increase of frequency.

(2) The magnitude of the dielectric constant has been found to decrease faster with initial rise of frequency from 1 KC/S to 9 KC/S and then decrease becomes
Fig. 7.5 Dielectric constant versus log of frequency.
slower with further increase of frequency in the range 9 KC/S to 15 KC/S (figure 7.6).

(3) A plot of dielectric constant versus log of frequency is shown in figure 7.5. The dielectric constant shows a linear dependence as a function of log of frequency with almost same slopes.

(4) The value of dielectric constant varies from 56.43 to 49.27 at temperature 35°C while the variation is from 66.56 to 58.91 at temperature 90°C for the variation of frequency from 1 KC/S to 15 KC/S.

No change in dielectric constant is observed in acenaphthene sample after polarization under different fields and temperatures.
Fig. 7.6 Variation of dielectric constant with frequency at various temperature.