CHAPTER IV

DIELECTRIC CONSTANT
4. A Introduction :

Various phenomena occurring in dielectrics under the action of electric field are for example electrical conduction, polarization and dielectric losses. If the electric field is either static or alternating with a frequency below $10^2$ Hz conductance or dielectric phenomena behaviour is the most important one. This response of a dielectric to an electric field consists of two parts, one direct current and the other the transient current. The accepted dielectric approach regards direct current invariably due to some form of carriers while the other component is due to dipolar mechanism in the material. This dipolar mechanism, especially in certain conjugated macro-molecular solids display unusually intense polarization in electric field. It turns out that this greatly increased polarization response is due to exciton mechanism.

The polarization of a material by the displacement of the electrons in the atoms is a process requiring about $10^{-10}$ sec, whereas the polarization of atoms in the molecules requires about $10^{-14}$ to $10^{-10}$ sec. Orientation polarization involving rotation of dipolar molecules is a process requiring usually $10^{-12}$ to $10^{-10}$ sec, but for very large molecules or very viscous materials, the time required may be much larger when a field is applied to a
dielectric is removed, the decay of the polarization with time is called "dielectric relaxation. The alignment of the dielectric polarization with the applied field cannot occur without part of the energy being irreversibly converted into heat, it thus gives rise to dielectric absorption or dielectric loss, i.e., this absorption gives a loss of power known as dielectric loss $\varepsilon''$, most of which occurs within a frequency range of about a decade on each side of a characteristic angular frequency $\omega_m$ (2$\pi$ no. of cycles/sec.), which is the reciprocal of the relaxation time $\tau$, i.e.

$$\tau = \frac{1}{\omega_m}$$

This loss becomes a maximum at a certain resonance frequency. This absorption maximum is often referred to as resonance absorption. This subject has been reviewed by Nelson and by Cole. Smyth and his group have studied group rotation in aromatic methoxy - compounds and in aromatic ethers where there are sometimes two relaxation times, a long one due to molecular rotation and a short one arising from intramolecular rotation. These workers have also studied the absorption by rigid molecules in viscous solvents. Solutions of alcohols have been examined by Lefevre and his group and crystals of long-chain secondary alcohols by Powlegs and Kail. The dielectric loss has been found in microwave frequency range in compressed gaseous propane, isobutane and isopentane and interpreted in terms of small permanent dipole moments; that of isobutane is 0.132 D in excellent agreement with the value obtained through stark splittings.
The dielectric constant of organic materials have been studied by several workers.\textsuperscript{10-16} Fuoss and coworkers\textsuperscript{17} and others\textsuperscript{18-20} have done a good amount of work on high polymers. Huggins and Sharbaugh\textsuperscript{21} investigated the dielectric properties of some organic semiconductors using elaborate a.c. analysis. Different theories were proposed for the dielectric behaviour of the substance.\textsuperscript{22,23} Kronberger and Weiss\textsuperscript{24} reported some of the dielectric properties of a number of molecular compounds and of their components. They measured the (mean) dielectric constants of these substances in the form of crystalline powders. The measurements were carried out - by an immersion method which was originally proposed by Starke\textsuperscript{25} and later used by Eucken and Buchner\textsuperscript{26} and by Hojendahel\textsuperscript{27} for the determination of dielectric constants of inorganic salts. They also calculated molecular polarizations of the molecular compounds $P_{AB}$ and of the components $P_A$ and $P_B$ according to the formula of Lorentz and of Drude respectively. All measurements were carried out at a temperature of $17 \pm 1^\circ$C and at radio frequency (about 800 Kc/sec), a double heterodyne method being used. They found that molecular polarization of the molecular compound $P_{AB}$ is entirely different from the sum of polarization $P_A$ and $P_B$ of the components. For illustration Anthracene and picric acid has molecular polarization 64.1 and 60.1 respectively whereas complex of Anthracene-picric acid has molecular polarization 117. It was first shown by Fairbrother\textsuperscript{28} that
iodine is subjected to substantial polarization when it interacts with non-polar solvents or solvents of low polarity to form non-violet solutions. In the case of a complex such as benzene-iodine, in which both compounds are non-polar, the observed dipole moment (1.8 D in dilute solution in cyclohexene) must result entirely from the dative form (D^+A^-) which contributes to the structure of the ground state (Chap. 1, Eqn. 1.1); the no bonded form has no moment. On the other hand when one or both the components is polar, the moment of the complex may be larger or smaller than the sum of the moments of the components.

Dielectric study also gives an insight into the mechanism of electrical conduction in the dielectric. Its variation with temperature and frequency yields interesting information about the structure of the dielectric. Cohn and Edsall have used the dielectric increments and losses of solutions in the investigation of the structure of amino acids, peptides and proteins.

Since electrical parameters, dielectric constant depends on the changeable external factors such as the frequency of voltage applied to the dielectric, temperature, pressure, humidity, field etc. Numerous workers have reported that dielectric constant of a material depends strongly on the frequency of applied potential and on temperature. In a number of cases their dependence are of paramount practical importance.
4. B Parameters influencing dielectric constant and loss

4.B.1 Frequency — The most striking characteristic of dielectric is the relationship between dielectric constant, dielectric losses and frequency. Each type of polarization has a characteristic frequency response and gives rise to power losses in the characteristic frequency ranges. The time required for electronic or ionic polarization to set in, is very small as compared with the time of the voltage sign change even for the highest frequencies which find practical use in electrical and radio engineering. For this reason the polarization of dielectrics distinguished only by a deformation mechanism of polarization completely settles itself during a very short period of time as compared with the voltage half-period and there is no practically essential dependence of on the frequency in such dielectrics. It is not so in the case of dipole polarization. When the frequency of alternating voltage increases the value of ε of a polar dielectric at first remains invariable but beginning with a certain frequency to when polarization fails to settle itself completely during the one half-period, ε begins to drop approaching at very higher frequencies the values typical of non-polar dielectrics.

The dielectric constant when absorption occurs is treated as a complex quantity:

\[ \varepsilon = \varepsilon' - i\varepsilon'' \]  \hspace{1cm} (4.1)
where $\varepsilon'$ is the measured dielectric constant and $\varepsilon''$ is the loss factor or loss. The classical development of the relation between dielectric constant, dielectric loss and frequency is due to Debye as follows

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \left( \frac{\omega}{\gamma} \right)^2} \quad ... \ (4.2)$$

and

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty) \frac{\omega T}{1 + \left( \frac{\omega^2}{\gamma^2} \right)}} \quad ... \ (4.3)$$

where $\varepsilon_0$ - the static dielectric constant and $\varepsilon_\infty$ - the instantaneous or optical dielectric constant.

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

The ratio $\frac{\varepsilon''}{\varepsilon'}$ is called the dissipation factor or loss tangent, which is tangent of phase angle $\delta$ between the vector for displacement and that for the applied electric field. Thus

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad \text{....................... (4.4)}$$

As $\varepsilon''$ and $\varepsilon'$ are frequency dependent, $\delta$ is also frequency dependent. Equ. (4.3) shows that $\varepsilon''$ approaches to zero both for small and large value of $\omega T$, while it is maximum for $\omega T = 1$.

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

4. B. 2 Temperature

The simplest form of the Debye equation\textsuperscript{38} which relates the dielectric constant of a substance to its structure and temperature is,

$$\frac{\varepsilon^{-1}}{\varepsilon + 2} + \frac{4\pi N_1}{3} \left( \chi_0 + \frac{\mu^2}{3KT} \right) \ldots (4.5)$$

where $N_1$ is the number of molecules per cc, $\chi_0$ is the polarizability of the molecule, that is, the dipole moment induced per molecule by unit electric field, $\mu$ is the permanent electric dipole moment of the molecule, $K$ is the molecular gas constant equal to $1.38 \times 10^{-10}$ erg/degree and $T$ is the absolute temperature.

Equ. (4.5) satisfactorily represents the behaviour of non-polar substances but is inadequate in case of polar substances with few exceptions. This suggests that the dielectric constant of polar substances is temperature dependent\textsuperscript{40,41} and that of non-polar substances is temperature independent.\textsuperscript{42}

For non-polar substances, however, due to thermal expansion of matter, the ratio of the number of molecules to the
effective length $L$ of the dielectric diminishes, when
temperature increases, for which reason $\varepsilon$ should also
diminish in this case according to Equ. (4.5). The failure
of above dielectric constant-temperature curve is due to the
fact that the material is usually frozen between the fixed
plates of a condenser so that decreasing density does not alter
the amount of material between the plates.

The nature of dependence of dielectric constant on
temperature may be different in solid ionic dielectric. In
most cases an ionic mechanism of polarization increases $\varepsilon$
when the temperature grows. Examples are alkali halogenide crystal
of rock salt,\textsuperscript{43} inorganic glasses of various composition. It
may be due to the loosening of the bonds which hold the ion in
place. However, at the same time the value of $\varepsilon$ diminishes when
the temperature rises due to the decrease in the number of
molecules per cubic centimeter as in the case of non-polar solids.
In the case of calcium fluoride and sodium chloride examined by
Bretscher,\textsuperscript{37} the calculated increase of dielectric constant due
to weakening of the interionic forces is nearly three times as
large as the decrease caused by decreasing density. In ionic
crystals that have been treated to introduce a relatively large
number of lattice defects, small loss maxima have been observed
in the kilocycle region.\textsuperscript{44}

Solids consisting of polar molecules, that is molecules
possessing permanent dipole moments, commonly behave like those
consisting of non-polar molecules, because solidification usually fixes the molecules with such rigidity in the lattice that lattice or no orientation of the dipoles in an externally applied field is possible. Near melting point polar molecules acquire freedom of rotation thus $\varepsilon$ abruptly changes from lower to higher value. Thus very slight increase in dielectric constant with temperature at low temperatures and the more pronounced rise just below the melting point are typical in polar solids.

If the dielectric is semiconductor, temperature increase may raise the free carrier density to introduce conduction losses and the effect was observed in terms of reduction of dielectric constant.$^{45-47}$

As a general rule $\tan \delta$ appreciably increases when temperature rises. This growth in $\tan \delta$ is brought about by an increase both in the conduction of residual current and the conduction of absorption current. The dielectric losses caused by the dipole mechanism reach their maximum at a certain definite temperature $T_K$.

Temperature and frequency dependence of dielectric constant of organic substances have been studied by several workers.$^{10-13,48,49}$ William $^{50}$ studied the properties of some organic compounds over a wide range of frequency, temperature and pressure. Dufour et al.$^{51}$ measured the dielectric constant
of PVC at very low frequency between 25° to 105°C. The value of dielectric becomes greater as the temperature increases and frequency decreases. Saraf 52 has measured the temperature and frequency dependence of dielectric constant and loss for pyrene while Das 53 measured it for copper-phthalocyanine.

4.8.3 Field  — Dielectric constant in most cases may be assumed practically independent of the applied field for ordinary strength. For strong field saturation effects are detectable. Bottcher 54 has examined the work of Debye 55 and of Vanvleck 56 on the saturation effect and derived a new expression for the change of dielectric constant \( \varepsilon_0 \) produced by a field:

\[
\frac{\Delta \varepsilon}{E^2} = - \frac{4\pi N_1 \mu^4}{45 k^3 T^3} A \quad \ldots (4.6)
\]

where \( \varepsilon \) is the dielectric constant, \( E \) is the applied field, \( N_1 \) is the number of molecules per cc., \( \mu \) is the permanent electric dipole moment of the molecule, \( T \) is the absolute temperature and \( K \) is the Boltzmann constant. \( A \) has the different values according to Debye, Vanvleck and Bottcher which are as follows:

\[
A = \frac{(\varepsilon_0 + 2)^4}{81} \quad \ldots \text{Debye.}
\]

\[
A = \frac{27 \varepsilon_0^4}{(2 \varepsilon_0^2 + 1)(2 \varepsilon_0 + 1)^2} \quad \ldots \text{Vanvleck.}
\]
\[
A = \frac{(\varepsilon_{\infty} + 2)^2 \varepsilon_0^2}{(2 \varepsilon_0^2 + \varepsilon_{\infty}^2)(2 \varepsilon_0 + \varepsilon_{\infty})(6 \varepsilon_0 + 1)} \quad \text{... Bottcher}
\]

Malsch \(^{57}\) did not observe any change in the dielectric constant of ether, water and glycerine using a field of intensity 100,000 V/cm. In an improved method, \(^{58}\) he found that a field of 250,000 V/cm produced a decrease of 0.7% in the dielectric constant of water, 1% in introbenezene and 1.5% in ethyl alcohol. Kautzsch \(^{59}\) found the expected decrease in the dielectric constants of ethyl ether, chloroform and chlorobenzene, whose molecules are polar. For non-polar hexane, no change in dielectric constant was observed.

According to dipole orientation theory, in polar dielectrics, there exist permanent dipoles and therefore they tend to orient when such a dielectric is placed in an electric field. The direction of orientation may be parallel, antiparallel or in some other direction. Direction depends upon the applied field strength. If the field strength is increased continuously the breakdown is reached much earlier before the saturation reaches. When the direction of orientation of permanent dipoles is at right angles to the direction of applied field, the dielectric constant is vanished. Orientation of permanent dipoles parallel to the direction of the applied field gives a high dielectric constant accompanied by a large dielectric loss due to hysteresis in the direction of the field. The orientation of the dipoles is proportional to the applied field strength and therefore a greater increment in the value of
the dielectric constant is to be expected with increasing field strength.

Numerous workers $^{45,45,50}$ have studied the variation of dielectric constant with applied field. It was found that the dielectric constant increases in the direction of the field and decreases for higher fields. However, the increase is not so large as expected from the dipole orientation theory. At higher fields trapped electrons are supposed to be released from the potential well and excited to the conduction band. This results in the decrease of polarization and therefore the dielectric constant. Robert $^{45}$ and Sawaguchi et al. $^{46}$ observed such a decrease in the case of ceramic based dielectrics.

Srivastava and Bhatnagar $^{61}$ showed that the value of dielectric constant of sugar-cane wax is increased by a very small amount on application of the d.c. field. Jangvir Singh $^{62}$ showed that the value of dielectric constant of $\beta$-naphthol thermoelectric to be maximum just immediately after the polarization of the sample and then it decays to the normal value corresponding to the unpolarized state. Seitz et al. $^{63,64}$ observed the change in dielectric constant for certain inorganic materials with frequency and field and concluded that barrier layer polarization is responsible for the dielectric behaviour.
Bhadra and Chatterji 55 and Bhadra 66 have observed an anisotropy in dielectric constant in case of carnuba wax. Mc Mahon 67 observed this for nitrowax. Lal 68 showed good interest in the static dielectric constant at various field strengths (0-16 kV/cm) for K₂NiF₄ single crystal in frequency ranges from 40 to 2 \times 10⁴ c/s and also 10⁶ and 10¹⁴ c/s.

4.8.4 **Humidity** - Dielectric constant may considerably increase due to the presence of water vapour or water molecules inside the dielectrics as its molecules are strongly polar. The value of tan δ also noticeably increases in hygroscopic dielectrics when humidity grows.

4. C **General Measurement Technique** :

A wide variety of methods 69-71 are available for the measurement of the dielectric constant and dielectric loss. The choice of method of measurement depends largely on the frequency at which the values are required and on the nature of the specimen.

The most generally used methods for measuring dielectric constant \( \varepsilon' \) (or static dielectric constant \( \varepsilon_s \)) at low frequencies consist of the measurement of the capacitance \( C_0 \) of an empty condenser and the capacitance \( C \) and the resistance \( R \) of the condenser filled with the
dielectric material. Thus determination of dielectric constant depends on accurate capacitance measurement.

A simple method for determining dielectric constant is to measure the time constant for the discharge of a condenser, through a standard resistor with and without dielectric present. The applicability of this method is limited to the case for which the time constant can be made long enough to permit observation. When this is of the order of milli-seconds the discharge can be observed using a cathode ray oscillograph with a long persistence screen. However, errors in the determination are associated with the measurement of the voltage reached after a given time, with the time measurement itself and with the difficulty in knowing precisely the moment of commencement of the discharge. Cole and Cole 72 developed a method in which the charging current of the condenser containing the dielectric is observed. The accuracy of this method depends on the accuracy of current and time measurements.

Bridge method 73-78 is the most generally useful method for the measurement of dielectric constant in the audio to high frequencies ( $10^2$ to $10^7$ c/s ). Generally these methods are based on the null balance principle. These types of instrument have been selected as representative of this
group, namely the Schering bridge, the transformer of hybrid coil bridge and the parallel T. The schering bridge is important one. It can be calibrated for direct reading of \( \tan \phi \) and it is suitable for higher frequencies. The General Radio Company (USA) has developed sophisticated and modified capacitance bridges to measure the dielectric constant and loss over a wide range of frequencies. 79

For frequency in the range of 10 Mc/s to 100 Mc/s bridge method are generally difficult due to increasing importance of effects of stray capacitance. In this region resonance method is used in which a very precise determination may be effected by tuning a circuit to resonance. This method has been used rather widely for the dielectric constants of liquids and is of such accuracy that it has also been applied for measurement of gases. Hartshorn and Ward 80 developed a resonance apparatus which has been used for dielectric constant and losses of solids and liquids of rather low loss at frequencies up to 100 Mc/s. A double resonance method has been used for measurement of \( \varepsilon' \) in the presence of high losses.

In all these methods accuracy of measurement depends critically on the measuring cell in which the specimen is mounted. Different measuring cells, i.e. cells with fixed electrodes, 81 cells for microwave frequencies 82-84 have been used earlier to observe the dielectric constant variation of
solids and liquids. Cells with adjustable electrode are used for materials that can be formed into disks. Measurement on single crystal can also be carried out with the type of cell if the crystal can be grounded with two parallel faces and if the dimensions of the sample can be accurately measured. The usual arrangement of cell for solids consists of flat parallel plates of known area and separation between which the specimen is inserted in the form of parallel sided disc. Errors in this arrangement are associated with the inductance and resistance of the leads to the electrodes, stray capacitance from these leads to earth and fringe fields at the edges of the electrodes. The effect due to stray capacitance and fringe fields can be eliminated by using micrometer electrodes or a suitably shielded three electrodes system. All the above effects referred to above are eliminated as they are practically kept constant, in the micrometer electrode method but however does not remove the effect caused by dc surface conductivity and by surface polarization resulting from moisture films. In the three electrodes system one of the measuring electrodes is connected to a suitable terminal of the measuring circuit.

In the very high frequency range 100-1000 Mc/s; the tuned circuit technique cannot be employed due to the impossibility of realizing a lumped resonant circuit at these frequencies. Distributed circuits are therefore used, the
common forms of which are transmission-lines and waveguides. In the frequency range above 1000 Mc/s resonance cavity and waveguide methods are employed. The particular mode of measurement employed depends upon the nature and quantity of material to be measured.

Other methods for the measurement of dielectric constant and loss tangent in the microwave region have been tabulated by Redheffer. 85

Proper electrical contact between the surface of the sample and that of the electrode is essential for accurate measurements. For this purpose some type of thin metallic electrodes are applied to the specimen before it is placed between the rigid electrodes of a measuring cell. Any air gap between specimen and electrodes provides a serious air capacitance and the dissipation factor. To avoid this, the electrodes are deposited on the specimen.

4. D. Present Technique for Measurement of Dielectric Constant:

The experimental technique used for determination of dielectric constant and dielectric loss of all picrates, consists of the following parts:

4. D. 1 Preparation of Sample - The sample in the form of circular pellets has been prepared under suitable pressure as described in previous chapter.
The thickness and area of each sample of different picrate has been kept to be the same and equal to 0.08 cm and 1.452 sq. cm respectively.

4.D. 2 Electrode Assembly and its constant

Electrode assembly used for dielectric constant and dielectric loss measurement is the same as described in the previous chapter. The inner diameter of the guard ring and the diameter of the guarded electrode are 1.48 cm and 1.28 cm respectively. The effective radius $r$ of the guarded electrode is given by Amery-Hamburger formula $86$ (Equ. 3.5 Chap. III). The effective radius comes out to be 0.681 cm and the effective area of the guarded electrode is 1.452 cm.

4.D. 3 Temperature Control

- The dielectric constant of any substance depends on the temperature of the specimen and it is very necessary to obtain the stability of temperature during the course of measurement. The thermostat used for this purpose is supplied by M/S Industrial Corporation, Bombay (India) capable of giving temperature up to $250^\circ + 1^\circ C$ was used.

4.D. 4 Dielectric constant Measuring Bridge

- Systronics LCR Bridge type 921, supplied by SYSTRONICS, 80-92 Naroda Industrial Area, Naroda P.O., Ahmedabad has been used for measurements. This is
Fig. 4.11

BASIC CAPACITANCE BRIDGE
designed for the precise measurement of capacitors and capacitance standards. This bridge can be used either on the production line or in laboratories.

4. D. 5 Bridge Circuit - The Systronics LCR Bridge is a development of the Wheatstone Bridge. One of the bridge diagonals is powered either by a DC or AC voltage according to the nature of the component to be tested. The other diagonal is a zero detector that includes an amplifier powering a meter. The bridge balance is determined by a meter preceded by a null amplifier. The amplified voltage and the A.F. bridge input voltage (100 Hz - 1 KHz - 10 KHz) are both available at terminals and allow the display of Lissajous figures so as to facilitate balancing the bridge when the minimum is difficult to obtain by means of the meter. This detector allows an external source to be used to energize the bridge for measurements over a more representative range of frequencies (from 100 Hz to 10 KHz). Eight separate fixed capacitance standards are used, where values in range in decade steps from 0.1 pf to 10,000 uf.

Bridge is operated by Philips A.F. generator GM 2308/90 supplied by Philips India Ltd., was used as external frequency source. The audio frequency generator provides an a.c. voltage with which measurements can be carried out in the audio frequency range.

An isolating transformer TM 7120 supplied by Marconi
Fig. 4.12
Instrument Ltd., England used as an optional accessory. Fig. 4.11 shows the basic bridge configuration used for these measurements.

4.D.6 Circuit Arrangement and Operating Procedure

The assembly containing the pellet of picrate as a dielectric was kept inside the thermostat. The two main electrodes of the assembly are connected across jacks - and +. To avoid the stray capacitance and mains hum pick-up, the shortest possible length of the connecting leads, which are grounded and shielded have been used for all circuit connections.

For measurement using the internal oscillator, the following instructions are followed.

(i) Set DC bias control to 0.
(ii) Set RLC control to C, \[ \tan \phi = \text{WCR} (0-\infty-0) \].
(iii) Set source control to either \( X \) 0.1 - 10 KHz; \( X \) 1 - 1 KHz; or 100 Hz.
(iv) Set excitation voltage control above halfway up.
(v) Adjust the sensitivity control until the meter indicates 30 graduations.
(vi) Set ranges control to a range providing minimum reading on meter. The balance is not far off when pointer approaches zero.

Then the sensitivity may be increased. Now the bridge is balanced with the main balance and loss balance controls. The
capacitance value $C$ is obtained on the bridge for the capacitance assembly with picrate as dielectric. At the same time dielectric loss tangent is also obtained from the bridge.

For measurements using an external AC source, source switch is set to $X$-INPUT to cut the internal source off and to allow the use of an AF external source (50 Hz to 10,000 Hz) to power the bridge.

This external source has to be connected to jacks source out. It must be asymmetrical with one lead grounded and with a voltage between 0.2 to 2 V r.m.s. The excitation level varies with frequency. The external a.f supply is connected via isolating transformer. The use of transformer eliminates the possibility of measuring low impedance at high frequency.

Now the frequency is set to desired value, DC bias control is set to zero, RLC control to $C$, $\tan \delta$ on $\frac{\omega}{\omega_0}$. Same procedure is applied for obtaining value of capacitance and $\tan \delta$ loss as described above in the case of measurement using an internal source.

The vacuum capacitance $C_0$ of the assembly is given by:

$$C_0 = 0.08854 \frac{\pi r^2}{d} \text{ uuf}$$

where $r$ = effective radius
$d$ = thickness of the sample.

The static dielectric constant is then simply obtained by the
formula \( \varepsilon = \frac{C}{C_0} \).

4. E Details of Measurement:

For each picrate variation of dielectric constant and loss are measured with temperature and frequency. Frequency is varied from 200 c/s to 10 kHz in 14 steps. Temperature variation is different for different picrates according to their melting point. The details of measurement are as follows:

4. E. 1 Variation of dielectric constant and loss with temperature at fixed frequency.

In this part of experiment effect of temperature on dielectric constant and dielectric loss at constant frequency is measured. Frequency is kept fixed and temperature is raised in steps for the whole range. At each temperature, thermal equilibrium of the specimen is obtained by keeping the assembly in thermostat for at least five hours and the steady value of capacitance of the specimen is measured along with dielectric loss by the method as used earlier. When whole temperature range is applied other frequency is set on the bridge and the same process is repeated.

4. E. 2 Variation of dielectric constant and loss with frequency at fixed temperature.

To observe this variation of dielectric constant and
dielectric loss the temperature is kept constant and frequencies varied. The steady value of capacitance and dielectric loss (tan δ %) of the specimen is observed directly on the bridge. The corresponding value of dielectric constant is calculated from the above observations. Frequencies are varied from 200 c/s to 1 Kc/s in steps of 200 c/s and from 1 Kc/s to 10 Kc/s in steps of 1 Kc/s. Now temperature is increased in steps for full range and the same process of measurement is repeated. At each temperature, the assembly is allowed to remain in thermostat for five hours before the frequency is applied. This period is sufficient for the specimen to attain equilibrium.

Following information is known from the literature.

<table>
<thead>
<tr>
<th>1. α-Bromo naphthalene - C_{10}H_{8}Br</th>
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</thead>
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<tr>
<td>Temperature</td>
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<td>22.7°C</td>
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<table>
<thead>
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</tr>
<tr>
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continued ....
Naphthalene - C₁₀H₈

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<th>Dielectric constant</th>
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<tr>
<td>60</td>
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<td>&quot;</td>
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<td>&quot;</td>
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<td>180</td>
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Phenanthrene

<table>
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<th>Dielectric constant</th>
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4. Results:

The nature of variation of dielectric constant and
dielectric loss of all picrates with temperature and frequency is shown in Figs. 4.1 to 4.10. The values of dielectric constant and dielectric loss for different picrates in the frequency range from 200 c/s to 10 KHz are as follows:

<table>
<thead>
<tr>
<th>Picrate of</th>
<th>Frequency</th>
<th>Temp. °C</th>
<th>Dielectric Constant</th>
<th>Dielectric Loss</th>
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<td>Naphthalene</td>
<td>200 c/s to 10 KHz.</td>
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<td>2.40 - 14</td>
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<td>4.52-18.75</td>
<td>2.40 - 14</td>
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<td></td>
<td>35-115</td>
<td>4.35-9.06</td>
<td>2.40 -14</td>
</tr>
<tr>
<td>α-Naphthol</td>
<td></td>
<td>35-140</td>
<td>4.90-23.75</td>
<td>2.25 - 14</td>
</tr>
<tr>
<td>β-Naphthol</td>
<td></td>
<td>35-135</td>
<td>4.40-15.70</td>
<td>2.30 - 14</td>
</tr>
<tr>
<td>α-Naphthyl-amine</td>
<td></td>
<td>30-125</td>
<td>3.90-6.90</td>
<td>2.40 - 14</td>
</tr>
<tr>
<td>β-Naphthyl-amine</td>
<td></td>
<td>35-145</td>
<td>4.60-16.39</td>
<td>2.20 - 14</td>
</tr>
</tbody>
</table>

4.4.1 Variation of Dielectric Constant and Dielectric Loss with temperature at fixed frequency.

The results obtained during the measurement of dielectric constant and dielectric loss as the temperature was varied from 30° to 115° at fixed four frequencies, 0.2 KHz, 0.8 KHz, 2.0 KHz and 8.0 KHz. are shown in Figs. 4.1 to 4.4. After careful observation of these figures following inferences can be drawn.
VARIATION OF DIELECTRIC CONSTANT WITH TEMPERATURE AT DIFFERENT FREQUENCIES.

\[ \begin{align*}
\Delta & \rightarrow \Delta \quad \text{PHENANTHRENE PICRATE} \\
\Delta & \rightarrow \Delta \quad \text{NAPHTHALENE PICRATE} \\
\bullet & \rightarrow \bullet \quad \text{\(\alpha\) - CHLORO-NAPHTHALENE PICRATE} \\
\bigcirc & \rightarrow \bigcirc \quad \text{\(\alpha\) - BROMO-NAPHTHALENE PICRATE}
\end{align*} \]

FREQUENCY

1 = 0.2 KHz
2 = 0.8 KHz
3 = 2.0 KHz
4 = 8.0 KHz

ORIGIN IS SHIFTED BY 6 CMC FOR EACH NEXT PICRATE

Fig. 4.1
VARIATION OF DIELECTRIC CONSTANT WITH TEMPERATURE AT DIFFERENT FREQUENCIES.

\[ \begin{align*}
\text{FREQUENCY} \\
1 &= 0.2 \text{ KHz} \\
2 &= 0.8 \text{ KHz} \\
3 &= 2.0 \text{ KHz} \\
4 &= 8.0 \text{ KHz}
\end{align*} \]

ORIGIN IS SHIFTED BY 6 CMS FOR EACH NEXT PICRATE

Fig. 42
(i) Figs. 4.1 and 4.2 show that in all picrates dielectric constant increases with temperature at all frequencies.

(ii) The rate of increase of dielectric constant in lower temperature region up to 70°C for naphthalene, 80°C for phenanthrene, α-naphthyl-amine, β-naphthyl-amine, α-chloro-naphthalene and α-bromo-naphthalene and 85°C for α-naphthol and β-naphthol picrate is slower than that at higher temperature region.

(iii) For all the picrates, curves are closer at lower temperature region than that at higher temperature region. As temperature is increased the spacing between curves of different frequency is increased. It shows that at lower temperature the difference between values of dielectric constants at different frequencies is small but as the temperature increased difference between the values of dielectric constant at different frequencies is increased.

(iv) From the curves in Figs. 4.3 and 4.4, it is clear that dielectric loss in % i.e. tan δ % increases with increasing temperatures at fixed frequency.

(v) The increase in dielectric loss with temperature is more marked at lower frequencies.

(vi) The rate of increase of dielectric loss in lower temperature region is slower than that of higher temperature region. In
VARIATION OF LOSS (TAN $\delta \%$) WITH TEMPERATURE AT DIFFERENT FREQUENCIES.

- $\Delta$ NAPHTHALENE PICRATE
- $\Delta$ $\beta$-NAPHTHYL AMINE PICRATE
- $\bullet$ $\alpha$-NAPHTHYL AMINE PICRATE
- $\bigcirc$ PHENANTHRENE PICRATE

FREQUENCIES
1 = 8.0 KHz
2 = 4.0 KHz
3 = 1.0 KHz
4 = 0.8 KHz

TAN $\delta \%$

TEMPERATURE °C

ORIGIN IS SHIFTED BY 6 CMS. FOR EACH NEXT PICRATE.

Fig. 4.3
VARIATION OF LOSS (TAN δ %) WITH TEMPERATURE AT DIFFERENT FREQUENCIES

- ▲ ▲ ▲ - BROMO NAPHTHALENE PICRATE
- △ △ △ - CHLORO NAPHTHALENE PICRATE
- ● ● ● - NAPHTHOL PICRATE
- ○ ○ ○ - NAPHTHOI PICRATE

FREQUENCY
1 = 80 KHz
2 = 40 KHz
3 = 10 KHz
4 = 0.8 KHz

ORIGIN IS SHIFTED BY 6 CMS FOR EACH NEXT PICRATE.
the lower frequency region, a faster increase of 
dielectric loss is observed above temperature, 75°C 
for α-naphthol, β-naphthol, α-naphthyl-amine, 
β-naphthyl-amine, 70°C for α-chloro-naphthalene, 
β-bromo-naphthalene, 80°C for naphthalene and phenanthrene 
picrate. In the frequency region from 4 to 8 KHz, a 
faster increase of dielectric loss is observed above 
temperature, 105°C for α-naphthyl-amine, 
β-naphthyl-amine; 95°C for α-naphthol, β-naphthol and 
naphthalene and 100°C for α-chloro-naphthalene picrate. 
In the above frequency region, for α-bromo-naphthalene 
picrate the rate of increase of dielectric loss with 
temperature is so small that it appears to be almost 
constant.

(vii) At lower frequency, the rate of increase of loss with 
temperature in the lower temperature region is so small 
that it appears to be constant. The value of dielectric 
loss in % after which the nature of constancy appear 
is different for different picrates.

(viii) In case of phenanthrene picrate tan δ % increases 
with temperature up to 80°C at each frequency; at 80°C 
the value of tan δ % is maximum and then it decreases 
up to 90°C. After 90°C the value of tan δ % further 
increases with temperature at a faster rate than that at 
lower temperature region.
4.F. 2 Variation of Dielectric Constant and Loss with frequency at fixed temperature.

Fig. 4.5 shows the frequency dependence of dielectric constant of naphthalene picrate, phenanthrene picrate, \( \alpha \)-chlore-naphthalene picrate, \( \alpha \)-bromo-naphthalene picrate at four fixed temperatures 40\(^\circ\)C, 95\(^\circ\)C, 105\(^\circ\)C and 115\(^\circ\)C. Fig. 4.6 shows the frequency dependence of dielectric constant of \( \alpha \)-naphthyl-amine picrate, \( \beta \)-naphthyl-amine picrate, \( \alpha \)-naphthol picrate and \( \beta \)-naphthol picrate at temperatures 40\(^\circ\)C, 95\(^\circ\)C, 115\(^\circ\)C and 125\(^\circ\)C.

From these curves it is clearly observed that :-

(i) Pattern of frequency dependence of dielectric constant for all picrates and for all temperatures remains almost the same.

(ii) Dielectric constant decreases with frequency at all temperatures for all picrates and the values of dielectric constant becomes almost constant after 5 Kc/s for all picrates, except in case of phenanthrene in which at temperature 115\(^\circ\)C, the values of dielectric constant becomes constant after 7 Kc/s.

(iii) At higher temperature and in low frequency region the rate of decrease of dielectric constant with frequency is faster than that at lower temperature for all picrates.
VARIATION OF DIELECTRIC CONSTANT WITH FREQUENCY.

- ▲▲▲▲ CHLORO NAPHTHALENE PICRATE
- ○○○○ BROMO NAPHTHALENE PICRATE
- ●●●● PHENANTHRENE PICRATE
- ○○○○ NAPHTHALENE PICRATE

TEMPERATURES
1 = 40 °C
2 = 95 °C
3 = 105 °C
4 = 115 °C

Dielectric Constant

Frequency KHz

Origin is shifted by 6 CMS for each next picrate

Fig. 4.5
VARIATION OF DIELECTRIC CONSTANT WITH FREQUENCY

- ▲: NAPHTHYL AMINE PICRATE
- △: NAPHTHYL AMINE PICRATE
- ●: NAPHTHOL PICRATE
- ○: NAPHTHOL PICRATE

TEMPERATURES
1 = 40 °C
2 = 95 °C
3 = 115 °C
4 = 125 °C

DIELECTRIC CONSTANT

FREQUENCY KHz

ORIGIN IS SHIFTED BY 6 CMS FOR EACH NEXT PICRATE

Fig. 4.6
(iv) Figs. 4.7 to 4.10 show the variation of \( \tan \delta \) with frequency at fixed temperatures 40\(^\circ\)C, 75\(^\circ\)C, 95\(^\circ\)C, and 105\(^\circ\)C. From these curves it is clear that:

(i) Pattern of frequency dependence of \( \tan \delta \) for all picrates remains almost the same at all temperatures.

(ii) For all the picrates, the value of \( \tan \delta \) decreases with frequency and becomes almost constant after 4 Kc/s at temperatures 40\(^\circ\)C and 75\(^\circ\)C and after 7 Kc/s at temperatures 95\(^\circ\)C and 105\(^\circ\)C.

(iii) At each temperature and for all picrates, \( \tan \delta \) decreases at a faster rate in the low frequency region than that comparatively at higher frequency region.
VARIATION OF LOSS (TAN δ%) WITH FREQUENCY

- ▲ PHENANTHRENE PICRATE
- ▲ NAPHTHALENE PICRATE
- ● α - NAPHTHYL AMINE PICRATE
- ● β - NAPHTHYL AMINE PICRATE

TEMPERATURES
1 - 40°
2 - 75°

ORIGIN IS SHIFTED BY 4 CMS. FOR EACH NEXT PICRATE

Fig. 4.7
VARIATION OF LOSS (TAN $\delta\%$) WITH FREQUENCY.

- $\Delta\Delta$ - CHLORO NAPHTHALENE PICRATE
- $\Delta\cdot\Delta$ - BROMO NAPHTHALENE PICRATE
- $\bullet\cdot\bullet$ - NAPHTHOL PICRATE
- $\circ\cdot\circ$ - NAPHTHOL PICRATE

TEMPERATURES

1 = 40 $^\circ$C
2 = 75 $^\circ$C

TAN $\delta\%$

FREQUENCY KHz

ORIGIN IS SHIFTED BY 4 CMS FOR EACH NEXT PICRATE.

Fig. 4.8
VARIATION OF LOSS (TAN δ %) WITH FREQUENCY.

TEMPERATURES
1 = 95°C
2 = 105°C

Fig. 4.9
VARIATION OF LOSS (TAN $\delta$ %) WITH FREQUENCY.

- $\alpha$ - CHLORO NAPHTHALENE PICRATE
- $\alpha$ - BROMO NAPHTHALENE PICRATE
- $\alpha$ - NAPHTHOL PICRATE
- $\beta$ - NAPHTHOL PICRATE

TEMPERATURES

1 = 95 $^\circ$C
2 = 105 $^\circ$C

ORIGIN IS SHIFTED BY 4 CMS. FOR EACH NEXT PICRATE.

Fig. 4.10
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