CHAPTER I

A BRIEF SURVEY OF THE THEORIES OF DIELECTRIC POLARIZATION, DIELECTRIC CONDUCTION TOGETHER WITH A BRIEF REVIEW OF PREVIOUS WORKS

1.1. Debye Theory of Dielectric Polarization and Complex Dielectric Constant:-

All matter is built up from electrically charged particles; negative electrons and positive nuclei, combining some times to neutral atoms and molecules, but in other case the particles with a net charges, such as ions in solution and in crystal. When a material is bring into an external electric field, then every particles in the material is subjected to an "internal field" which is proportional to applied electric field. Under the influence of external field in some materials the electrons in metals and ions in solution moved over a long distance, such materials are called conductors. But in the case of insulators or dielectries, a very small displacement of charges occurs. When an electric field is applied to the dielectric material the force acting upon the charges bring about a small displacement of the electrons relative to the nuclei, as the field tends to shift the positive and negative charges in opposite direction. This displacement is limited since the electrons are bound to the nuclei and therefore, reactive forces arise, which are proportional to the displacements for not too high field intensity. Thus when electrons of an atom are displaced by the electric field the dielectric is said to be polarized and this type of polarization is called electronic polarization. Another form of polarization is due to the fact that the applied fields tends to direct the permanent dipoles. During the formation of this polarization a certain amount of dielectric charges is transported through every plane elements in the dielectric. This transport is called the displacement current. After reaching the state of equilibrium in an applied electric field every volume element of the dielectric has aquired an induced moment.

The moment of a set of charges relative to a fixed point is defined by relation

$$\vec{m} = \sum_i e_i \vec{r}_i \qquad \ldots\ 1.1$$

where $\vec{r}_i$ is the radius vector, pointing from the chosen point to the ith. charge. The induced dipole moment in a volume element ΔV around a point is denoted by

$$\vec{m}_{ind} = \vec{p}\Delta V = \sum_i N_i e_i \vec{s}_i \Delta V \qquad \ldots\ 1.2$$

where $N_i \Delta V$ is the average number of charges e_i with displacement $\vec{s}_i$, in the volume element ΔV.

The vector $\vec{P}$ is generally called the "electric polarization" and it is the induced dipole moment per unit volume. The vector $\vec{P}$ is connected with the dielectric displacement vector $\vec{D}$ as

$$\vec{D} = \vec{E} + 4\pi\vec{P} \qquad \ldots 1.3a$$

or, $$\vec{P} = \frac{\vec{D} - \vec{E}}{4\pi} = \left(\frac{\epsilon - 1}{4\pi}\right)\vec{E} \qquad \ldots 1.3b$$

where $\vec{D} = \epsilon\vec{E}$, ϵ = dielectric permittivity and $\frac{\epsilon - 1}{4\pi} = \chi$ is the dielectric succeptibility $\vec{E}$ is the applied electric field.

Now, it consider that a dielectric sphere of radius 'a' in vacuum, then the formula for dipole moment becomes

$$\vec{m} = \frac{\epsilon - 1}{\epsilon + 2} a^3 \vec{E}_0 \qquad \ldots 1.4$$

when a dielectric is placed in an electric field, $\vec{E}_0$ in vacuum, then due to induction, its polar molecules orientate themselves along the direction of the applied field. Each molecule is an electric dipole possessing an electric moment. This moment $\vec{m}$ is proportional to $\vec{E}_0$. So it can be written as

$$\vec{m} = \alpha\vec{E}_0 \qquad \ldots 1.5$$

where α is a constant called polarizability of the dielectric, which is given by

$$\alpha = \frac{\epsilon - 1}{\epsilon + 2} a^3 \qquad \ldots 1.6$$

Thus polarizability has the dimension of volume. For conducting sphere polarizability $\alpha = a^3$.

The concept of the polarizability is very important for the molecular description of matter, since all atoms, ions and molecules are polarisable.

Polarisation $\vec{P}$ is divided into two parts $\vec{P}_\mu$ caused by the orientation of permanent dipoles and $\vec{P}_\alpha$ caused by the translational effect.

Thus

$$\vec{P} = \vec{P}_\alpha + \vec{P}_\mu \qquad \ldots 1.7$$

Then term

$$\vec{P}_\alpha = \sum_k N_K \alpha_K (\vec{E}_i)_K \qquad \ldots 1.8$$

and

$$\vec{P}_\mu = \sum_k N_k \bar{\vec{\mu}}_k \qquad \ldots 1.9$$

where N is the number of perticles per unit volume, α the average polarizability of a particle and $\vec{E}_i$ the average field strength acting upon the particle. The index K refers to the k th. kind of particle. ($\vec{E}_i$ is the internal field which is equivalent to that of applied field $\vec{E}$). $\bar{\vec{\mu}}_k$ is the average value of permanent dipole moment for k th. molecule.

Now, in an uniform directing field $\vec{E}_r$ the average dipole moment vector $\overline{\vec{\mu}}$ of a dipole molecule in thermal equilibrium with a large number of other molecules is,

$$\overline{\vec{\mu}} = \frac{\mu^2}{3kT}\vec{E}_r \qquad \ldots\ 1.10$$

In the other theories $\vec{E}_r$ was taken equal to $\vec{E}_i$. However, Onsagar showed that this is only satisfactory for gases at low pressure, since in the general case only a part of the internal field $\vec{E}_i$ has a directing influence upon the permanent dipoles.

Combining eq. (1.9) and (1.10)

$$\vec{P}_\mu = \sum_k N_k \frac{\mu_k^2}{3kT}\left(\vec{E}_r\right)_k \qquad \ldots\ 1.11$$

From eq. (1.7), (1.8) and (1.11)

$$\vec{P} = \frac{\epsilon - 1}{4\pi}\vec{E} = \sum_k N_k\left[\alpha_k\left(\vec{E}_i\right)_k + \frac{\mu_k^2}{3kT}\left(\vec{E}_r\right)_k\right] \qquad \ldots\ 1.12$$

This is the fundamental equation.

To describe the dielectric behaviour of gases and polar molecules in a static and in a low frequency alternating field Debye equation is used. To obtain Debye equation by substituting $\vec{E}(\epsilon+2)/3$ both for $\left(\vec{E}_i\right)_k$ and $\left(\vec{E}_r\right)_k$ in eq. (1.12).

The result is

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_k N_k \left(\alpha_k + \frac{\mu_k^2}{3kT}\right) \qquad \ldots \; 1.13$$

The Debye equation is used for calculation of dipole moments from measurements on dilute solutions of a polar compound in a nonpolar solvent. But this is not very accurate method. Now introducing the molar polarization $[P]$ of the solution $[P] = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{\bar{M}}{d}$ where d = density and $\bar{M} = \sum_k x_k M_k$, average molecular weight, x_k are the molar fraction of the components and M_k their molecular weights. The Debye equation (1.13) becomes

$$[P] = \frac{4}{3}\pi N_A \sum_k x_k \left(\alpha_k + \frac{\mu_k^2}{3kT}\right) \qquad \ldots \; 1.14$$

where

$$N_A = \sum N_k \frac{M}{d}$$

is Avogardo's number.

In the solution of polar compound in nonpolar solvent

$$[P] = \frac{4}{3}\pi N_A \left[(1-x)\alpha_o + x\left(\alpha + \frac{\mu^2}{3kT}\right)\right] \qquad \ldots \; 1.15$$

where α_o is the polarizability of the solvent molecules, α, μ and x are the polarizability, permanent dipole moment and molar fractions of the solute respectively.

If $[P_s]$ is molar polarization of the pure solvent the Clausius-Mosotti equation becomes

$$[P_s] = \frac{4}{3}\pi N_A \alpha_0$$

or,

$$\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} = \frac{4\pi N_A}{3}\alpha_0 \qquad \dots 1.16$$

Further introducing the ideal molar polarization $[P]_d^o$ of the polar compound.

$$[P]_d^o = \frac{4\pi}{3} N_A\left(\alpha + \frac{\mu^2}{3kT}\right)$$

or,

$$\frac{\epsilon_1 - 1}{\epsilon_1 + 2}\cdot\frac{M_1}{d_1} = \frac{4\pi N_A}{3}\left(\alpha + \frac{\mu^2}{3kT}\right) \qquad \dots 1.17$$

Debye formula can be written in different form by eliminating α with the help of the Lorentz-Lorentz equation,

$$\frac{n_\infty^2 - 1}{n_\infty^2 + 2} = \frac{4\pi}{3} N\alpha \qquad \text{where} \qquad \epsilon = n_\infty^2$$

$$\therefore \mu^2 = \frac{9kT}{4\pi N}\cdot\frac{(\epsilon - n_\infty^2).3}{(\epsilon + 2)(n_\infty^2 + 2)} \qquad \dots 1.18$$

Considering the correction for the reaction field and taking $\frac{4}{3}\pi a^3 N = 1$ Onsager reduced the eq.(1.18) to

$$\mu^2 = \frac{9kT}{4\pi N}\cdot\frac{(\epsilon - n_\infty^2)(2\epsilon + n_\infty^2)}{\epsilon(n_\infty^2 + 2)^2} \qquad \dots 1.19$$

This is an important formula of Onsager's theory for calculating the dipole moments. But the difficulty is that, for determing the value of n_∞ the atomic polarisation should be known.

1.2. Physical Interpretation of Dielectric Loss (ϵ'') and Loss 'Tangent' ($\tan\delta$):

Wnen a dielectric is subjected to an alternating electric field there are two possibilities are found, which depends on the frequency of the applied field, the temperature and the kind of material.

a) In some cases there are no measurable phase difference between $\vec{D}$ and $\vec{E}$ then the relation $\vec{D} = \epsilon \vec{E}$ is also valid for alternating field.

b) In other cases there is a suitable phase difference between $\vec{D}$ and $\vec{E}$. Then the simple relation $\vec{D} = \epsilon \vec{E}$ is not valid for and the phase difference between the potential and the true charges of the condenser makes it impossible to use the simple formula $C = \epsilon C_0$ for the capacity of the condenser.

The important difference between these two possibilities that in the first case no energy is absorbed by the dielectric from the electromagnetic field whereas in the second case there is a dissipation of energy in the dielectric. The dissipation of energy in the dielectric due to the absorption of electromagnetic wave is called the "dielectric loss".

A phase difference between $\vec{D}$ and $\vec{E}$ can be due to three different mechanisms:

I) Electrical conductivity (II) Relaxation effect due to permanent dipoles and (III) Resonance effect due to rotation or vibration of atoms, ions or electrons.

All alternating fields are associated with electromagnetic waves, thus the theory of dielectric loss is closer related to the theory of the absorption of electromagnetic waves by dielectric materials.

In the case of phase difference between $\vec{D}$ and $\vec{E}$ it is useful to describe the relationship between the scalars D and E with the aid of complex notation as

$$E^* = E_o e^{j\omega t} \quad \text{and} \quad D^* = D_o e^{j(\omega t - \delta)}$$

where δ is the phase difference and $\omega = 2\pi f$ is the frequency of the electromagnetic wave; But $D^* = \epsilon E^*$ or,

$$\epsilon = \frac{D^*}{E^*} = \frac{D_o}{E_o} e^{-j\delta} = \frac{D_o}{E_o}\left(\cos\delta - j\sin\delta\right) \qquad \ldots 1.20$$

Thus the dielectric constant becomes complex at high frequency. The complex dielectric constant ϵ^* can be split up into real and imaginary part ϵ' and ϵ'' respectively

$$\epsilon^* = \epsilon' - j\epsilon'' \qquad \ldots 1.21$$

where $\epsilon' = \frac{D_o}{E_o}\cos\delta$ and $\epsilon'' = \frac{D_o}{E_o}\sin\delta$

The dielectric loss at a certain frequency is often indicated by the value of $\tan\delta$

where $\tan\delta = \frac{\epsilon''}{\epsilon'}$ ... 1.22

Again, the dissipated energy per unit volume per second of the electric field is

$$W = \frac{\omega E_o^2}{8\pi}\epsilon\sin\delta = \frac{\omega E_o^2}{8\pi}\epsilon'' \qquad \text{... 1.23}$$

Thus the energy is directly proportional to ϵ'' and hence to $\sin\delta$. Therefore ϵ'' is generally called the loss factor and $\sin\delta$ the power factor.

1.3. DIELECTRIC CONSTANT AND LOSS:

1.3a. Dielectric loss and relaxation time:-

Let in the static field the polarisation is

$$\vec{P}_s = \frac{\epsilon_s - 1}{4\pi}\vec{E}, \text{ then } \quad \vec{P}_s = \vec{P}_\infty + (\vec{P}_s)_{dip} \qquad \text{... 1.24}$$

where $(\vec{P}_s)_{dip}$ indicates the part of $\vec{P}_s$ due to permanent dipoles and $\vec{P}_\infty$ the part due to the polarizability of the particles

$$\vec{P}_\infty = \frac{\epsilon_\infty - 1}{4\pi}\vec{E} \qquad \text{...1.25}$$

The time in which the permanent dipoles needs to reach the equilibrium distribution subsequent to the application of a static electric field is of the order of magnitude between 10^{-6} and 10^{-13} seconds. This time depends on the temperature, the chemical composition and the structure of the dielectric molecules. During this time interval the part $(\vec{P}_s)_{dip}$ of $\vec{P}_s$ is build and polarisation increases from $\vec{P}_\infty$ to $(\vec{P}_s)$. Since the time required to established $\vec{P}_\infty$ relative to time required to build up $(\vec{P}_s)_{dip}$ is neglected. Then after a certain time t during this interval the relation becomes

$$\vec{P}_t = \vec{P}_\infty + \vec{P}_{dip} \qquad \ldots\ 1.26$$

where $\vec{P}_{dip}$ is the part of $(\vec{P}_s)_{dip}$ that has already been build up. Assuming the increase of $\frac{d\vec{P}_{dip}}{dt}$ is proportional to the difference between the final value $(\vec{P}_s)_{dip}$ and the actual value of $\vec{P}_{dip}$. Thus

$$\frac{d(\vec{P}_{dip})}{dt} = \frac{1}{\tau}\left\{ (\vec{P}_s)_{dip} - \vec{P}_{dip} \right\} \qquad \ldots\ 1.27$$

τ is a constant which measures the time lag, so it is called the relaxation time.

The relaxation time τ may be defined as the time in which the polarisation is reduced to $\frac{1}{e}$ th. times of its original value, where e is the base of the natural logarithm.

Now integrating the eq. (1.27) and using the condition

$$(\vec{P}_{dip})_{t=0} = 0$$

$$\vec{P}_{dip} = (\vec{P}_s)_{dip}\left(1 - e^{-t/\tau}\right) \qquad \ldots 1.28$$

At the alternating field at a time t,

$$(P_s^*)_{dip} = \frac{\epsilon_s - 1}{4\pi} E_t^* - \frac{\epsilon_\infty - 1}{4\pi} E_t^* \qquad \ldots 1.29$$

from eq. (1.27) and eq. (1.29)

$$\frac{d(P_{dip}^*)}{dt} = \frac{1}{\tau}\left[\frac{\epsilon_s - \epsilon_\infty}{4\pi} E_0 e^{j\omega t} - P_{dip}^*\right] \qquad \ldots 1.30$$

the general solution of the above equation is

$$P_{dip}^* = Ce^{-t/\tau} + \frac{1}{4\pi}\frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} E_0 e^{j\omega t} \qquad \ldots 1.31$$

The first term on the right hand side will decrease to an infinitely small value after some time and therefore it may be neglected.

Thus the total polarisation is given by

$$P^* = P^*_\infty + P^*_{dip}$$

or,

$$P^* = \left[\frac{\epsilon_\infty - 1}{4\pi} + \frac{1}{4\pi} \cdot \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau}\right] E_0 e^{j\omega t} \qquad \ldots\ 1.32$$

This formula indicates that P^* is a sinusoidal function of the time with the same frequency of the applied field. Now the dielectric displacement can be calculated from eqn (1.32) and $D^* = \epsilon^* E^*$,

$$D^* = E^* + 4.\pi.P^*$$

or, $$D^* = \left[\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau}\right] E_0 e^{j\omega t} \qquad \ldots\ 1.33$$

Thus the complex dielectric constant ϵ^* is

$$\epsilon^* = \left[\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau}\right] \qquad \ldots\ 1.34$$

or,

$$\epsilon^* = \left[\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2}\left(1 - j\omega\tau\right)\right] \qquad \ldots\ 1.35$$

The real part of the eqn. (1.35) is

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \qquad \ldots\ 1.36$$

and the imaginary part is

$$\epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{1+\omega^2\tau^2} \cdot \omega\tau \qquad \ldots\ 1.37$$

1.3b. Distribution of relaxation time:-

According to the equations (1.36) and (1.37) it is possible to deduce

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{1+\omega^2\tau^2} \qquad \ldots\ 1.38$$

and

$$\frac{\epsilon''}{\epsilon_s - \epsilon_\infty} = \frac{\omega\tau}{1+\omega^2\tau^2} \qquad \ldots\ 1.39$$

By plotting the left hand side of these equations against log $\omega\tau$ symmetrical curves are obtained as shown in Fig. 1.1 and Fig. 1.2 respectively. The maximum value of absorption is reached for log $\omega\tau$ = 0. Thus the angular frequency corresponding to the maximum value of absorption is

$$\omega_m = \frac{1}{\tau} \qquad \ldots 1.40$$

This result can also be obtained from eq.(1.37) by taking $\frac{d\epsilon''}{d\omega} = 0$. The corresponding values ϵ'_{max} and ϵ''_{max} of ϵ' and ϵ'' are obtained by introducing $\omega\tau = 1$ in eq. (1.36) and eq. (1.37).

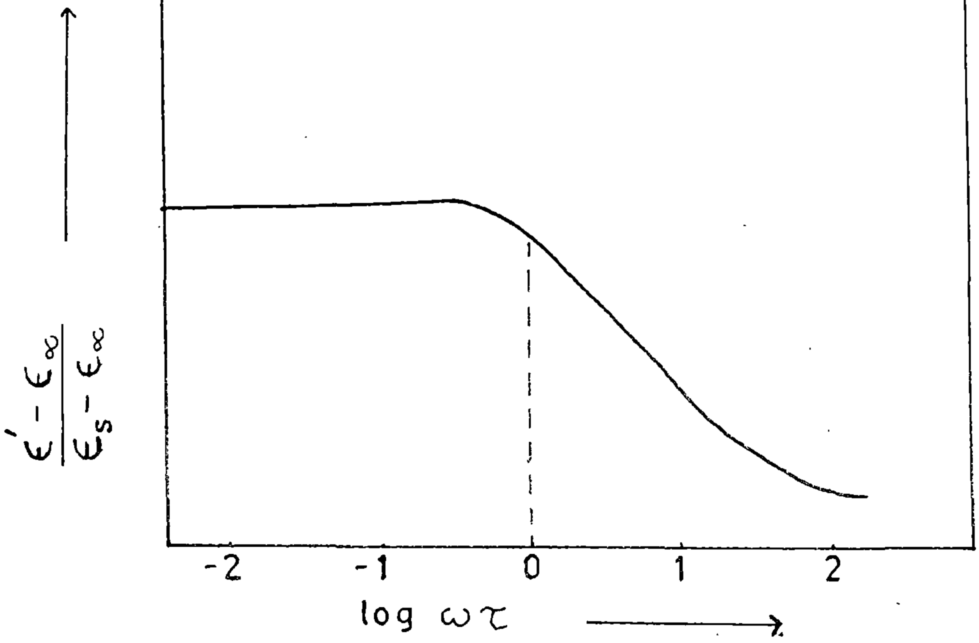

Fig -1.1 Plot of $\frac{\epsilon' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty}$ versus $\log \omega\tau$.

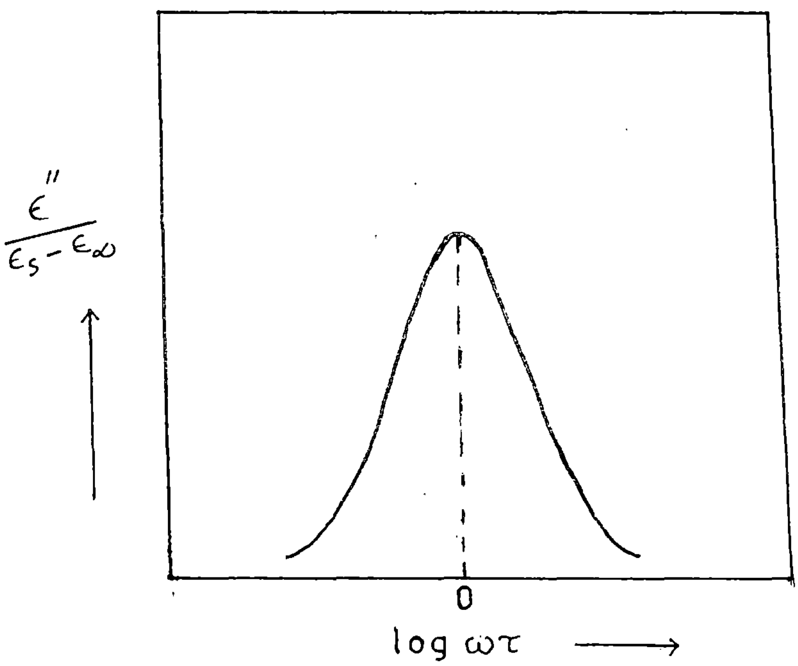

Fig-1.2 Plot of $\frac{\epsilon''}{\epsilon_s - \epsilon_0}$ versus $\log\omega\tau$.

$$\epsilon'_{max} = \frac{\epsilon_s + \epsilon_\infty}{2} \qquad \ldots\ 1.41$$

and

$$\epsilon''_{max} = \frac{\epsilon_s - \epsilon_\infty}{2} \qquad \ldots\ 1.42$$

The cyclic frequency $f = \frac{\omega_m}{2\pi}$ corresponding to the angular frequency $\omega_{max} = \omega_m$ is generally called as critical frequency. The curves of Fig. 1.3 and Fig. 1.4 obtained from eq. (1.36) and eq. (1.37) are generally called Debye curve.

1.3c. Representation of permittivity in the complex plane:-

Debye Semi Circle

The equations for the complex permittivity

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{1+\omega^2\tau^2}, \quad \frac{\epsilon''}{\epsilon_s - \epsilon_\infty} = \frac{\omega\tau}{1+\omega^2\tau^2}$$

are the parametric equation of a circle in the ϵ' and ϵ'' plane, on eliminating the parameter $\omega\tau$ between two equations and rearranging

$$(\epsilon_s - \epsilon'')(\epsilon' - \epsilon_\infty) = \epsilon''^2 \qquad \ldots\ 1.43$$

$$\left(\epsilon' - \frac{\epsilon_s + \epsilon_\infty}{2}\right)^2 + \epsilon''^2 = \left(\frac{\epsilon_s - \epsilon_\infty}{2}\right)^2 \qquad \ldots\ 1.44$$

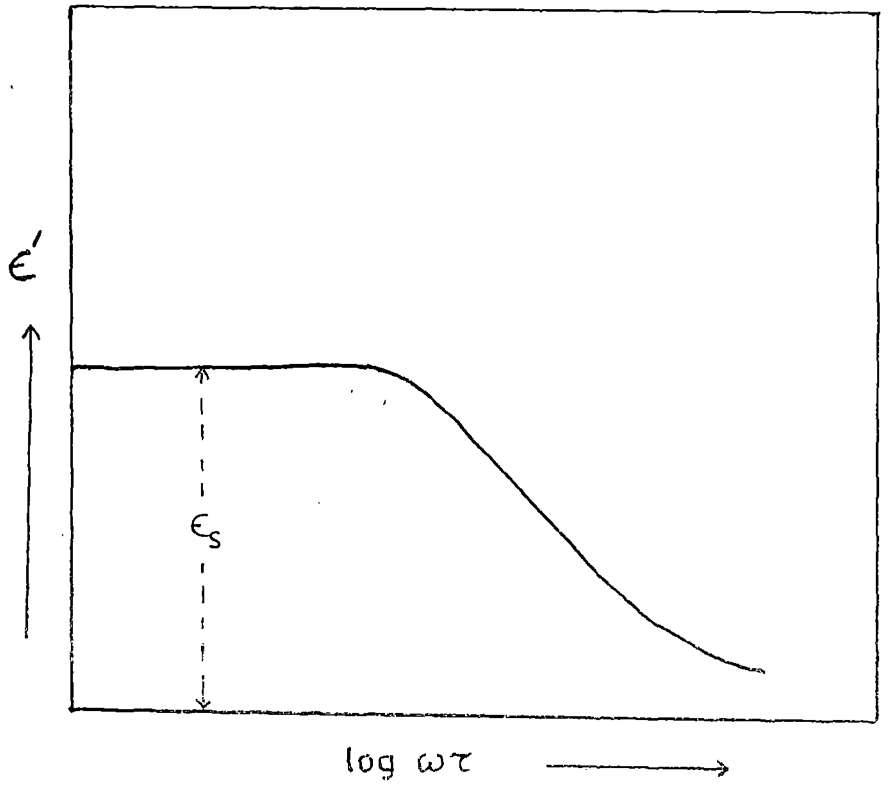

Fig-1.3 Plot of ϵ' versus log $\omega\tau$.

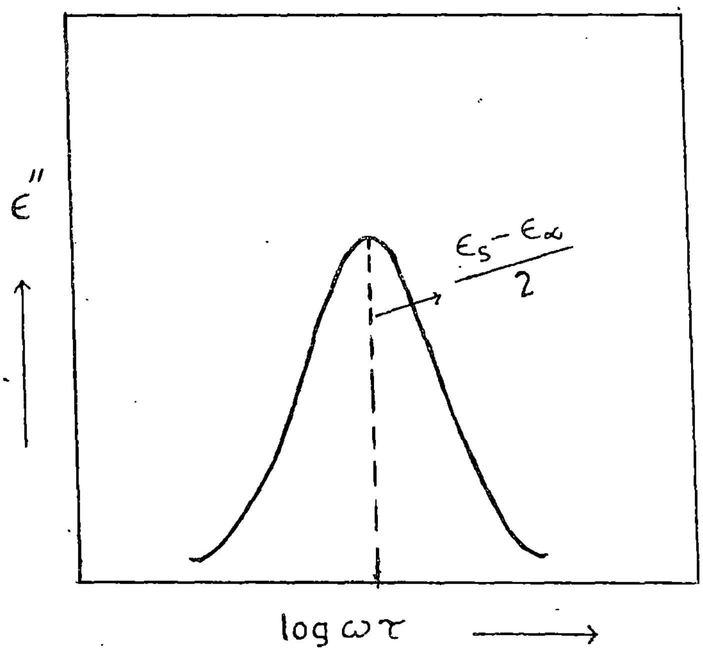

Fig-1.4 Plot of ϵ'' versus $\log\omega\tau$.

which is the equation of a circle whose centre is $\left\{\frac{\epsilon_s + \epsilon_\infty}{2}, 0\right\}$ and radius $\left(\frac{\epsilon_s - \epsilon_\infty}{2}\right)$.

The intersection points with the abscissa are characterised by $\epsilon' = \epsilon_\infty$ and $\epsilon' = \epsilon_s$ respectively. This semi circle is shown in Fig. 1.5. This semi circle is called Debye Semi Circle.

1.3d. Cole-Cole Distribution:-

The arc dispersion function of Cole and Cole has been applied to analysis the experimental dielectric data most frequent because of the attractively simple graphical form by which data of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ can be analysis in its term. Cole and Cole have shown that the Fig. (1.6) Debye semi circle centre of which the arc is a part is depressed below the abscissa axis and the diameter drawn through the ϵ_∞ point makes an angle $\alpha < \frac{\pi}{2}$ with the abscissa axis. The angle α gives the measure of distribution of relaxation time which may vary with temperature but not with frequency. The value α lies between (0 and 1).

The Debye equation is modified by them as

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (j\omega\tau_0)^{1-\alpha}} \quad \ldots 1.45$$

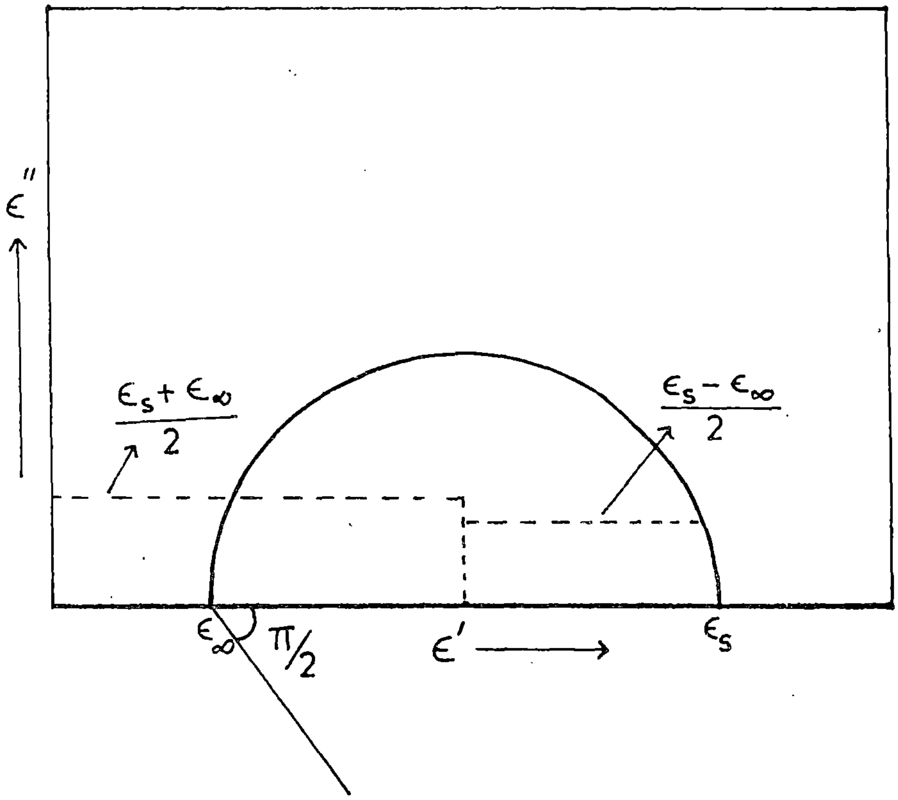

Fig-1.5 Plot of ϵ'' versus ϵ'.

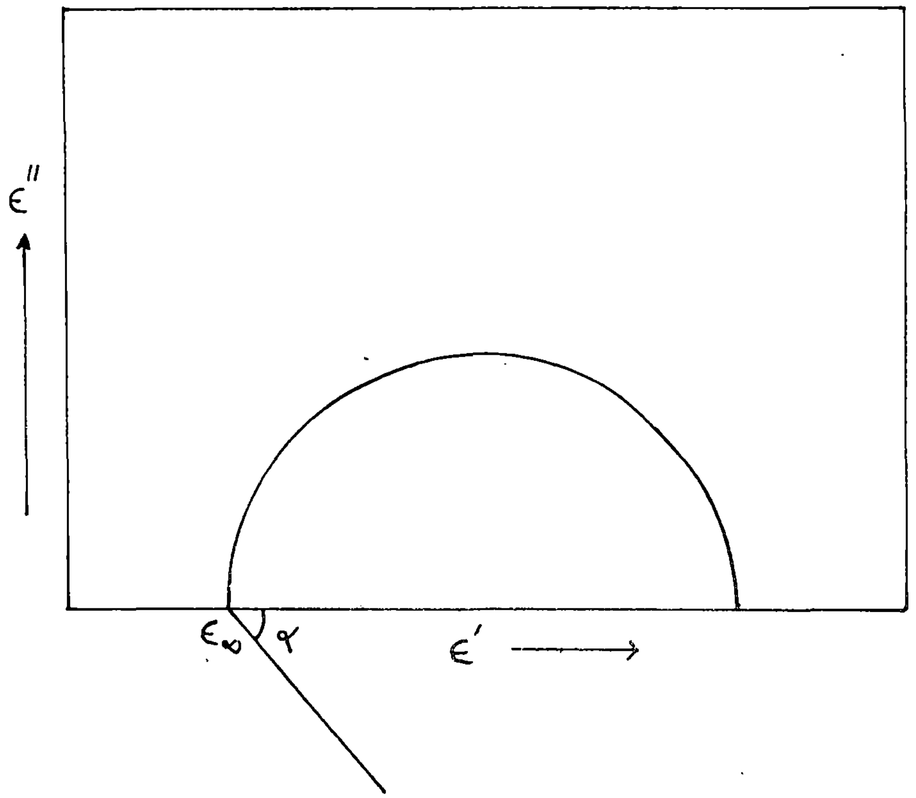

Fig-1.6 Cole-Cole Plot of ϵ'' versus ϵ'.

with the most probable relaxation time τ_0 which can be calculated from the relation

$$\frac{v}{u} = (\omega\tau_0)^{1-\alpha} \qquad \ldots 1.46$$

where v is the distance on the Cole-Cole plot from ϵ_s point to experimental point and u is the distance from the same experimental point to the ϵ_∞ point, if α is zero $\frac{v}{u}$ becomes equal to $\omega\tau_0$ which is the true Debye equation.

1.4. Expression for Dielectric Relaxation in Dilute Solution of Polar Molecules in Nonpolar Solvent:-

The expression for ϵ' and ϵ'' have already been derived and if ϵ' and ϵ'' are determined separately at certain frequency of the applied electric field the relaxation time τ may be determined.

If α_1 be the polarizability of a molecule of the first component (non-polar solvent) and α_2 that of a molecule of the second component (polar solute), and if n_1 and n_2 represent the number of molecules present in 1 c.c. of the solution then

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{\rho} = \frac{4\pi}{3} N f_1 \alpha_1 + \frac{4\pi}{3} N f_2 \alpha_2 \qquad \ldots 1.47$$

and

$$\frac{\epsilon_s-1}{\epsilon_s+2}\cdot\frac{f_1M_1+f_2M_2}{\rho}=\frac{4\pi}{3}Nf_1\alpha_1+\frac{4\pi}{3}Nf_2\alpha_2+\frac{4\pi}{3}Nf_2\frac{\mu^2}{3kT} \qquad \ldots 1.48$$

where ϵ_∞ and ϵ_s are the dielectric constant of the solution for infinite frequency and static field respectively. M_1 and M_2 are the molecular weights of the two components. The density of the solution is denoted by ρ , f_1 and f_2 the mole fractions of the two components are given by

$f_1=\frac{n_1}{n_1+n_2}$, $f_2=\frac{n_2}{n_1+n_2}$ respectively,

from eq. (1.47) and (1.48) we get

$$\epsilon_s-\epsilon_\infty=\frac{4\pi NC\mu^2}{27kT}(\epsilon_\infty+2)(\epsilon_s+2) \qquad \ldots 1.49$$

where C denotes the concentration of the solute molecules in mole/c.c.

Substituting the values of ($\epsilon_s-\epsilon_\infty$) in eq. (1.37) i.e.

$$\epsilon''=\frac{\epsilon_s-\epsilon_\infty}{1+\omega^2\tau^2}\cdot\omega\tau$$

or, $$\epsilon''=\frac{4\pi NC\mu^2(\epsilon_\infty+2)(\epsilon_s+2)}{27kT(1+\omega^2\tau^2)}\cdot\omega\tau$$

or,

$$\epsilon'' = \frac{(\epsilon_\infty+2)}{3}\cdot\frac{(\epsilon_s+2)}{3}\left[\frac{4\pi N C \mu^2}{3}\right]\frac{\omega\tau}{1+\omega^2\tau^2} \qquad \ldots 1.50$$

In case of dilute solution of polar solute in nonpolar solvent it is assume that $\epsilon_s \approx \epsilon_\infty$ and without causing much error ϵ_s and ϵ_∞ each can be taken equal to ϵ'.

Hence,

$$\epsilon'' = \left(\frac{\epsilon'+2}{3}\right)^2 \frac{4\pi N C \mu^2}{3kT}\,\frac{\omega\tau}{(1+\omega^2\tau^2)} \qquad \ldots 1.51$$

It is seen from the above equation (1.51) that for fairly low concentration the value of ϵ'' is linearly dependent on the concentration of polar solute molecules in nonpolar solvent and in the case of infinite dilution i.e. as $C \rightarrow 0$ the value of ϵ' may be replaced by ϵ_s the static dielectric constant of the solvent and eq. (1.51) becomes

$$\epsilon'' = \left(\frac{\epsilon_s+2}{3}\right)^2\cdot\frac{4\pi N C \mu^2}{3kT}\cdot\frac{\omega\tau}{1+\omega^2\tau^2} \qquad \ldots 1.52$$

The eq. (1.52) has been used in the present investigations for determining the value of dipole moment and also relaxation time, whenever possible from experimentally determined value of dielectric loss ϵ'' at different frequencies, temperature and concentrations.

1.5a. Dielectric Loss and High Frequency Conductivity:

The experimental determination of dielectric absorption is a measure of energy dissipation in the medium and in practice most system show energy loss from this process other than dielectric relaxation. Generally these will be small and related to the d.c. conductivity of the medium. Assuming a homogenious medium of conductivity K (ohm^{-1} cm^{-1}) the Joule heating arising from the conductivity contributes a loss factor ϵ_c'' (conductance). So at a particular frequency,

$$\text{Total dielectric loss} = \epsilon''(\text{total}) = \epsilon''(\text{dielectric}) + \epsilon_c''(\text{conductance}) \quad \ldots\ 1.53$$

In an ideal dielectric there would be no free ions conduction but in actual insulating material Joules heat may be developed by the drift of free electrons and free ions in the applied field. Therefore, the total heat developed is the sum of the dielectric loss and Joule heat.

If a potential E is established between the parallel plate condenser whose dielectric material constant ϵ and distance between the plates and surface area are d and A respectively then a charge q per unit area will appear on each plate and a polarisation p will be created in the dielectric. The current flowing in the lead of the condenser is ($A\frac{dq}{dt}$). If it is assumed that conductivity due to free ions may be neglected then the conductivity is

$$K = \frac{1}{E}.\frac{dq}{dt} \qquad \ldots 1.54$$

Since $E = \frac{V}{d} = \frac{D}{\epsilon}$ and $D = 4\pi q = E + 4\pi P$

The eq. (1.54) becomes

$$KE = \frac{dq}{dt} = \frac{1}{4\pi}\frac{dD}{dt} = \frac{\epsilon}{4\pi d}\cdot\frac{dV}{dt}.$$

where all the electrical quantities are expressed in e.s.u.

When the applied potential is alternating then V may be expressed as the real part of $V = V_0 e^{j\omega t}$ where $\omega = 2\pi f$ and the dielectric constant as complex $\epsilon^* = \epsilon' - j\epsilon''$.

Then the total current density in dielectric

$$I = \frac{dq}{dt} = \frac{\epsilon^*}{4\pi d}\frac{dV}{dt} = j\omega\frac{\epsilon^*}{4\pi d}\cdot V_0 e^{j\omega t}$$

$$= j\omega\frac{\epsilon' - j\epsilon''}{4\pi}\cdot\frac{V_0}{d}e^{j\omega t}$$

$$= \left(\frac{j\omega\epsilon' + \omega\epsilon''}{4\pi}\right)\cdot E_0 e^{j\omega t} \qquad \text{where } E_0 = \frac{V_0}{d}$$

$$\therefore \quad I = \left(\frac{\omega\epsilon''}{4\pi} + j\frac{\omega\epsilon'}{4\pi}\right)E_0 e^{j\omega t} \qquad \ldots 1.55$$

The total current density 'I' in the dielectric can be considered as the sum of displacement or capacitive current and conduction current

$$I = I_d + I_{cond} \qquad \ldots 1.56$$

Murphy and Morgan (1939) deduced an expression on total conductivity K which is a complex quantity and is the sum of conductivity due to displacement current (K") and conductivity due to conduction (K')

$$\therefore \quad K = K' + jK'' \qquad \ldots 1.57$$

Now comparing the eq. (1.55) and eq. (1.57), the real part of eq. (1.55) can be considered to

$$K' = \frac{\omega \epsilon''}{4\pi} \qquad \ldots 1.58$$

and the imaginary part $K'' = \frac{\omega \epsilon'}{4\pi}$ ... 1.59

Therefore, $I = \left(K' + jK''\right) E_o e^{j\omega t}$ ... 1.60

For convenience in connection with subsequent account of methods of measurement, the admittance of the condenser may be expressed in terms of an equivalent parallel capacitance C_p and conductance G_p so that

$$\frac{dq}{dt} = \frac{0.9 \times 10^{12}}{A} \left(G_p + j\omega C_p\right) E_o e^{j\omega t} \qquad \ldots 1.61$$

where G_p in mhos, C_p in farads and 0.9×10^{12} is the ratio of the farad to the e.s.u. of capacitance and also of mhos to the e.s.u. of conductance. By using the expression for empty condenser capacitance C_o in farad

$$C_o = \frac{A}{4\pi d \times 0.9 \times 10^{12}} \quad \ldots\ 1.62$$

So we can write,

$$\frac{dq}{dt} = \frac{1}{4\pi C_o}\left(G_p + j\omega C_p\right) E_o e^{j\omega t} \quad \ldots\ 1.63$$

Comparing eq. (1.55) and (1.63) it is possible to get

$$\epsilon' = \frac{C_p}{C_o} \quad \ldots\ 1.64$$

$$\epsilon'' = \frac{G_p}{\omega C_o} \quad \ldots\ 1.65$$

and

$$K' = \frac{G_p}{4\pi C_o} = \frac{\omega \epsilon''}{4\pi} \quad \ldots\ 1.66$$

The K' in ohm^{-1} cm^{-1} can be written as

$$K' = \frac{\epsilon'' \omega}{4\pi \times 0.9 \times 10^{12}} = \frac{f \epsilon''}{1.8 \times 10^{12}} \quad \ldots\ 1.67$$

where f is the frequency of the applied field.

The instantaneous power or heat developed per second, which is the multiplication of current given in eq. (1.55) and voltage given by $E_0 \cos \omega t$ and integrating over half period, the mean power or heat developed

$$\overline{W} \text{ per second} = K' \frac{E_0^2}{2} = \frac{\omega \epsilon''}{4\pi} E_0^2 \text{ ergs/sec} \qquad \ldots 1.68$$

Heat developed per cycle in the dielectric

$$\overline{W} \text{ per cycle} = \frac{\epsilon'' E_0^2}{4} \text{ ergs/sec} \qquad \ldots 1.69$$

Eq. (1.68) and eq. (1.69) shows that K' is proportional to the heat developed per second and ϵ'' is proportional to the heat developed per cycle.

1.5b. High Frequency Conductivity of Dielectric Polar Molecules:-

In $K' = \frac{\omega \epsilon''}{4\pi}$, ϵ'' is substituted from the Debye equation (1.37) i.e.

$$\epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau$$

the high frequency conductivity K' becomes

$$K' = \frac{1}{4\pi} \cdot \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \omega^2 \tau \qquad \ldots 1.70$$

This equation shows that K' does not pass through maximum as ϵ'', but increase with ω, approaching to limiting value K_∞, the infinite frequency conductivity, which is reached when 1 can be neglected in comparison with $\omega^2\tau^2$ that is as $\omega \to \infty$, $\omega^2\tau^2 \gg 1$, so that

$$K_\infty = \frac{\epsilon_s - \epsilon_\infty}{4\pi\tau} \qquad \ldots 1.71$$

1.5c. High Frequency Conductivity of Dilute Solution of Polar Molecules in Non-polar Solvent:-

It is seen in eq. (1.51) that for fairly low concentration the ϵ'' is linearly dependent on the concentration of polar solute molecules in nonpolar solvent

$$\epsilon'' = \left(\frac{\epsilon'+2}{3}\right)^2 \frac{4\pi N C \mu^2}{3kT} \cdot \frac{\omega\tau}{1+\omega^2\tau^2}.$$

But at very low concentration that is at $C \longrightarrow 0$ the ϵ' may be replaced by ϵ_s dielectric constant of the solvent. Then the above equation becomes

$$\epsilon'' = \left(\frac{\epsilon_s+2}{3}\right)^2 \frac{4\pi N C \mu^2}{3kT} \cdot \frac{\omega\tau}{1+\omega^2\tau^2}$$

Substituting this value of ϵ'' in $K' = \frac{\omega\epsilon''}{4\pi}$

The high frequency conductivity of solution becomes

$$K' = \left(\frac{\epsilon_s+2}{3}\right)^2 \cdot \frac{NC\mu^2}{3kT} \cdot \frac{\omega^2\tau}{1+\omega^2\tau^2} \qquad \ldots 1.72$$

This eq. (1.72) has been used in the present investigation for determining the value of relaxation time τ and as well as the dipole moment (μ) of polar molecules.

1.6a. Relaxation Time (τ) and its Relation with Microscopic and Macroscopic Properties:-

In the previous sections the expression for ϵ' and ϵ'' have been given in terms of the relaxation time τ.

In Debye theory the turning couple on dipolar molecule caused by the applied field is opposed by a torque proportional to the angular velocity of the dipole and this constant denoted by ζ is dependent on the surrounding medium. Debye shown that if the dipoles are regarded as spheres of radius 'a' immersed in the medium with internal viscosity coefficient η_{int} the constant ζ is given by the stokes formula

$$\zeta = 8\pi\eta_{int}a^3 \qquad \ldots 1.73$$

and the relaxation time is obtained as

$$\tau = \frac{\zeta}{2kT} \qquad \ldots 1.74$$

combining eq. (1.73) and eq. (1.74) we get

$$\tau = \frac{4\pi a^3}{kT}\eta_{int}$$

Debye assumed that the internal viscosity η_{int} which is a microscopic property is equal to the macroscopic viscosity (η) of the polar liquid and thus the Debye relation can be written as

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad \ldots\ 1.75$$

The above equation (1.75) shows that from the measured value of the relaxation time τ and the coefficient of viscosity η at a certain temperature T the size of the rotating polar molecule may be calculated from the equation

$$a^3 = \frac{\tau kT}{4\pi\eta} \qquad \ldots 1.76$$

where a = radius of the polar polecule. Alternatively if the size of the polar molecule is known from measurements, the determination of the value of the relaxation time τ afford a method of obtaining the value of η_{int} from which information on the structure of the polar medium may be obtained.

1.6b. Modification of Debye's relation:-

Perrin (1934) modified the Debye relation eq.(1.76) which is applicable for the spherically symmetric molecule. Perrin treated the rigid dipolar molecule as an ellipsoid with molecular dipole moment $\vec{\mu}$ having component μ_a μ_b and μ_c along the three principal axes (a, b, c) of the ellipsoid and obtained an expression for the average moment per molecule in which the term $\mu^2/1+j\omega\tau$ of equation

$$P^* = \frac{4\pi N_A}{3}\left[\alpha + \frac{\mu^2}{3kT}\cdot\frac{1}{1+j\omega\tau^*}\right] \quad \ldots 1.77$$

is replaced by

$$\left[\frac{\mu_a^2}{1+j\omega\tau_a} + \frac{\mu_b^2}{1+j\omega\tau_b} + \frac{\mu_c^2}{1+j\omega\tau_c}\right] \quad \ldots 1.78$$

So the eq. (1.77) becomes

$$P^* = \frac{\epsilon^* - 1}{\epsilon^* + 2}\cdot\frac{M}{\rho}$$

Or,

$$P^* = \frac{4\pi}{3}N_A\left[\alpha + \frac{1}{3kT}\left(\frac{\mu_a^2}{1+j\omega\tau_a} + \frac{\mu_b^2}{1+j\omega\tau_b} + \frac{\mu_c^2}{1+j\omega\tau_c}\right)\right] \ldots 1.79$$

where τ_a , τ_b and τ_c are the relaxation times of the dipole moment components along the three axes.

In many cases the rigid polar molecules is approximated by an ellipsoidal shape instead of being a perfect sphere. Moreover, the dipole may be along one of the axes of consideration. In such a case the time of relaxation is given by Fischer as

$$\tau = \frac{4\pi abcf}{kT} \eta_{int} \qquad \ldots \; 1.80$$

where a, b, and c are the semi axes of the ellipsoid and f is a structure factor.

1.7 Radiofrequency Conductivity of Polar Dielectric Liquids and Relaxation Time:-

In an actual dielectric when a radiofrequency field ($E = E_0 e^{j\omega t}$) is applied, the total heat produced is due to the combined effect of dielectric loss and Joule's heating. Thus the radiofrequency conductivity measurement provides an information regarding the displacement current and conduction current in a dielectric liquid.

In reference to the previous theory of the dielectric conductivity eq. (1.58) it is observed that the product of angular frequency and loss factor is equivalent to a dielectric conductivity ($K' = \frac{\omega \epsilon''}{4\pi}$) The dielectric conductivity K' may represent as well an actual ohmic conductivity caused by migrating charge carrier as refer to an energy loss associated with a frequency dependence (dispersion) of ϵ'' , for example, the friction accompanying the orientation of dipoles.

Sen and Ghosh (1974, 1978) put forward a theory on conductivity based on the assumption of existence of free ions in polar dielectric liquids, so that when a radio frequency field is applied in the polar liquid, there is not only the displacement component contributing to the conductivity as assumed by Murphy and Morgan, but the conduction current due to free ions plays a dominant role. Using Murphy and Morgan's eq. (1.58) of conductivity and Debye's dielectric loss equation (1.37) a general equation for conductivity has been obtained,

$$K' = \frac{1}{4\pi} \cdot \frac{(\epsilon_s - \epsilon_\infty)\omega^2\tau}{1 + \omega^2\tau^2} \qquad \ldots 1.81$$

Substituting the relaxation time $\tau = \frac{4\pi\eta a^3}{kT}$ in eq. (1.58) which is in most cases of common dielectric liquids is of the order of 10^{-11} secs. The eqn.(1.37) of the radio frequency conductivity becomes

$$K' = \frac{(\epsilon_s - \epsilon_\infty)}{kT}\omega^2 a^3 \eta \qquad \ldots 1.82$$

Here at radiofrequency stage $\omega^2\tau^2$ considered to be very small i.e. $\omega^2\tau^2 \ll 1$.

Thus it is evident that if measurement of radio-frequency conductivity are made at gradually higher and higher temperature then as ($\epsilon_s - \epsilon_\infty$) and η/T are both decreasing factor of temperature, therefore K' should decrease with the increase of temperature. But the experimental results showed that the radio frequency conductivity increases with the increase of temperature. It is well known that in case of electrolytes where conductivity is mainly due to ions, Walden's rule is valid, which states that the product of equivalent conductance at infinite dilution and the viscosity of the solvent is approximately constant and independent of the nature of dielectric.

A similar relation observed in case of polar dielectric liquids where $K'\eta$ = constant and it follows Walden's rule.

Taking the analogy from the motion of an electron in an ionized gas when the degree of ionization is small and assuming the resistive force as due to viscosity, the equation of motion of the ions is given by

$$M\frac{dv}{dt} = eE_0e^{j\omega t} - 6\pi\eta a v \qquad \ldots 1.83$$

where "a" is the radius of the molecule and η the coefficient of viscosity then

$$v = \frac{eE_0 e^{j\omega t}}{M(\nu + j\omega)} \qquad \ldots 1.84$$

where

$$\nu = \frac{6\pi\eta a}{M}$$

Now,

$$v = \frac{eE_0}{M}\left[\frac{\nu}{\nu^2+\omega^2} - j\frac{\omega}{\nu^2+\omega^2}\right]e^{j\omega t} \qquad \ldots 1.85$$

if n denotes the number of free ions/c.c. and the current $i_c = nev$

Then the conduction current

$$i_c = \frac{ne^2}{M}\left[\frac{\nu}{\nu^2+\omega^2} - j\frac{\omega}{\nu^2+\omega^2}\right]E_0 e^{j\omega t} \qquad \ldots 1.86$$

finding the real part of the conductivity

$$\sigma = \frac{ne^2\nu}{M(\nu^2+\omega^2)}$$

or,

$$\sigma = \frac{ne^2}{M}\cdot\frac{6\pi\eta a/M}{(6\pi\eta a/M)^2+\omega^2} \qquad \ldots 1.87$$

as $a = 10^{-8}$ cm, $\eta = 10^{-3}$ poise and $M = 10^{-28}$ gms.
then $\frac{6\pi\eta a}{M} \gg \omega$.

Thus conductivity due to free ions is

$$\sigma = \frac{ne^2}{6\pi\eta a} \qquad \ldots 1.88$$

Now, the total conductivity is given by K' = dielectric conductivity + ionic conductivity. Thus from eq. (1.70) and eq. (1.88)

$$K' = \left[\frac{(\epsilon_s - \epsilon_\infty)}{4\pi} \cdot \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} + \sigma \right]$$

or,

$$K' = \frac{(\epsilon_s - \epsilon_\infty)}{4\pi} \omega^2 \tau + \left(\frac{n e^2}{6 \pi a} \right) \frac{1}{\eta} \qquad \ldots \; 1.89$$

or, $$K' = A + B/\eta \qquad \ldots \; 1.90$$

This is the fundamental equation for radiofrequency conductivity, where $A = \frac{1}{4\pi} \cdot (\epsilon_s - \epsilon_\infty) \omega^2 \tau$, $B = \frac{n e^2}{6 \pi a}$ and $\omega = 2\pi f$ and considering $\omega^2 \tau^2 << 1$, B is the slope of the curve K' against $1/\eta$ and A is the intercept. From these values dielectric relaxations can be determined.

1.8. Ultra High Frequency Conductivity or Microwave Conductivity of Polar Molecules in Dilute Solution of Nonpolar Solvent:-

At the very dilute solution of the polar solute in nonpolar solvent the percentage of free ions present in solution is negligible. Again at U.H.F. and microwave field there will be no displacement of existing ions present in the dilute solution but only the oscillation can be expected. So the second part of the eq. (1.90) may be omitted. So at infinite dilute solution of polar solute in nonpolar solvent the equation (1.90) becomes,

K' = A' = The U.H.F. or microwave conductivity at infinite dilution,

or,

$$K' = \left(\frac{\epsilon_s + 2}{3}\right)^2 . \frac{NC\mu^2}{3kT} . \frac{\omega^2\tau}{1+\omega^2\tau^2} \qquad \ldots\ 1.91$$

since

$$A' = \left(\frac{\epsilon_s + 2}{3}\right)^2 . \frac{NC\mu^2}{3kT} . \frac{\omega^2\tau}{1+\omega^2\tau^2} \qquad \ldots\ 1.92$$

this eq. (1.91) is same as eq. (1.72).

In our present investigation this eq. (1.91) is used for determining the time of relaxation τ or dipole moment μ of the polar liquids.

1.9. A Brief Review of the Early Works:-

Dielectric Dispersion and Absorption and Some Related Phenomena of Some Organic Polar Dielectric Liquids:-

In the year 1850 Mossotti and in 1879 Clausius established a quantitative relation to reveal the nature of the liquid dielectrics in presence of an external electric field.

Lorentz (1892), Von-Helmholtz (1892) and Drude (1904) independently explained the anamolous dispersion of refractive index of dielectric liquids at optical frequencies. Similar anomalous dispersion of dielectric constant at very high frequency electric field was also modified by Drude in (1904).

Most of the earlier works were centered round the studies of applicability of Debye's equation in determining the molecular radii from the measurement of relaxation times and macroscopic viscosity and the experiments were done mainly on the polar rigid and non rigid molecules in nonpolar solvents.

In general the high frequency absorption in liquid system studies may be classified in two categories:

(a) Solution of polar rigid and non rigid molecules in non polar solvents.

(b) Pure polar liquids.

The first quantitative verification of Debye theory was attempted by Mizushima. He in 1926 carried out the investigation on dielectric dispersion of several alcohols and Ketones in metre wave length region and over a wide range of temperature and observed absorption peak at low temperature. He verified Debye theory in the case of alcohol by calculating molecular radii and found them to be almost of the right order with glycerine as an exception having too small a value for molecular radius.

J.D. Stranathan (1928) studied the dielectric behaviour of dilute solution of several alcohols in benzene solution. He found that the zero concentration (molecular volume Vs concentration curve at different temperatures) intercepts for methyl, ethyl, propyl and amyl alcohol lead to the values of electric moment of molecules which are essentially independent of temperatures thus is in agreement with Debye theory, it is contrast to the behaviour of the pure liquid alcohols.

Debye himself (1929) successfully explained the anamolous dispersion observed by Drude (1904) and postulated that the characteristic property of the liquid responsible for anamolous dispersion at radiofrequency range is the polarity of their molecules.

Fischer (1939) measured the relaxation times of a number of liquid compounds in dilute solutions and in pure liquid and found for the alephatic chain molecules (Ketones, monohalogenides, alcohols) the relative time increases in sequence alcohol, ketones, halogenides. The absolute values of relaxation times can be evaluated by introducing molecular viscosity which is smaller than macroscopic viscosity. The result show for acetone, nitrobenzene and monochlorobenzene in undiluted state in agreement with Debye theory of quasicrystalline structure of liquids, but the general theory does not explains the behaviour of alcohol with their strong interaction of (- OH) groups.

Spengler (1941) showed relaxation time as a function of concentration with two liquids C_6H_5NO and C_6H_5Cl. He pointed out that according to Debye's law, relaxation time (τ) varied with viscosity (η) holds for dilute solution where Brownian movement is a major factor in the arrangement of the dipole, with high concentration the mutual action between the dipoles is more important and the ratio (τ / η) the reduced relaxation time decreases.

Jackson and Powels (1946) determined the value of relaxation time in benzene and in paraffin solution and observed that the values only increased by 4 - 7 fold for an increase in viscosity of eight fold.

Curties (1952) and Smyth (1954) observed that although the viscosity of the liquid was same, value of relaxation time was different in solutions and in liquid state.

Müller (1956) observed that molecular radii calculated by using Debye equation for few molecules from experimental values of critical wavelength and critical frequency were too low compared with values obtained from other method. He further observed that the molecular radii becomes still lower with the increase of viscosity of the medium.

Sinha et al (1966) studied the influence of viscosity on relaxation time and concluded that the macroscopic viscosity did not correctly represent the internal viscosity of the liquid.

Mehrotra (1972) determined the relaxation time τ and mutual viscosity η_{12} of seven substituted benzene p-toludine, O-nitroaniline etc. in the microwave region at various temperatures and concluded that the mutual viscosity is a better representation of the resistance of the rotation of the individual solute molecules.

P.C.Gupta (1978) measured the dielectric loss (ϵ'') and dielectric permittivity in dilute solution of benzene in 3 cm. microwave region of benzoylacetone, p-fluoro, p-chloro, p-bromo and p-methyl benzoylacetones at 40°C and calculated the relaxation times, the dipole moments, the free energies of activation for dielectric relaxation and viscous flow.

Dielectric Dispersion and Absorption of Non-rigid Molecule in Nonpolar Solvents:-

Fischer and Frank (1939) using thermal method of measuring dielectric loss at 4.3 meter wavelength obtained relative values of relaxation times of some aromatic halides. The shorter relaxation times in larger molecules were explained by them as being associated with orientation of CH_2X group rotation around their bond ring.

F.R. Goss (1940) analysed the dielectric polarization of certain binary mixtures of polar with nonpolar liquids and showed that the solvent effect can be resolved into contributions depending on the anisotropy of the electric fields which varies with the shape of the non spherical molecules and on induction effect related to the dielectric constant of the liquids and arising both from the reaction field and from permanent dipoles.

Schallamarch (1946) experimentally showed that dielectric relaxation time and viscosity of a number of long chain liquids are not generally equal, in contradiction to the behaviour of liquids of low molecular weights.

Gopala Krishna (1957) gave a method for determining the dipole moment and relaxation time of polar substances in nonpolar solvents at microwave range of frequency. The special advantage of his method is that it need not required the density and concentration of solution for determining the relaxation time.

Since after the development of Budo's theory the molecular and intermolecular rotations have been observed in large number of molecules like $-OCH_3$, $-NH_2$, $-CH_2Cl$, $-CH_2Br$, $-CH_2CN$, $-OH$ by Fong and Smyth (1963).

Jaiprakash (1969) developed a method based on Frolich's equation for calculating the relaxation time of spherical polar molecule in nonpolar solvent. The calculated relaxation time of five molecules were comparable with those calculated from Gopala Krishna's method.

Tay and Gossley (1972) analysed bromoalkanes and Ketones, interms of rotation of molecules as a whole but in amines the $-NH_2$ group rotation has been attributed to be responsible for dielectric relaxation.

Arrawatia et al (1977) determined the dielectric permitivity ϵ' and dielectric loss ϵ'' of O-Chlorobenzene, 4-chloro-3-nitrobenzotrifluoride and 4-chloro-3-nitrotoluene at 35°C in dilute solution of benzene and carbon tetrachloride in microwave region. The relaxation time (τ), the distribution parameter (α) and the dipole moment (μ) have been evaluated from the measured dielectric data.

Gupta et al (1978) studied the dielectric absorption of some simple liquids viz. fluorobenzene, O-dichlorobenzene and O-chlorotoluene and their binary mixtures in dilute benzene solutions at the 3 cm. microwave region over the temperature range 20°C - 60°C and determined the relaxation time and the thermodynamic parameters viz. free energy, enthalpy and entropy of activation.

The results obtained are explained on the basis of polarity, size of the molecules and the change in the molecular environment. Wassink and Bordeijk (1978) determined the dielectric relaxation times for mixtures of N-methylformide, N-ethyl acetamide in carbontetrachloride by time domain reflectometry.

Sharma et al (1985) used a standard microwave X-band technique and Gopala-Krishna's single frequency concentrational variational method determined the dielectric relaxation times (τ) of the dilute solutions of N,N-dimethyl formamide (DMF), methanol and several DMF + MeOH mixtures in benzene at different temperatures and also calculated the thermodynamical parameters.

Agarwal (1986) measured the dielectric constant (ϵ') and dielectric loss (ϵ'') of four different compounds of different shapes viz. n-butyl chloride (linear) chlorobenzene and bromobenzene (planer) and tert-butyl chloride (nearly spherical) in benzene solution at $32^{\circ}C$ and 9.96 GHz and observed that for nearly the same molar volume of the solute molecule the relaxation time (τ) is affected by molecular shape in the following manner

$$\tau_{\text{linear}} > \tau_{\text{planner}} > \tau_{\text{spherical}}.$$

Madan (1987) studied the dielectric absorption of thiophone, acetone, benzophenon and their mixtures in dilute solutions in the microwave region over a wide range of temperatures and developed a relation for calculating the relaxation times and thermodynamic parameters. The values agrees with the given data.

Pure Liquids:-

The earlier studies of molecular shape and dielectric relaxation have been reviewed comprehensively by Smyth. According to simple dielectric theory the dielectric constant of the polar liquids should be directly derivable from their chemical structures. But Morgan and Yger (1940) observed these values greatly different. They explain the depertures may be due to association or interaction causing the molecules to act as anassociated pairs in which the electric moment is low because the dipoles are so directed (a) to oppose one another or (b) the effect of internal friction or viscosity is restricting the motion of the molecules. Whiffen and Thomson (1946) from dielectric measurement obtained (τ) value for toluene, O-xylene, p-cyanine etc. in pure liquid state, which are in according to the size of the molecules.

Hiafelin (1946) determined permittivity of isobutyl alcohol in pure and in viscous solvents. Strong and weak solution in benzene behaved in accordance with

Debye theory but the medium solution behaved differently from the simple theory.

Petro and Smyth (1948) observed the same effect as observed by Whiffen and Thomson in (1946), Garner (1948) showed that simple Debye theory does not hold for many insoluting liquids such as glycerine, phenolic resines and suggested an equation

$$\frac{1}{\epsilon''} = B\left(x^n + \frac{1}{x^n}\right) \qquad \ldots 1.93$$

when $0 < n < 1$ represents dielectric behaviour more correctly the loss factor ϵ'' and $x = \omega\tau$ where τ = relaxation time.

From dielectric loss measurement of some rigid molecules of monosubstituted benzene in liquid state, Poley (1955) obtained the relaxation times which increases with the molecular sizes.

Müller and Smyth (1956) examined the direction of dipole moment with respect to the molecular plane on the relaxation behaviour of the molecules of different shapes and size in liquid state and showed that though the molecules 2, 4, 6 trimethyl pyridine and 2, 4, 6-trimethyl 1,3,5-trioxane are of equal size, dipole moment and viscosity in the liquid state, the two molecules have quite different (τ) values, because of the direction of the dipole moment were parallel and perpendicular respectively to the spheroidal molecular plane.

Petro and Smyth (1957) from the investigation in substituted benzene and pyridine in the liquid state observed a regular increase in the (τ) values with the increase in the size of the substituents.

Higasi et al (1960) reanalysed the experimental data of n-alkyl bromide in liquid state in terms of distribution betwene two limits given by Frolich (1949). The (τ) values in lower limit was associated with the relaxation time of internal rotation of $-CH_2Br$ group, while the upper limit to the orientation of the whole molecule.

Relaxation time (τ) and viscosity (η) has been experimentally determined by Bhanumati (1963) at different temperatures for a few liquids, such as α - chloronapthalenes, butyl-phthalene and iso-anylphthalene etc. The values of potential barrier heights for dipole relaxation (ΔH_τ) and that for viscous flow (ΔH_η) were evaluated from the linear plots of log (τT) versus ($\frac{1}{T}$) and log (η) versus ($\frac{1}{T}$) respectively. The calculated values of (ΔH_η) were found to be greater than (ΔH_τ) as the phenomenon of viscous flow considered the process of translation as well as rotation but only rotational process was considered in dipole relaxation .

Krishnaji and Manshingh (1964) reported that the dielectric relaxation of alkyl cyanides and of alkylthiols in liquid state. The relaxation time was in the order of increasing size of the molecules in former case and more than two relaxation behaviour in the latter case was found.

Bhattacharyya et al (1966) reported in polar liquids with rigid dipoles having moment (μ = 1.5 D or less), the effect of dipole interaction was negligible.

Sinha, Roy and Kastha (1967) showed in 7 mm microwave region the temperature dependence of relaxation time of a number of polar molecules of different shape, size and dipole moments in very dilute solution of non-polar solvents. The dependence of (τ) at any temperature (T) on viscosity (η) of the solution is represented by τT = (constant) η^{γ}, where γ is the ratio of the heats of activation for dielectric relaxation and viscous flow.

Garg and Smyth (1973) reanalysed the dielectric data of anisole and aniline in liquid state. They obtained values for methoxy group rotation as 3.2 p. sec. and its weight fraction as 0.2 while these values in dilute solution are about 8 to 0.8 respectively.

Molecular Association of Associated and Associato-Associated Polar Liquids:

Molecular association may be expected to influence dielectric relaxation by modifying the structure of the liquid. The investigation of dielectric relaxation in this connection continued actively in recent years.

Mecke and Reuter (1949) made precision measurements of permittivity on various solution of CH_3OH, C_2H_5OH, nC_4H_6OH, $nC_8H_{17}OH$, C_6H_5OH, $PC_6H_4(ON)CH_3$ in C_6H_6, CCl_4 and cyclohexane at 20°C and 40°C. They computed the molecular association and found for alcohols and phenols dipole moment is reduced by association and the binding moment of oil group is usually not much more than half the value of the free unassociated molecules.

Kremmling (1950) made absorption measurements on aliphatic chloride and alcohols. He found difficult to sort out the effects due to polar association, H-bond formation, change of molecular shape, internal rotation, multiple relaxation times etc.

Brot (1956) made a conclusions from his measurements on straight chain alcohols $CH_3(CH_2)_nOH$ with n = 5-9 and 11. In second dispersion region the principle of superposition of relaxation time did not hold good. A third dispersion region near λ = 1 cm was assigned to the reorientation of the dipoles in the interior of the polymeric species.

Schellman (1957) developed equations which take into account the association in liquids on dielectric saturation. Srivastava and Varshni (1957) also suggested an equation for variation of dielectric constant of mixture of polar liquids (associated-associated) with concentration C and temperature $T^{o}K$

$$\epsilon = \left(l + \frac{m}{T}\right) + \left(p + \frac{q}{T^{1/2}}\right) \times C + Z C^{2} \qquad \ldots 1.94$$

where p, q, l, m and z are constants, variation of ϵ with C is linear, the equation has been illustrated for water methyl alcohol and water butyl alcohol mixtures with satisfactory results.

Conway (1959) examined theory of absolute reaction rate for the case of relaxation in associated polar liquids and showed the mechanism of absolute reaction rate to be consistent with other theoretically derived quantities and with mechanism of proton mobility in water. Muralidhara, Rao (1959) studied the dielectric loss and dielectric constant of two liquid mixtures n-butyl alcohol + glycerol (both associated) and Isobutyl alcohol + n propyl bromide (asso-non-associated). Two picks were observed in both the cases in ϵ'' - frequency and ϵ'' - temperature curves. Schallamarch's (1946) suggestion was that the process of dielectric relaxation cannot be directly connected with individual molecules but is an disturbance over an appreciable region in the liquid does not appear to be valid in the said mixture.

Mc.Duffie Jr. and Litovitz (1962) studied the dielectric properties of the associated liquids such as butanediol, 1, 3, 2-methyl pentanediol 2,4,glycerol and hexanetriol, 1,2,6 over the temperature range - 20°C to + 10°C and over a frequency range of 0.01 to 1200 MHz. Dielectric relaxation times and their distributions have been determined and observed that (a) all four liquids exibit an assymetric distribution of relaxation times of the Davidson and Cole form, (b) with the exception of hexanetriol 1,2,6, the distribution of relaxation times becomes narrower with increasing temperatures. They concluded that the dielectric orientation is closely related to the structural breakup of the group and the structural break up is a co-operative process. They explained the temperature dependence on the width of the distribution may be due to decrease of group size with increase of temperature and as the groups become smaller, the structural decay process becomes more exponential. McDuffie Jr, Quinn and Litovitz (1962) measured the dielectric relaxation time in MHz region and at low temperature for glycerol water mixture. The mixtures ranging from relatively pure glycerol to equal molar concentration of glycerol and water. From the data a single distribution of relaxation times was infered for these mixtures rather than two individual distributions. They explained their experimental findings in terms of the group concept of Schallamach in which it was assumed that in a mixtures of associated-associated liquids, such as glycerol and water dielectric orientation occurs through co-operative effect in groups of molecules and these groups containing molecules of both kinds.

Dielectric measurements of Garg and Smyth (1965) on the normal alcohol form propyl to dodecyl in pure liquid state have shown three distinct dispersion regions as was previously reported by other workers. The relaxation times for 1st, 2nd, and 3rd. were 1 to 2.2 x 10^{-10} secs. 1.7 to 5 x 10^{-11} and 1.7 to 4 x 10^{-12} secs. respectively. The long relaxation times are associated with polymeric clusters resulting from the strong hydrogen bonding between (-OH) group shortest relaxation times was ascribed to the orientation of the (-OH) group and the intermediate relaxation time was attributed to the rotation of the free alcohol molecules.

Barbenza (1968) reported the dielectric property of methyl alcohol (pure) in temperature range 5° to 55°C and at wave length from 15 to 5 cm. Can be represented by a single relaxation time. The strong temperature dependence of extrapolated values of ϵ_{∞} leads to a second dispersion region. Moreover, the measurement show that the main dispersion can be described as a rate process with an activation energy of 3.4 K Cal/mol.

Rizk, I. Elanwar (1970) measured the frequency dependence of complex dielectric constant of glycerol-Iso propyl alcohol and glycerol-Isobutyl alcohol within the frequency band 10^5 to 10^7 c/s and the range of temperature -19 to + 50°C for entire concentration range. It is found for each mixture there is one main relaxation process. The average relaxation time in each system is found to vary exponentially with the molecular concentration of glycerol. The increase of glycerol content in each system is accompanied by a linear increase of the activation enthalpy and entropy change for dielectric relaxation. It is suggested that the dielectric relaxation in these mixtures occurs through a co-operative effect in groups containing molecules of both kinds and that the interaction between these molecules are stronger in glycerol-isobutyl alcohol system than in glycerol iso-propyl alcohol system.

Purohit and Sharma (1971) determined the dielectric constant (ϵ') and dielectric loss (ϵ'') of methanol, ethanol, 2-propanol, 3-methyl-1-butanol and 1-butanol in benzene solution for concentration varying from 0.004 to 0.08 weight fraction in the X-band. They found in all cases except 1-butanol, the tan δ - concentration curve shows a marked increase in the concentration range 0.03 - 0.04 mol. fraction and this behaviour has been explained as due to the formation of dimers by association and due to solute-solvent interaction.

Sen and Ghosh (1972) and Ghosh and Sen (1980) calculated the dielectric relaxation time of some normal primary alcohols in nonpolar solvents from radiofrequency conductivity measurements. They observed that the rate of breakup of the cluster of molecules is affected with dilution in different nonpolar solvents.

Van-Gemert and Deloor (1973) investigated dielectric relaxation and activation energies of some normal alcohols in nonpolar solvents. The relaxation time for alcohol benzene mixtures are found in all cases smaller than those observed for other solvents, the energy of activation in different solvents do not differ significantly, but are constantly higher than for the pure alcohols.

Rajyan, Ramasastry and Murthy (1977) studied dielectric dispersion of two pure liquids glycerol and diethylene glycol at radiofrequency, Uhf and microwave region at 80°C and confirmed the Cole Davidson type dispersion.

Mulecki and Balamicka (1980) studied the self association of t-butyl alcohol and developed a method for a simultaneous determination of three independent values of free energy of self association from experimental datas.

Prakash and Rai (1986) determined dielectric constant (ϵ'_{12}) and dielectric loss (ϵ''_{12}) at different concentration of five mixture of aniline and nitrobenzene mixture I (25% nitrobenzene and 75% aniline), mixture II (50% nitrobensene + 50% aniline) and mixture III (75% nitrobenzene + 25% aniline) and also of pure nitrobenzene using benzene as a nonpolar solvent at different temperatures and frequencies. ϵ'_{12} and ϵ''_{12} found to increase linearly with the addition of nitrobenzene in the aniline - nitrobenzene mixture except for mixture III. Similar deviation have also been recorded in relaxation times and thermodynamic parameters. These deviations may be attributed either to the existance of interassociation or to the complex formation in the last mixture (III).

Electrical Conductivity of Dielectric Liquids in D.C. And High Frequency Electric Fields:-

Quincke (1895) first showed that the current through the liquid depends upon voltage, gap width and nature of the liquid and concluded that the current is non-ohmic and probably electrolytic in origin.

Curie (1902) observed that the electrical conductivity of petroleum ether, carbon tetrachloride carbondisulphide and benzene was increased by exposure to gamma rays or X-rays.

Schweilder (1907) showed experimentally that the conductivity of saturated hydrocarbons decreased with increased purification.

Jaffe (1906) studied the current voltage characteristic of hexane when irradiated by gamma-ray and considered that the current as the sum of the two separate currents, one rising to a saturation value like the current in the gas, while the second is the ohmic current. In 1909 he succeded in measuring the small current developed when a voltage was impressed on highly purified hexane in a brass conductivity cell. His result shows that in pure state the conductivity of hexane was due to cosmic radiation and near about 146 ions were produced per c.c. per sec. similar result was obtained for heptane and petroleum ether, but Jaffe (1913) discarded this view of separate currents, in favour of a theory according to which the ions are produced in very densely packed column isolated from each other. The columns are the tracks of the photoelectrons reacted by γ -rays and he concluded that the field of less than 100 V/cm, a large part of the current is caused by external ionising radiation.

Nikuradse (1932) studied the current in liquid dielectrics over the wide range of field strength and gap width. He observed that current depends on the purification of the liquid, electrode geometry and electrode material, but independent of pressure but when all the ionizing agents such as X-rays and other radio active sources were removed there still exists a residual or natural conductivity in these liquids. The residual conductivity of a supposedly pure insoluting liquid has been reduced by a factor of a thousand or more by treating it in such a way as to remove traces of water. When a reasonable low limiting value of conductivity has been reached, the next problem is to find out, how it originates. However, there is no general agreement as to its characteristics.

Baker and Boltz (1937) and Dronte (1940) interpreted their investigation to mean that the conductivity is due to thermoionic emission from the cathode combined with Schottky effect. Lepage and Dubridge (1940) observed that log (I) is a linear function of (E) and later concluded that the current is due to field enhanced thermoionic emission and derived the following relation

$$J = AT^2 \exp\left[-\frac{\phi e}{kT} + \frac{1}{2.3RT}\left(\frac{e^3 E}{K'}\right)^{1/2}\right] \qquad \ldots\ 1.95$$

where K' is the dielectric constant of the liquid.

Plumley (1941) and Pao (1943) interpreted with experimental supports that the potential dissociation theory originally proposed by Onsager (1934) for very weak electrolytes. According to their view there are even in purest hydrocarbon such as hexane, a very small number of ions exist resulting from the sponteneous dissociation of molecules.

Ruhle (1943) developed the idea of induced conduction and Eck (1949) showed that the variation of current strength with time can be represented by the equation

$$\left(I - I_{\infty}\right) = \left(I_0 - I_{\infty}\right) e^{-kT} \qquad \ldots 1.96$$

where I_0 is the initial current, I_{∞} is the limiting current and K is the constant which contains the ionic mobilities. The effect is assumed to be due to initial existence of the ionic clusters in the body of the liquid which gradually disperse. He performed experiments on acetone, nitrobenzene and acetone substituted compounds.

Goodwin and Mac-Fadyen (1953) showed that the current is a function of electrode gap width and field strength. Extrapolation to zero gap width showed the existence of a zero width current that obey a field emission relation of the form

$$J = \left[A E^2 \exp\left(-b/E\right)\right] \qquad \ldots 1.97$$

Jaffe and LeMay (1953) studied time dependent current in hexane for wide gap and voltage of low value and concluded that the current are ionic. The breakdown in dielectric liquid gives additional information concerning the conduction current in dielectric liquid.

Green (1955) has studied the conduction and breakdown in hexane and assumed that positive ions are always present in the liquid, because of external radiation or dissociation of impurity molecules. When an external field is applied, these ions drift towards the cathode but the cathode surface layer impedes their immediate neutralization. The ions then set up a local field across the surface layer that tend to produce electron emission. The size of the local field depends upon the magnitude of the ionic current and the probability of neutralisation of the ions.

Standthammer and Sayer (1957) have obtained evidence for the formation of pure ions in cyclohexane and cyclohexane saturated with water.

Riehl (1955) and Keepler (1960) observed that the level of conduction of some polynuclear aromatic compounds, such as napthalene and anthracene increases by a factor 10^3 to 10^6 on melting. It has been suggested that the higher conduction in molten form is due to higher mobility of the charge carrier.

Hart and Mungali (1957) observed that the conduction current in chlorobenzene continued to decrease even after continuous distillation for as long as three months.

Le Blance (1959) suggest that electrons exist in n-hexane in quasi trapped state.

Forster (1962) studied the nature of conduction in pure hexane and benzene and also at different concentrations of n-hexane-benzene mixture and obtained a relation $\sigma_S = \sigma_H \cdot e^{CK}$ where σ_H is the conduction of n-hexane, K is the constant and C is the concentration. He further suggested that the transformation of electron from one benzene molecule to another is a function of the number of molecules located between the electrodes and assumed that only electron migration rather than electron diffusion is valid in the conduction process. The increase of conduction due to increase of temperature of the liquid would be the result of enhanced transfer probabilities resulting from an increase of molecular collision leading to electron transfer.

Forster (1964) again showed that conduction in alephatic hydrocarbons is most probably related to the presence of polar impurities or trapped electron present in the liquid or generated at the electrode surface. In unsaturated hydrocarbons experimental evidence suggested the existance of electronic conduction. He suggested an empirical relation for the activation energy of quasitrapped mechanism $\epsilon_a = 0.067\ P$ eV, where P is the number of peripherial π electrons and thus confirmed the electronic nature of the conduction current.

Silver (1965) has developed a theoretical model for conduction of current in insulating liquids which shows that it is possible to calculate from the measurement of potential distribution, the rate of formation and motion of charges. One consequence of his theory is that the conductivity is a function of electrode spacing and the form

$$V = \left(AJ^2 + BJL\right) \qquad \ldots\ 1.98$$

where A and B are constants, V is the applied voltage, J is the current density and L is the gap length. This theory explained successfully the variation of conductivity with electrode spacing at various constant voltage in benzene, but the result in nitrobenzene suggested that the cathode acts as an injector of electrons.

Felsenthan and Vonne Gut (1957) concluded that the enhancement of conductivity in insulating liquid may be due to the presence of depressed conducting particles in the insulating liquids.

Adamczewski and Jachym jointly (1968) investigated the electrical conductivity on number of saturated hydrocarbons which are characterised by the conductivities of two order of magnitude lower than those of other liquids and concluded that the natural conductivity values of organic liquids is a function of temperatures. They further observed that among all the investigated organic compound which occurs in liquid state the lowest conductivity values are found in nonpolar liquids.

Adamczewski (1969) measured the ionic mobilities in hexanes, heptanes and nonane, and other mixtures. He observed that mobility value in all cases lies between 7.2×10^{-5} to 5.8×10^{-4} $cm^2V^{-1}sec^{-1}$.

Gaspard and Gosse (1970) gave a clear evidence of ionic conduction in polar dielectric. They used membranes electrodes and gave evidence for three distinct regions of conduction and in each case the conduction is ionic in nature. It is due to the impurities at low and medium fields and injections of ions at high fields. They observed considerable erratic variation of current with time under electric field.

Lohneysen and Nagerl (1971) determined the mobility of polar liquids by temporal variation of current method and concluded that the existance of natural charge carriers in liquids are of two kinds having mobilities μ_1^+ and μ_2^-.

Nicolan, Secareanu and Moisescu (1971) studied the electrical conductance of n-butyl and amyl alcohol in the temperature range of 0-97°C. The variation of conductance with temperature for those alephatic alcohols was explained in the light of intermolecular hydrogen bonding and concluded that intermolecular hydrogen bonding plays an important role in the mechanism of electrical conduction.

Sen and Ghosh (1974) and Ghosh and Sen (1980) determined the r.f. conductivity of some polar associating and non-associating dielectric liquids in the solution of different non-polar solvents and temperatures and calculated the free ion density, ionic mobility and energy of activation for conductivity.

Ghosh, S.K., Ghosh A.K., and Acharyya S. (1980) established a relation for calculating the h.f. conductivity of polar liquids in infinitely dilute nonpolar solvents at microwave region and showed that the h.f. conductivity varies linearly with concentration.

Ghosh and Choudhury (1982) measured the r.f. conductivity of pure glycerol and glycerol water mixture at 1 MHz frequency and at various concentrations over the temperature range of 20° to 50°C and calculated the ionic mobility and the average ion number density. They observed a marked decrease in electrical resistance with the addition of water as impurity and thus confirmed that the impurity conduction prevails in pure polar liquid and the conduction of glycerol water mixture is an exponential function of concentration.

Critical Point Phenomena in Electric Resistivity of Binary Liquid Systems:

The phenomena of critical opalescence was first observed by Andrews (1869) in connection with his classical investigation of carbon-dioxide isothermal. After that many investigators came forward to unveil the different properties such as scattering, change of dielectric constant, viscosity, ultrasonic absorption and electrical resistance or conductivity of critical opalescent binary liquid mixture at and very near to critical temperature.

Friedlander (1901) probably the first worker to report on the study of transport phenomena for a binary liquid mixture near the critical point and showed qualitatively that the electrical conductivity is less sensative to critical behaviour than the viscosity in isobutyric acid-water mixture.

Gammel and Angell (1972) studied the temperature dependence of the resistivity for the system isobutyric acid + water but could not detect any influence due to critical fluctuations. Stein and Allen (1972) established the existance of a strong divergence in the temperature derivative of the resistivity for the same binary liquid mixture very close to critical temperature T_c.

Again Stein and Allen (1973) measured the electrical resistance of sealed solutions of isobutyric acid water at the critical composition in the reduced temperature range $3.3 \times 10^{-7} \leq \epsilon \leq 6.6 \times 10^{-2}$, using a Jones a.c. bridge and lock the amplifier. The temperature derivative of the resistance exhibits a strong divergense very close to T_c.

Further, Gammell and Angell (1974) measured the electrical conductivity of the same system for several concentration and also at critical concentration. Measurement were made using a hybrid conductance/viscosity cell a modified ubbelhode viscometer which permitted almost simultaneous measurements of viscosity and conductance. The results of their measurement indicated that, the electrical conductivity does not exhibit any critical anomaly down to $T_c + 0.03^{\circ}C$ even which it is well into the region (T_c to $T_c + 2^{\circ}c$), when the viscosity anomaly becomes apparent.

Jasnow, Goldburg and Samura (1974) analysed the data of Stein and Allen and showed that the data below a value of $\epsilon = \frac{T - T_c}{T_c} = 5 \times 10^{-5}$ may be influenced by gravitational effects which has been not accounted for the original analysis. They suggested a fit equation of the form $\frac{R_c - R}{R_c} \approx At^{1-\alpha} + Bt$ (where α is the specific heat exponent), when the temperature range is above the value $\epsilon = 5 \times 10^{-5}$.

Shaw and Goldburg (1976) measured the electrical conductivity of several binary liquid systems such as pure phenol-water, Kcl doped phenol water and isobutyric acid-water near their critical point. All the measurements were made within the reduced temperature range $10^{-5} \leqslant \epsilon \leqslant 10^{-2}$ and all the systems showed clearly the existance of a singular contribution to the conductivity. A least squares fit of the data for the equation $\left(\frac{\sigma - \sigma_c}{\sigma_c}\right) \propto \epsilon^{\theta} + \sigma_{bkg}$ showed that the singularity could be characterised by a critical exponent $\theta = 0.70^{+0.15}_{-0.10}$ Critical point phenomena in the electrical resistivity of binary liquid system $CS_2 + CH_3CN$ and $CS_2 + CH_3NO_2$ studied by Gopal et al (1976). They reported that the liquid mixture at the critical composition, the resistance of the system above T_c follow the relation $R = R_c - A(T - T_c)^b$ with the critical exponent $b = 0.6 \pm 1$ and below the conductivity of the two phases obey a relation

$$(\sigma_2 - \sigma_1) = B(T_c - T)^{\beta}$$

with critical exponent $\beta = 0.34 \pm 0.02$.

Kumar and Gopal (1979) measured the electrical resistance of the binary liquid system, cyclohexane + acetic anhydride in the critical region ($\epsilon \approx 10^{-6}$) both in the pure mixture and when the mixture is doped with small amount ($\approx$ 100 ppm) of H_2O/D_2O impurities.

They showed that the critical exponent $b \approx 0.35$ in the fit of the resistance data to the equation appreciably by the impurities, but there is a sign reversal of $\frac{dR}{dT}$ in the non-critical region.

Sen and Ghosh (1980) measured the r.f. conductivity for methyl alcohol + nhexane, methyl alcohol + carbondisulphide and methyl alcohol + cyclohexane at critical temperature. Ghosh and Datta (1985) measured the electrical conductivity and mobility at critical solution temperature of five binary liquid systems and observed a sudden change in ionic mobility and viscosity of binary liquid solution at the critical point.

1.10. SCOPE AND OBJECT OF THE PRESENT INVESTIGATION-

It is evident from the brief review of the earlier works in both theoretical and experimental aspects on dielectric relaxation time and electrical conductivity of polar liquids that it is possible to obtain certain informations regarding the state of a system and the structure of the molecules. The interaction of electromagnetic field with polar molecules results into the orientation polarization of molecules which gives rise to dielectric relaxation. It has been admitted that dielectric relaxation offer an important method to study the dipole-moment and the shape and size of the molecule in the pure and dilute state.

Various methods have been reported for determining the relaxation time (τ) of pure liquids and even the relaxation time in dilute solution of nonpolar solvents, but it invites a slight personal error within a certain range. Recently in the process of determination of dipole moment (μ) of polar liquids in nonpolar solvent from the r.f. conductivity measurement shows that the relaxation time (τ), plays a very significant role in yielding the proper value of dipole moment (μ). This particular idea open the door to evaluate the relaxation time at dilute solution (τ_s) from the high frequency or microwave conductivity data. The method of determination of τ based on sound mathematical foundation. The accurate value of τ_s of the polar solute is of much importance as it throw much light on the structure of the molecule and also for calculating the exact value of dipole moment.

The ultra high frequency (UHF) and microwave conductivity data in the low concentration region are of much interest as they reveal a completely different situation in comparison to those of high concentration region.

The dipole-moment calculation from the value of relaxation time (τ_s) of polar solute in non polar solvent at lower and higher concentration gives an idea of the formation of monomer and dimer. It also predict the association of polar unit.

Thus it may be concluded that the variation in the value of dipole moment (μ_j) at different concentrations for the substituted molecules in benzene may be due to (i) the difference in the value of group moments and (ii) inductive effect.

Further the variation of r.f. conductivity, relaxation time and thermodynamical parameters of some alephatic monohydric alcohol in a nonpolar solvent at various concentrations and temperatures gives an idea of the rate of breaking of hydrogen bonding of the liquids with dilution and also the dipole orientation at infinite dilution.

Thus the scope and object of the present investigations were as follows : -

(I) To study the microwave conductivity and dipole-moment of polar dielectrics, it is expected that the experimental results will reveal some fresh ideas on the variation of dipolemoment with temperature of organic polar liquids.

(II) To study the microwave conductivity and dipole-moment of substituted benzenes, the experimental conductivity data of polar, nonpolar liquid mixtures at lower and higher concentration region may give some suggestion on the formation of dimer and monomer at higher and lower concentrations of the mixture.

(III) The ultra high frequency conductivity data of polar-nonpolar liquid mixtures at infinite dilution may be used to estimate the temperature and concentration dependence of dipole moment of the following liquids (a) N-methyl acetamide in benzene (b) N-methyl acetamide in dioxane and (c) p-Bromonitrobenzene in benzene.

(IV) The conductivity, relaxation time and energy of activation of some aliphatic alcohol in benzene at infinite dilution may suggest that the rotation of dipole molecule is not hindered by the interaction with the other neighbouring dipole molecules, the rotation is due to rotational orientation of the (-OH) group of a molecule.

(V) The experimental data of energy of activation and dipole moment of water may be used to calculate the correlation factor 'g' of water, which may be used to compute the bending of the bond angles with temperature.

(VI) The electrical conductivity of binary opalescent liquid mixture near critical temperature measured at radio frequency (400 KHz) in order to study the high frequency effect on critical exponent θ and to show that the results are consistent with the existance of a conductivity singularity of the form $\sigma_{\text{sing}} = A\epsilon^{\theta}$

The experimental results and discussions of the works have been presented in chapter III to chapter VIII and a summary of the results is given in chapter IX.

BIBLIOGRAPHY

Adamczewski I and Jachym B (1968): Acta Phys Polan 6 34 1015.

Adamczewski I (1969): Ionisation conduction and Breakdown in dielectric liquids, Taylor and Francis Ltd. (London).

Agarwal C B (1986): Ind J of Pure & Appl Phys 24 204.

Andaut A (1924): Jr de Phys et rad 5 193.

Andrew T H (1869): Phil Trans 159 575

Arrawatia M L, Gupta P C and Sisodia M L (1977): Ind J Pure & Appl Phys 15.

Baker E B & Boltz H A (1937): Phys Rev 51 275

Barbenza G H (1968): J Chim Phys (France) 5 65 906-10.

Bassler H and Richi N (1964): Phys Letter (Netherland) 12 101

(1965): Naturforch 1 20a 85.

Bhanumati A (1963): Ind J Pure & Appl Phys 1 79

Bhattacharyya J, Roy I B and Kastha G S (1966): Ind J Phys 40 187

Bhattacharyya D K (1923): Proc Ind Assoc Cultv Sc 8 227

Bialobrzeski M C (1936): J De Phys et rad 7 329

Brere, Gand Gaspard F (1968): Chem Phys Letter (Netherland) 11, 706

Böttcher C J F (1952): Theory of Electric Polarization Elsevier Publishing Company, New York.

Böttcher C J F and Bordewjk P (1978): Theory of electric Polarization, Elsevier Scientific Publishing Co. Vol. II, New York.

Briere G, Canquis G, Rose B, and Serve D (1969): J Chem Phys 66 44.

Briere C B (1960): J Phys D (G B) 3 9 144.

Brisks J B (1960): Modern dielectric materials, Heywood and Company Ltd. (London).

Brot C (1956): Arch Sci Geneve 9 49.

Brot C (1956): C R Acad Sci (Paris) 239, 160

Brown P L, and Parry Jone G (1975): J Chem Soc Farad Trans II (G B) 71 1657-1666.

Choudhury I and Ghosh R (1980): Ind J Pure and Appl Phys 18 669-672

Cole K S & Cole R H (1941): J Chem Phys 9 341

Cole R H and Davidson D W (1952): Ibid 210 1389

Conway B E (1959): Canad J Chem 37 3 613-628

Clausius R (1979): "Die Mechanishe Warmetheorie" 11 62-Vieveg.

Crossley J (1972): J Chem Phys 56 2549.

Curie P (1902): Comptes rendus 134 420

Curties A J McGreer P L, Rathmann G B, Smyth C P (1952): J Amer Chem Soc 74 644-648

Dalbart R, Magat M and Surduts A (1949): Bull Soc Chem France 16D 345.

Danney D J & Cole R H (1955): J Chem Phys 23 10, 1767-1772.

Davidson D W and Cole R K (1950): J Chem Phys 18 1417

(1951): J Chem Phys 19 1484-1491.

Debye P (1929): Polar Molecules, Chemical Catalogue, New York.

Debye P and Huckel E (1923): Z. Physik 24 185, 305.

Dineal F, Mathews J H, Bender P and Alberty R A (1956): Experimental Physical Chemistry, McGraw Hill Book Company, Inc, New York.

Dronte R W (1940): Ind Eng Chem 32 1529.

Drude P (1904): Ann Phys LPZ 14 667.

Eck J L (1949): Ann Phys 4 12.

Eyring H (1936): J Chem Phys 4 283

Eyring H, Glasstone S & Laidlar K J (1941): The theory of rate process, McGraw Hill Book Co. Inc New York 548.

Felici R J (1959): C r Acad Sci (Paris) 249 264.

Felici R J (1971): Direct current 2 90.

Felsenthan and Vonnecut B (1957): Brit J Appl Phys 18 1801.

Fischer E, Frank F C (1939): Physik Z 40 345.

Fong and Smyth E P (1963): J Phys Chem 67 226.

Foster E O (1962): J Chem Phys 37 5 1021.

Foster E O (1964): Electo Chim Acta 9 1319.

Friedlander J (1901): Z Phys Chem (Leipz) 38 385.

Frohlich H (1949): Theory of Dielectrics (Oxford University Press, London) Sec. 12

Gammell P M and Angel C A (1972): Phys Lett 40A 49.

Gammell P M and Angell C A (1974): J Chem Phys 584.

Garg S K, Lovell N S, Clematt G J and Smyth C P (1973): J Chem Phys 77 232.

Garg S K and Smyth C P (1965): J chem Phys (USA) 42, 4,1397.

Gaspard F and Gosse J P (1970): Electro chim Acta (G B) 15 4, 599

Garner, J (1948): C R Acad Sci Paris 226 1354.

Ghosh A K and Sen S N (1980): Ind J Pure & Appl Phys 18 8, 588-592.

Ghosh S K, Ghosh A K and Acharyya S (1980): Ind. J Pure and Appl Phys 18 8.

Ghosh R and Choudhury I (1981): Pramana (India).

Ghosh R and Choudhury I (1982): Ind Jour Pure & Appl. Phys 20 717.

Ghosh R and Datta (1985), Proc Nat Acad Sci (India) 55A, III

Girad P and Abadie P (1945): Bull Soc Chem France 27 207.

Girad P and Abadie P (1946): Trans Fad Soc 42A 40, 143

Girad P and Abadie P (1947): J Chem Phys 44 313.

Glasstone S, Laidler K J and Eyring H (1941), The theory of rate process, McGraw Hill Book Co. New York.

Gopal E S R, Lele M V, Ramkrishna J, Chandrasekhar P and Subramonyam S V (1976): Pramana 7 266.

Gopala Krishna (1957): Trans Faraday Soc (London) 53 767.

Gopala Krishna V K (1958): Ind J Phys 32 387.

Goodwin D W and Macfadyen K A (1953): Proc Phys Soc (London) B66, 85.

Goss F R (1940): Chem Soc J 752-758.

Green W B (1955): Jr Appl. Phys 26 10, 1257

Groof Wassink R and Bordewijk (1978): Advance in Molecular Relaxation and Interaction Processes 13 Elsevier Scientific Publishing Co. Amsterdam.

Gupta P C et al (1978): Ind J Pure & Appl Phys 16 10.

Gupta P C et al (1978): Ind J Pure & Appl Phys 16 7

Hiafelin J (1946): Arch Sci Phys Nat 28 19-59

Hart J and Mungali A G (1957): Trans Am Inst Elect Engrs 76 1295.

Hassion F X and Cole R H (1955): J Chem Phys 28 10 1756-1761.

Hasted J B (1953): Aqueous Dielectric, Chapman and Hall, London 173.

Higasi K, BergmannK and Smyth C P (1960): J Chem Phys 64 880

Jackson W and Powles J G (1946): Trans Fad Soc 42A 101.

Jachym A and Jachym B (1967): Acta Phys Pol 31 4, 733.

Jaffe G (1906): J de Phys. 5 263 (1908) Annd Physik, 25 257 (1913) Le Radium 10 126.

Jaffe G and Lamay C Z (1953): J Chem Phys 21 920.

Jasnow D, Goldburg W I and Samura J S (1974): Phy Rev A 9 11, 355.

Kalman O F and Smyth C P (1961): J Am Chem Soc 83 571

Kanzman W J (1942): Amer Chem Soc 64 1626-1629
Revs Mod Phys 14 12.

Keepler R G (1960): Phys Rev 119 1226.

Khastry K and Gandhi J M (1987): Ind J Pure & Appl
Phys 25 3, 140-2.

Kremmling G (1950): J Naturforsch 5a 675-682.

Krishnaji and Mansingh A (1964): J Chem Phys 41 827.

Kumar A and Gopal E S R (1979): Pramana 12 511.

Lange N A and Foker G M (1961): Hand Book of Chem
McGraw Hill Inc, New York.

Le BlanceO H Jr (1959): J Chem Phys 30 6, 1443.

Leirs T J (1959): Prog. Dielect 1, 97.

Le Page W R and Dubrige (1940): Phys Rev 58 61.

Lohneysen H V and Negerl H (1971): J Phys D Appl Phys
4 1718.

Lorentz H A (1892): Arch Neerl Sci 25 363.

Mac Fadyan K A (1955): J Appl Phys 6 1.

Madan M P (1987): J Mol Liq (Netherlands) 33 2-3,203-11

Mulecki S and Balanicka S and Nowak J (1980):
J Chem Soc Faraday Trans 11 (G B) 1 42-50.

Mc Duffie G E (Jr), Litovitz J A (1962): J Chem Phys
378 1699-1705.

Mc Duffie G E (Jr), Quim R G & Litovitz T A (1962):
J Chem Phys 37 239.

Mecke R and Reuter A (1949): Z Naturforsch 4a 368-78.

Mehrotra N K, Pant T C and Saxena M C (1972): Bulletin of the Chem Soc. Jpn. 45

Mizushima S I (1926): Phys Z 28 418.

Mizushima S I (1927): Sci ~~Papers-Inst~~ Phys Chem Research (Tokio) 5 201
(1928): Ibid 9 201.

Morgan S O and Yager W A (1940): Industry In Chemistry 32 1519.

Mosotti O E (1850): Mem Soc Ital Sc (Moneda) 14 49.

Müller R C & Smyth C P (1956): J Chem Phys 24 814.

Murphy E L & Morgan S O (1939): Syst Tech J 18 501.

Muralidhara and Rao V (1959): J Sci Industr Res 18B 3, 103-8.

Naokazu ~~and~~ W and Moizumi (1957): J Chem Phys 27 3, 625

Nicolau A, Secarcanu I and Moisescu D (1971): Ind J Pure & Appl Phys 9 4, 263-264.

Nicolan A, Marinescu A and Pascu E (1968): Rev, Rowm Phys 13 9, 799-801.

Nikuradse A (1932): Z Physik 77 216.

Nowak W (1963): Thesis ~~Technical~~ Unit Szeecin Poland.

Onsager L J (1934): J Chem Phys 2 509.

Organische & Helbleiter (1966): Academic Verlag, Berlin.

Pao C S (1943): Phys Rev 64 60.

Petro A J, Smyth C P (1948): J Am Chem Soc 70 4047

(1957): J Am Chem Soc 79 6142.

Plumley H J (1941): Phys Rev 59 200.

Poley J Ph (1955): J Appl Sci Res 4 337.

Prakash Jai (1969): Thesis, University of Gorakhpur.

Prakash, J and Rai B (1986): Ind J Pure & Appl Phys, 24 4, 187-91.

Purohit H D and Sharma H S (1971): Ind J Pure & Appl Phys 9 7, 450-452.

Quincke G (1895): Wied Ann 54 385.

Rajyan B S, Ramsastry C R K and Murthy C R K (1977): Z Naturforsch A (Germany) 32A, 11, 1309-1312.

Ramkrishna J, Nagrajan N, Kumar A, Gopal E S R, Chandrasekhar P and Ananthakrishna G, (1978): J Chem Phys 68 4098.

Rao, P, Prakash and Govindaraju G,R (1970): J Phys D Appl Phys (G B) 3 341.

Riehl N V (1955): Zhur Fuz Khim 29 259

Rizk H A and Elanwar I M (1970): Z Phys Chem 245 5-6, 289-298.

Ryhle F (1943): Z Physik 44 89.

Schallamarch A (1946): Trans Fad Soc 42A 180-186.

Schellman J A (1957): J Chem Phys 26 5, 1225-1230.

Schewilder E V (1907): Ann Physic 5 483.

Sen S N, Ghosh R (1972): J Phys Soc (Japan), 33 838

(1974): J Phys Soc (Japan) 36 743.

(1975): J Phys Soc (Japan) 38 1445

(1978): Ind J Pure & Appl Phys 16 665.

Sen S N and Ghosh A K (1980): Ind J Pure & Appl Phys 18 977.

Sexton J A (1952): Proc Roy Soc (London) 213A 473.

Sharbaugh A H and Watson P K (1962): Prog Dielect 4 199.

Sharma A K and Sharma D R (1985): Ind J Pure & Appl Phys 23 8, 418-21.

Shaw C H and Goldburg, H I (1976): J Chem Phys 65 11, 4906

Sinha B, Roy S B and Kastha G S (1966): Ind J Phys. 40 101.

Sinha B, Roy S B and Kastha G S (1967): Ind J Phys 41 3, 183-198.

Silver M (1965): J Chem Phys 42 1011.

Smyth C P (1954): Dielectric Behaviour and Structure: McGraw Hill Book Company, Inc. New York 105.

Spengler H (1941): Phys. Z 42 134-143.

Srivastava G P and Vershni V P (1957): Physica 23 2, 173-178.

Standthammer P and Seyer W F (1957): J Appl Phys 2b, 4, 405.

Stein A and Allen G F (1972): Phys Rev Lett <u>29</u> 1236

Stranathan J D (1928): Phys Rev <u>91</u> 653-671.

Swan D W (1962): Br J Appl Phys <u>13</u> 308.

Tay S P and Crossley J (1972): J Chem Phys <u>50</u> 2031.

Van-Germet M J C and Delbor (1973): Adv Mole Relaxation Process (Netherlands) <u>5</u> 301-312.

Van Eick A J & Poley J P H (1957): Appl Sci Res <u>6B</u> 359.

Von Helmboltz H (1892): Berlin Ber 1892, 1093.

Watson P K (1963): Nature London <u>199</u> 646.

Wiffen D H and Thomson H W (1946): Trans Fad Soc <u>24</u> 114-122.

Zasky A A and Hawley R (1973): Conduction and Breakdown in Mineral Oil, Peter Peregrinus Ltd. London.