INTRODUCTION

1.0 The study of electrical conductivity in polar and non polar dielectrics provides an important approach to understand many concepts pertaining to the structure of the matter and also to estimate the degree of imperfection in the dielectrics. The subject of ionization and conductivity in polar and non-polar liquid dielectrics has been studied for a long time and has gained great interest in recent time. The subject is far from being exhausted and several aspects of the phenomena have received intensive attention in recent years and significant progress has also been made in this field. However much more investigation is necessary to understand completely the phenomena of ionization and conductivity of dielectric liquids, specially in radio frequency field. The object of the present work is to study some of the salient features of ionization and conductivity of organic polar liquid dielectrics and it is expected that this will enable us to understand the electric transport mechanism of ions in the associating dielectric liquids, molecular structure, intermolecular forces and lastly the causes of imperfection in the pure dielectric liquids.

CHAPTER - I

1.1: DEBYE THEORY OF DIELECTRIC POLARIZATION AND RELAXATION:

A : The idea of orientation polarization came into lime light after Debye (1929) assumed it as a third polarization occuring in addition to the normal electric and atomic polarization on placing the polar molecules in a steady electric field and calculated the total polarization (including the orientation polarization) as

$$P = \frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT}\right) \quad \ldots\ldots \quad (1.1)$$

Since in the high frequency alternating field the orientation polarization which arises due to the alignment of the polar molecules in the direction of the applied field, lags behind the field the dielectric constant of the substance under study becomes complex i.e.

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad \ldots\ldots \quad (1.2)$$

where ε' is the dielectric constant at high frequency ε'' the loss of electrical energy due to the above mention lagging and is dissipated in the form of heat.

On removing the external field, the polarization decays exponentially according to the relation

$$P = P_0 \, e^{t/\tau} \qquad \ldots\ldots \quad (1.3)$$

the time $t = \tau$ in which the polarization reduces to $\frac{1}{e}$ of the original value P_0 after removal of the field is called dielectric relaxation and is denoted by τ

Debye calculated the total polarization of dipolar molecules in the high frequency field of angular frequency $\omega = 2\pi f$ as

$$P^*_\omega = \frac{\varepsilon^* - 1}{\varepsilon^* + 2}\,\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT}\cdot\frac{1}{1+j\omega\tau}\right) \ldots\ldots \quad (1.4)$$

where $\varepsilon^* = \varepsilon' - j\,\varepsilon''$ which can explain well the behaviour of the dielectric as static as well as at high frequency alternating field. If we put $\varepsilon^* = \varepsilon_0$ at $\omega = 0$ and $\varepsilon^* = \varepsilon_\infty$ at infinite frequency $\omega = \infty$

the eqn. (1.3) reduces to

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\cdot\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT}\right) \qquad \ldots\ldots \quad (1.5)$$

and

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\,\frac{M}{\rho} = \left(\frac{4\pi N}{3}\,\alpha\right) \qquad \ldots\ldots \quad (1.6)$$

the dielectric constant ε_∞ denotes the value of dielectric constant at very high frequency and is called optical dielectric constant and the dielectric constant ε_0 at low frequency $\omega \simeq 0$ is called static dielectric constant. From eqn. (1.2) (1.5) and (1.6) and separating the real and imaginary parts we get

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\beta\omega\tau)^2} \qquad \text{.....} \quad (1.7)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\beta\omega\tau}{1 + (\beta\omega\tau)^2} \qquad \text{.....} \quad (1.8)$$

where $\beta = \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}$

Equation (1.7) requires that ε' decreases from ε_0 at $\omega = 0$ to ε_∞ at $\omega = \infty$ which accounts for the dielectric dispersion in polar liquids. From equation (1.8) $\varepsilon'' = 0$ both at $\omega = 0$ and $\omega = \infty$ and it is maximum at the critical frequency ω_m which is given by

$$\tau \simeq \frac{\varepsilon_\infty + 2}{\varepsilon_0 + 2} \cdot \frac{1}{\omega_m} \qquad \text{.....} \quad (1.9)$$

1.2: DERIVATION OF DEBYE EQUATION FROM A DIFFERENT CONCEPT.

Fröhlichs Phenomenological theory of dielectric dispersion.

From altogether different considerations (macroscopic point of view Frohlichs (1949) deduced the Debye's equations.

The properties of dielectric substances in an alternating field was considered by Frohlichs on the assumption of an exponential decay function

$$\alpha(t) \propto e^{-t/\tau} \qquad \text{.....} \quad (1.21)$$

where τ is independent of time, but may depend upon temperature.

He deduced the relation between the electric field $E(t) = E_0 e^{j\omega t}$ which is dependent on time and the corresponding electric displacement D (t). A field E (u) is applied during a time between (U) and $(U + du.)$

Then

$$D(t) = \varepsilon_\infty E(t) + \int_{-\infty}^{t} E(u)\alpha(t-U)du \quad \text{.....} \quad (1.22)$$

The first term of the equation (1.22) is the instantaneous displacement while second term is the absroptive term and α (t-u) is the decay function describing the gradual decrease of D.

Equation (1.22) is transformed into a differential equation

$$\tau = \frac{d}{dt} D(t) = \epsilon_{\infty} \tau \frac{d}{dt} E(t) - \int_{-\infty}^{t} E(t)\, \alpha(t-u)\, du + \alpha(0) E(t) \quad \ldots\ldots (1.23)$$

Since $\frac{d}{dt}\alpha(t) = \frac{1}{\tau}\alpha(t)$

on simplification

$$\tau \frac{d}{dt}\left(D - \epsilon_{\infty} E\right) + \left(D - \epsilon_{\infty} E\right) = \tau \alpha(0) E \quad \ldots\ldots (1.24)$$

in a constant electric field equation (1.24) becomes

$$\tau \frac{d}{dt}\left(D - \epsilon_{\infty} E\right)\left(D - \epsilon_{\infty} E\right) = \left(\epsilon_{0} - \epsilon_{\infty}\right) \quad \ldots\ldots (1.25)$$

So far the electric field is assumed constant. Now far a periodic field $E \propto \exp.(j\omega\tau)$ then

$$\frac{d}{dt}(E) = j\omega E, \quad D = \epsilon^{*} E$$

$$\frac{d}{dt}(D) = j\omega \epsilon^{*} E \quad \ldots\ldots (1.26)$$

Putting these values and separating the real and imaginary terms

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \qquad \ldots\ldots(1.27)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\,\omega\tau}{1 + \omega^2 \tau^2} \qquad \ldots\ldots(1.28)$$

examination of equation (1.28) shows that ε'' approaches zero both for small and large values of $\omega\tau$, while it is maximum when $\omega\tau = 1$.

It is seen that the difference between Debye's equations (1.7 & 1.8) and Frohlichs equation (1.17) and (1.18) is that Debye's equations contain the term $\beta\tau$ instead of τ. The difference is due to the fact that for Fröhlichs assumed τ to be macroscopic relaxation time whereas the relaxation time used by Debye is for the microscopic process. In case of dilute solution of polar molecules in non-polar solvents in which the difference between ε_∞ and ε_0 is very small and $\beta = \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}$ becomes almost unity and therefore, the microscopic or molecular relaxation time τ_{micro} of Debye equation becomes identical with the macroscopic relaxation time τ_{macro} defined by Frohlich.

1.3: KAUZMANN'S THEORY OF DIELECTRIC RELAXATION.

Kauzmann (1942) has given an extensive analysis of dipole orientation as rate phenomenon. He developed the theory of dielectric relaxation on the basis of rotational jumps of dipoles accross the potential barriers and obtained Debye equation both , when jumps are large and small. He also showed the probability of jumps across the potential barrier is smaller than in presence of an external field.

With the aid of the simplifying assumptions he obtained the polarization P (t) due to dipole orientation P(t).

$$P(t) = P_o e^{-K_o t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.31)$$

where P_o is the orientation polarization at $t = 0$ and K_o is the rate constant for activation of dipole i.e. the mean rate of jumping. When t has such values that

$$K_o t = 1 \quad \ldots\ldots (1.32)$$

P (t) must decayed to (P_o/e). This value of t is a relaxation time which may be defined as

$$\tau = \frac{1}{K_o} \quad \ldots\ldots (1.33)$$

Kauzmann used Lorentz expression for the internal field and obtained the total polarization of dipole under an external periodic field

$$P_{o\tau} = \frac{N_0 \alpha_{\mu}}{1 + j\frac{\omega}{K_o}} \left(\frac{\varepsilon_0 + 2}{3}\right) E_o + \alpha_{\mu} \left(E_o + \frac{4\pi}{3} P_{o\tau}\right) \quad \ldots\ldots (1.34)$$

putting $P_{OT} = \dfrac{(\varepsilon - 1)E}{4\pi}$ and $\alpha_{Y} = \dfrac{\mu^2}{3KT}$

and $\varepsilon = \varepsilon' - j\varepsilon''$

On simplification and separating the real and imaginary terms

$$\varepsilon' = \varepsilon_{\infty} + \frac{(\varepsilon_0 - \varepsilon_{\infty})}{1 + x^2} \quad \ldots\ldots (1.35)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_{\infty})x}{1 + x^2} \quad \ldots\ldots (1.36)$$

where $x = \dfrac{\omega}{K_0'}$ and $K_0' = \dfrac{\varepsilon_{\infty} + 2}{\varepsilon_0 + 2} K_0$

which are familiar Debye's equation. Following Eyring's (1936) treatment of activation of dipoles as a unionmolecular reaction he has further shown that

$$K_0 = \frac{1}{\tau} = \frac{KT}{h} \exp\left(\frac{-\Delta F^*}{RT}\right) \ldots\ldots (1.37)$$

where ΔF^* is the molar free energy of activation for dipole orientation. Since $\Delta F^* = \Delta H^* - T\Delta S^*$ where ΔS^* and ΔH^* are the entropy change and heat constant change for the process of activation

$$\tau = \frac{h}{KT} e^{-\Delta S^*/R} \cdot e^{\Delta H^*/RT} \quad \ldots\ldots (1.38)$$

which is of the form $\tau = \frac{A}{T} e^{E_\tau/RT}$ ..... (1.39)

where E_τ is the energy of activation for dipole relaxation.
A is a constant called the frequency factor.

1.4: RELAXATION TIME (τ) AND ITS RELATION WITH MICROSCOPIC AND MACROSCOPIC PROPERTIES.

Debye assumed that the torque applied to a dipole molecule by electric field is counter balanced by frictional forces which are proportional to the angular velocity of the dipolar molecule at steady state condition

$$M = \xi \cdot \frac{dv}{dt} V \qquad \text{.....} \ (1.41)$$

where ξ is the frictional co-efficient. Debye showed that if the dipoles are regarded as sphere of radius 'a' immersed in a medium of internal viscosity η the frictional co-efficient ξ is given by Stokes formula

$$\xi = 8\pi\eta a^3 \qquad \text{.....} \ (1.42)$$

The consideration of Brownian motion of dipole molecule in liquid state leads to the relationship between ξ and τ

$$\tau = \xi/_{2KT} \qquad \text{.....} \ (1.43)$$

from eqn. 1.43 and 1.43 the relation

$$\tau = \frac{4\pi a^3 \eta}{KT} \qquad \text{..... (1.44)}$$

is obtained. The eqn. (1.44) shows that from the measured values of the relaxation time τ and the co-efficient of viscosity η at certain temperature T, the size of the rotating molecule may be calculated from the equation

$$a^3 = \frac{\tau KT}{4\pi \eta} \qquad \text{..... (1.45)}$$

Alternatively as the size of the polar molecule is known from measurements, the determination of the value of the relaxation time τ afford a method for obtaining the value of η_{int} from which information on the structure of the polar medium may be obtained. In Kauzmann's theory the relaxation time τ is given by

$$\tau = \frac{A}{T} e^{E_\tau/RT} \qquad \text{..... (1.46)}$$

and from the eqn. (1.46) the activation energy is obtained which help us to interpret the structure of the liquid molecule.

1.5: COLE-COLE DISTRIBUTION:

The arc dispersion function of Cole-Cole has been applied to the analysis of experimental dielectric data most frequently because of attractively simple graphical form by which data of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ can be analysed in its terms.

Cole-Cole (1941) have shown that Debye equations (A) and (B)

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1+(\beta\omega\tau)^2} \quad \text{..... (A)}$$

and

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\beta\omega\tau}{1+(\beta\omega\tau)^2} \quad \text{..... (B)}$$

can be combined in the form of equation

$$\left[\varepsilon' - \frac{\varepsilon_0 - \varepsilon_\infty}{2}\right]^2 + (\varepsilon'')^2 = \left[\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right]^2 \quad \text{.....(1.51)}$$

which is the equation of a circle. The plot of ε and ε'' in a complex plain gives a semicircle. Such plots in the case of rigid polar molecules are semicircles which mean the dielectric data conforms to Debye equation. Cole-Cole have found for considerable number liquids that ε' vs ε'' plots represent arc of a circle intersecting the abscissa axis at the values of ε_∞ and ε_0. The center of the circle of which this arc is a part is depressed below the abscissa axis and the diameter drawn through the centre through the ε_∞ point makes an angle $\left(\frac{\alpha\pi}{2}\right)$ with abscissa axis. The value of α gives a measure of the distribution of relaxation times, which may vary with temperature but not with frequency. Values of α lies between 0 and 1, and except for polymers are commonly less than 0.3. The Debye equation is modified by them as

$$\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + (j\omega\tau_0)^{1-\alpha}} \qquad \ldots\ldots (1.52)$$

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

$$\frac{v}{u} = (\omega\tau_0)^{1-\alpha} \qquad \ldots\ldots (1.53)$$

where v is the distance on Cole-Cole plot from point to the experimental point and u is the distance from the same experimental point to the ε_∞ point. If $\alpha = 0$, v/u becomes equal to $(\omega\tau_0)$ which is true for Debye equation.

1.6: DAVIDSON AND COLE SKEWED ARC METHOD:

In some cases the plot of ε' against ε'' shows the form of skewed arc. For these molecules, Davidson and Cole suggested an modified of form Debye equation which is given by

$$\overset{*}{\varepsilon} = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{(1 + j\omega\tau)^{\beta}} \qquad \ldots\ldots (1.6.1)$$

where the distribution factor β is an emperical constant with a value between 0 and 1. When $\beta = 1$ the equation reduces to Debye equation.

I.B: DIELECTRIC CONSTANT, DIELECTRIC LOSS, RELAXATION TIME AND RADIO FREQUENCY CONDUCTIVITY OF THE POLAR LIQUID.

1.7: When an alternating electric field applied on a polar dielectric liquid, the permanent dipoles cannot follow the alternations of the field without measurable lag. This lag is commonly referred to as relaxation and the time in which the polarization is reduced to 1/e times its original value is called the relaxation time. The polarization acquires a component out of phase with field and the displacement current acquires a conductance component in phase with the field resulting in thermal dissipation of energy. To have an idea, let us consider a parallel plate condenser, of geometrical capacitance C_0, connected to an alternating source of e.m.f. (E) Where $E = E_0 \exp(j\omega t)$ of angular frequency $\omega = 2\pi f$ where f is the frequency.

The charge of the capacitor at any instant is $Q = C_0 E$ and the charging current $I_c = \left(d\theta/dt\right)$ which leads the applied voltage by a phase angle of 90°. If the space between the plates of the capacitor is now filled up with a dielectric liquid, the capacitor is increased to $C = \varepsilon' C_0$ where ε' is the (real) dielectric constant of the liquid. Due to presence of dielectric the charge on the capacitor is increased to $Q = \varepsilon' C_0 E_0$ and the charging current is increased to

$$I_c = J\omega\varepsilon' C_0 E \qquad \ldots\ldots (1.7.1)$$

It is well known that no dielectric liquid is a perfect insulator. Therefore in addition to I_0 which leads E by 90°, there is a loss current component I_1 in phase with E of magnitude

$$I_L = G E \qquad \ldots\ldots (1.7.2)$$

where $G = \frac{1}{R}$ is the equivalent conductance of the dielectric, R is the finite insulation resistance. Total current through the capacitor is therefore

$$I = I_c + I_l = (j\omega \varepsilon' C_0 E + GE)$$

$$= (j\omega C + G)E \quad \text{.....} \ (1.7.3.)$$

This is shown in the vector diagram in Fig. (1.1b). The current I leads E by a phase angle $\theta < 90^\circ$ where

$$\cos\theta = \left[\frac{I_l}{I}\right] = \frac{G}{\sqrt{G^2 + \omega^2 C^2}} \quad \text{.....} \ (1.7.4)$$

is the power factor. Alternatively the behaviour can be considered interms of loss angle δ and loss tangent $\tan\delta$ where

$$\delta = (90^\circ - \theta) \quad \text{and} \quad \tan\delta = \frac{I_l}{I_c} = \frac{G}{\omega C} \quad \text{.....} (1.7.5)$$

So it is observed that the loss current in a dielectric liquid is due to finite conductivity so that the capacitor can be represented as equivalent to a capacity C in parallel with resistance $R = 1/G$ as shown in Fig. (1.1 a).

In most materials, however the dielectric behaviour differs from this simple form, indicating the presence of other sources of dielectric loss. Without assuming the nature or

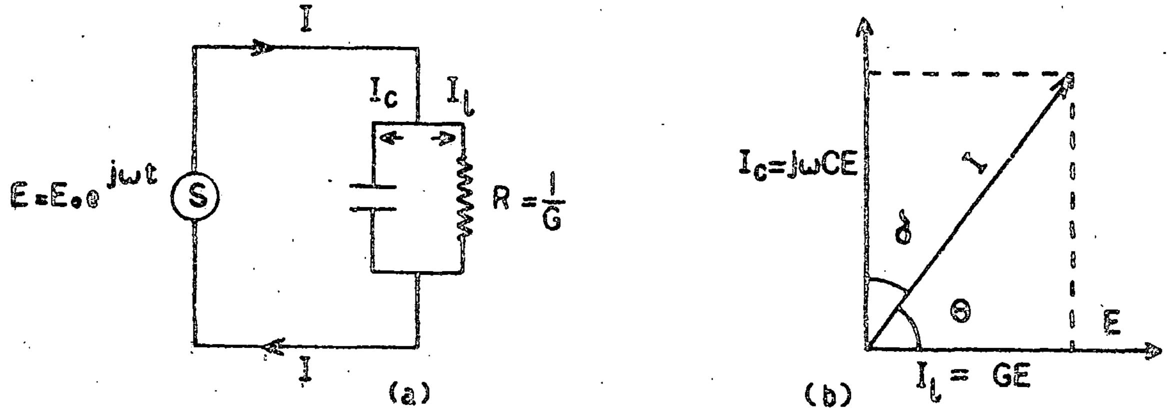

Fig. 1.1. Equivalent circuit, and (a) charging current I_c and loss curret I_l, of capacitor with lossy dielectric.

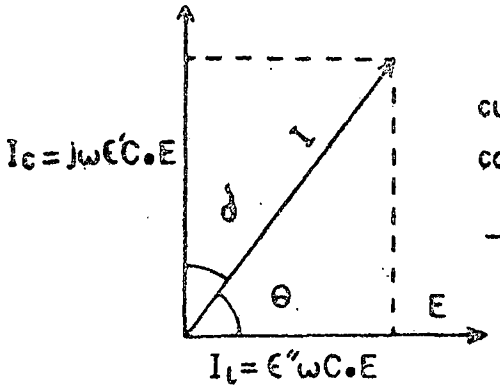

Fig. 1.2, Components of current through dielectric of complex dielectric constant

$\epsilon^{*} = \epsilon' - j\epsilon''$

origin of the dielectric loss, a complex dielectric constant can be defined as

$$\varepsilon^{*} = \varepsilon' - j\varepsilon'' \qquad \ldots\ldots (1.7.6)$$

where ε'' is the dielectric loss factor.

The total current thus

$$\begin{aligned} I &= j\omega\varepsilon^{*}C_o E \\ &= j\omega\left(\varepsilon' - j\varepsilon''\right)C_o E \\ &= j\omega\varepsilon' C_o E + \omega\varepsilon'' C_o E \qquad \ldots\ldots(1.7.7) \end{aligned}$$

Its components being represented vectorially in Fig. (1.2). Now comparing equation (1.7.3) with (1.7.7), we get

$$\begin{aligned} G &= \omega\varepsilon'' C_o \qquad \ldots\ldots(1.7.8) \\ C &= \varepsilon' C_o \end{aligned}$$

and loss tangent $\tan\delta = \dfrac{\omega\varepsilon'' C_o}{\omega\varepsilon' C_o} = \dfrac{\varepsilon''}{\varepsilon'}$

From equation (1.7.8)

$$\varepsilon'' = \frac{G}{\omega C_o} = \frac{\text{specific conductivity x 4}}{\omega = 2\pi f}$$

Therefore specific conductivity (real)

$$\frac{\varepsilon'' \omega}{4\pi} = K' \qquad \ldots\ldots(1.7.9)$$

For parallel plate capacitor, $C_o = \frac{S}{4\pi l}$ in vacuum, where S is cross section of the electrode pair and l is the distance of separation and $G = 1/R$ where $R = \rho \frac{l}{S}$ Equation (1.7.9) directly gives us the relation between the a.c. conductivity and dielectric loss. In this connection, it will be interesting to examine the relation between the apparent conductivity to dielectric constant and loss in the light of analysis given by Murphy and Morgan (1939).

For conductors, the conductivity (K) can be defined as the factor by which the voltage gradient E must be multiplied to give the current density (I)

$$I = KE \qquad \ldots\ldots(1.7.10)$$

or as the factor by which the square of the voltage gradient must be multiplied to give heat (W) developed per second in a unit cube of material

$$W = IE = KE^2 \qquad \ldots\ldots(1.7.11)$$

for the heat developed by a given voltage is proportional to the current, no matter of what material the conductor is composed.

However, the proportionality between the current and heat developed which is the characteristic of conductors does not hold in a dielectric material. When an alternating current flows in a dielectric it dissipates some energy as heat though the amount is generally much smaller than would be dissipated by an equal current flowing in a conductor. This heat which is developed in a dielectric by the polarization current is known as dielectric loss. In fact the complex conductivity represents the case of displacement of electric charge in a dielectric while its real part a-c conductivity is the factor which determines the rate of dissipation of electrical energy as heat in the material. In an ideal dielectric there should be no electron or free ion conduction but in actual practice there are some free ions or electrons and these produce Joule's heat as they drift towards the electrodes in the applied field. The total heat developed is the sum of the dielectric loss and Joule's heat and as the latter is proportional to the d-c- or free ion conductivity, the dielectric loss is proportional to the total a-c conductivity less the d-c conductivity.

Let a dielectric material of dielectric constant ε fill the space between the parallel plates of a two plates condenser, which has a distance "d" cm. between the plates, each plate having an area "A" sq. cm. on each side. If a potential difference V is established between the plates, the electric field intensity

$$E = \frac{V}{d} \qquad \ldots\ldots(1.7.12)$$

The effect of introducing a dielectric into the capacitor can be understood by considering the effect of the applied electric field on the bound charges in the dielectric. The very low conductivity of a dielectric material indicates that practically all the electronic charges are bound to their parent atoms or molecules by the electric fields due to the neuclear charges and they are not free to migrate under the action of an applied field. The action of the field E on the bound charges in the dielectric is to displace them slightly relative to one another, the positive charges being displaced in the direction of the field, the negative charges in the opposite direction. Each atom or molecule thus acquires an electric dipole moment parallel to and in the same direction as E. The effect is known as dielectric polarization, and an electric polarization vector P is defined as the electric dipole moment per unit volume. So if a potential difference V is established between the plates, a charge q per unit area will appear on each plate and a polarization P will be created in the dielectric. The displacement current flowing is $A \frac{dq}{dt}$ and if we assume that the dielectric liquid is free from ions, so that the conductivity due to free ions may be neglected then the conductivity is

$$K = \frac{1}{E} \frac{dq}{dt} \qquad \ldots\ldots(1.7.13)$$

$$\frac{dq}{dt} = K E$$

Since,

$$E = \frac{V}{d} = \frac{D}{\varepsilon}$$

$$D = \varepsilon V/d$$

$$dD/dt = \frac{\varepsilon}{d} \, dv/dt$$

$$D = 4\pi q = E + 4\pi P$$

$$dD/dt = 4\pi \, dq/dt$$

$$dq/dt = \frac{1}{4\pi} \frac{dD}{dt} = \frac{\varepsilon}{4\pi d} \cdot \frac{dv}{dt}$$

$$I = \frac{\varepsilon}{4\pi d} \frac{dv}{dt} \qquad \ldots\ldots(1.7.14)$$

where all the electrical quantities are expressed in electrostatic units. When the applied potential is alternating, V may be expressed as

$$V = V_c e^{j\omega t}$$

where V_o is the amplitude. The dielectric constant may then be written as the complex quantity. The current density in the dielectric is then

$$I = \frac{dq}{dt} = \frac{\varepsilon' - J\varepsilon''}{4\pi d} \cdot \frac{dV_0 e^{J\omega t}}{dt}$$

$$= \frac{\varepsilon' - J\varepsilon''}{4\pi d} \quad J\omega V_0 e^{J\omega t}$$

$$= \left(\frac{J\omega\varepsilon'}{4\pi} + \frac{\omega\varepsilon''}{4\pi}\right) \frac{V_0 e^{J\omega t}}{d}$$

$$= \left(\frac{\omega\varepsilon''}{4\pi} + J\,\frac{\omega\varepsilon'}{4\pi}\right) E_0\, e^{J\omega t} \quad \ldots\ldots(1.7.15)$$

If it is assumed that high frequency conductivity K is a complex quantity and is given by $K = K' + JK''$

$$I = \frac{dq}{dt} = \left(K' + JK''\right) E_0\, e^{j\omega t}$$

where $K' = \dfrac{\omega\varepsilon''}{4\pi}$ is the real part ......(1.7.16)

and $K'' = \dfrac{\omega\varepsilon'}{4\pi}$ is the imaginary part ......(1.7.17)

For convenience in connection with a subsequent method of measurement, the admittance of the condenser may be expressed in term of an equivalent parallel capacitance C_p and conductance G_p so that an alternate expression for I is

$$\begin{aligned} I &= \frac{dq}{dt} \\ &= \frac{0\cdot 9 \times 10^{12}}{A}\left(G_p + j\omega C_p\right)V_0 e^{j\omega t} \end{aligned} \quad \ldots\ldots(1.7.18)$$

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

$$C_o = \frac{A}{4\pi a \times 0\cdot 9 \times 10^{12}} \quad \ldots\ldots(1.7.19)$$

and using equations (1.7.15), (1.7.18) and (1.7.19)

$$\begin{aligned} \varepsilon' &= C_p / C_o \\ \varepsilon'' &= G_p / \omega C_o \\ K' &= \frac{G_p}{4\pi C_o} = \frac{\varepsilon''\omega}{4\pi} = \frac{\varepsilon'' f}{2} \\ K' &= \frac{1}{4\pi R C_o} \end{aligned} \quad \ldots\ldots(1.7.20)$$

To obtain K' in ohms^{-1} cm^{-1}, we can write

$$\begin{aligned} K' &= \frac{\varepsilon'' \omega}{4\pi \times 0{\cdot}9 \times 10^{12}} \\ &= \frac{\varepsilon'' f}{1{\cdot}8 \times 10^{12}} \\ &= \frac{G_p . f}{C_o . 2\pi f \cdot 1{\cdot}8 \times 10^{12}} \\ &= \frac{8{\cdot}85 \times 10^{-12} \times G_p}{C_o \; \mu\mu F} \end{aligned} \qquad \text{......(1.7.21)}$$

where ($C_o \, \mu\mu F$) is the capacitance in micro micro farads.

The dissipated energy per cm^3 of the dielectric placed inside the parallel plates of the plane condenser per second

$$W = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} I \, E \, dt \qquad \text{.....(1.7.22)}$$

and also we have the equation

$$I = \frac{1}{4\pi} \frac{dD}{dt}$$

We will first consider the case where D is in phase with E. Then we have

$$D = D_o \, Cos \, \omega t$$

$$I = - \frac{\omega D_o}{4\pi} . Sin \, \omega t$$

Thus the current density has phase difference with E. In this case no energy is dissipated in the dielectric and hence from equation (1.7.22).

$$W = -\frac{\omega^2}{8\pi^2} \cdot D_0 E_0 \int_0^{2\pi/\omega} \sin \omega t \cos \omega t \, dt = 0$$

where there is a phase difference δ between D and E while

$E = E_0 \cos \omega t$, we have

$D = D_0 \cos(\omega t - \delta)$

$= D_0 \cos \omega t \cos \delta + D_0 \sin \omega t \sin \delta.$

Apparently $D_0 \cos \omega t$ is in phase with E where $D_0 \sin \delta$ has a phase difference of $\pi/2$ with E. The phase difference δ is generally called the loss angle.

$$I = -\frac{\omega}{4\pi} D_0 \sin \omega t \cos \delta + \frac{\omega}{4\pi} D_0 \cos \omega t \sin \delta$$

By this equation I is split into two parts. The first part has a phase difference of $\pi/2$ with E and thus it does not lead to a dissipation of energy. The second part, however, is in phase with E. The dissipated energy per c.e. of the dielectric per second can be calculated as

$$W = \frac{\omega^2}{8\pi^2} D_0 E_0 \sin \delta \int_0^{2\pi/\omega} \cos^2 \omega t \, dt$$

leading to $W = \frac{\omega}{8\pi} D_0 E_0 \sin \delta$ ..... (1.7.23)

where the factor $\sin \delta$ is generally called the power factor.

If $D^* = D_0 e^{j(\omega t - \delta)}$ .....(1.7.24) where D* is the complex part of D_0 and D* $= \varepsilon^* E$ then

$$\varepsilon^* = \frac{D^*}{E} \cdot \frac{D_0 e^{j(\omega t - \delta)}}{E_0 e^{j\omega t}}$$

$$= \frac{D_0}{E_0} e^{-j\delta} \qquad .....(1.7.25)$$

But

$$\varepsilon^* = \varepsilon' - j\epsilon'' = \frac{D_0}{E_0}\left(\cos\delta - j\sin\delta\right) \qquad .....(1.7.26)$$

Then

$$\varepsilon' = \frac{D_0}{E_0}\cos\delta \qquad .....(1.7.27)$$

and

$$\varepsilon'' = \frac{D_0}{E_0}\sin\delta \qquad .....(1.7.28)$$

We find that the dissipated energy per cm^3 of the dielectric and per second is given by

$$W = \frac{\omega}{8\pi} \cdot \frac{D_0}{E_0}\sin\delta\, E_0^2$$

$$= \frac{\varepsilon''\omega}{4\pi} \cdot E_0^2/2$$

$$= \frac{K' E_0^2}{2} \qquad .....(1.7.29)$$

The heat developed per cycle in the dielectric is evidently

$$W \text{ per cycle} = \frac{\varepsilon'' E_0^2}{4} \text{ ergs per cycle} \qquad .....(1.7.30)$$

This demonstrates that K' is proportional to the heat developed per second and ε'' to that developed per cycle in the dielectric. In the above equation W is in ergs per second or per cycle when E_0, K' and ε'' are in e.s.u.

These equations also show that the total current flowing in the dielectric has a dissipative and a non-dissipative part: ε' is proportional to non-dissipative part and ε'' to dissipative part. The loss tangent $\left(\frac{\varepsilon''}{\varepsilon'}\right)$ may be interpreted as the ratio of the dissipative to the non-dissipative current and the power factor as the ratio of the dissipative current to the total current.

Under the influence of varying electric field each type of polarization takes some finite time to respond to applied field. This lag is known as relaxation. Considering Debye's expression for complex dielectric constant

$$\varepsilon^{*} = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + j\omega\tau} \qquad \text{.....} \; (1.7.31)$$

where ε_0 and ε_{∞} are the static and high frequency dielectric constant and τ is the time of relaxation and separating real and imaginary part

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + \omega^2\tau^2} \qquad \text{.....} \; (1.7.32)$$

Substituting the value of ε'' and ε' in the expression of $K' = \varepsilon''\omega/4\pi$ and $K'' = \varepsilon'\omega/4\pi$

we get

$$K' = \frac{1}{4\pi} \, \frac{(\varepsilon_0 - \varepsilon_{\infty})\,\omega^2\tau}{1 + \omega^2\tau^2} \qquad \text{.....} (1.7.33)$$

$$K'' = \frac{\omega}{4\pi}\left(\varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + \omega^2\tau^2}\right)$$

Differentiation of equation (1.7.32) w.r. to ω shows that the dielectric loss factor has a maximum which occurs when $\omega\tau = 1$. The value ω_m of the angular frequency for which the loss factor is maximum, is called the critical frequency. In that case

$$\omega_m = \frac{1}{\tau} \qquad \ldots\ldots (1.7.34)$$

Equation (1.7.34) has been utilized by many workers in determining the value of relaxation time. On the otherhand, differentiation of equation (1.7.33) with ~~reference~~ respect to ω shows that K' does not pass through a maximum as does ε'' but increases with ω, approaching a limiting value K'_{∞} the infinite frequency conductivity which is reached when 1 can be neglected in comparison with $\omega^2\tau^2$ so that

$$K'_{\infty} = \frac{\varepsilon_0 - \varepsilon_{\infty}}{4\pi\tau} \quad esu \qquad \ldots\ldots (1.7.35)$$

and

$$K'_{\infty} = \frac{(\varepsilon_0 - \varepsilon_{\infty})}{4\pi \times 0{\cdot}9 \times 10^{12}\tau} \qquad \ldots\ldots (1.7.36)$$

It is thus evident that from the measured value of radio frequency conductivity of pure polar liquid it is possible to calculate the time of relaxation which is a useful parameter in understanding the activation energy, inter-molecular field and the structure of the molecule concerned.

We have assumed in calculating the above expressions that there is no free ions or electrons in the dielectric liquids. In this case displacement current is the only factor contributing to the conductivity as has been tacitly assumed by Murphy and Morgan. In practice all dielectrics fall for short of this ideal requirement. The evidence for the existence of free ions and electrons has been shown by many workers in recent years such as Standhammer and Seyer (1957), Adamczewski (1969), Loheneysen and Nageral (1971), Sen and Ghosh (1974) etc. However, it has been found that in polar dielectric liquids, the percentage of ions is large in comparison to non-polar liquids. As the ion conduction produces Joule's heat, in an actual dielectric when an electric field is applied the total heat produced is due to the combined effect of dielectric loss and Joule's heating. Thus the radio frequency conductivity measurement provides us information regarding the displacement current and conduction current in a dielectric liquid. The generalised theory put forward by Sen and Ghosh (1974, 1978) is based on the assumption of the existence of free ions in polar dielectrics so that when a radio frequency field is applied to a polar liquid, displacement current is not only the factor contributing to the conductivity as has been assumed by Murphy and Morgan (1939) but the conduction current due to natural ionization plays a dominant role. Murphy and Morgan's expression assuming the absence of free ions for the conductivity is given by

$$K' = \frac{\varepsilon'' \omega}{4\pi} = \frac{1}{4\pi} \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \cdot \omega^2 \tau \ldots\ldots (1.7.37)$$

where the symbols have their usual significance. Substituting Debye's expression for the relaxation time

$$\tau = \frac{4\pi a^3 \eta}{K T} \quad \text{in equation} \quad \ldots\ldots(1.7.37)$$

$$K' = \frac{(\varepsilon_0 - \varepsilon_\infty)\, \omega^2 a^3 \eta / K T}{1 + \frac{16 \pi \eta a^6 \omega^2}{K^2 T^2}} \quad \ldots\ldots (1.7.38)$$

As in the case of most common dielectric liquids

$\tau = 10^{-11}$ sec. and considering the frequency range in the r.f. region so that $\omega^2 \tau^2 \ll 1$

$$K' = \frac{(\varepsilon_0 - \varepsilon_\infty)\, \omega^2 a^3 \eta}{K T} \quad \ldots\ldots (1.7.39)$$

Thus it is evident that if measurement of radio frequency conductivity are made at gradually higher and higher temperatures then as $(\varepsilon_0 - \varepsilon_\infty)$ and η / T are both decreasing functions of temperature, K' should decrease with the increase of temperature. But the experimental results show that radio frequency conductivity increases with the increase of temperature. It is well known that in case of electrolytes where the conduction 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 the later. To find out whether a similar relationship holds in case of radio frequency conductivity of polar dielectrics, K' has been plotted against $\frac{1}{\eta}$ and it has been observed that the variation is almost linear for all the frequencies investigated and can be well explained by assuming the presence of free ions in polar dielectrics.

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 ion is given by

$$M \frac{dv}{dt} = e E_0 e^{j\omega t} - 6\pi a \eta v \qquad .....(1.7.40)$$

where a is the radius of the molecule, η the co-efficient of viscosity of liquid. Then

$$v = \frac{e E_0 e^{j\omega t}}{M(\nu + j\omega)}$$

where

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

Then

$$v = \frac{\varepsilon E_0}{M}\left[\frac{\nu}{\nu^2+\omega^2} - J\frac{\omega}{\nu^2+\omega^2}\right] e^{j\omega t} \qquad .....(1.7.41)$$

If n denotes the number of free ions produced per unit volume then the current,

$$i_{(\text{conduction})} = \frac{n e^2}{M}\left[\frac{\nu}{\nu^2+\omega^2} - j\,\frac{\omega}{\nu^2+\omega^2}\right] e^{j\omega t} \quad \text{.....(1.7.41)}$$

If only the conduction current is present

$$K' = \frac{n e^2}{M}\cdot\frac{\nu}{\nu^2+\omega^2} = \frac{n e^2}{M}\,\frac{6\pi a\eta/M}{\left(6\pi a\eta/M\right)^2+\omega^2}$$

as $a \simeq 10^{-8}$ cm $\eta = 10^{-3}$ poise and $M = 10^{-24}$ gm

$$6\pi a\eta/M \gg M \qquad K' = \frac{n e^2}{6\pi\eta a} \quad \text{.....(1.7.42)}$$

where K' is the real part of the radio frequency conductivity. Further as the applied field is alternating, from Murphy and Morgan equation (1.7.15).

$$i_{(\text{displacement})} = \frac{\omega}{4\pi}\left(\varepsilon'' + j\varepsilon'\right)E_0\, e^{j\omega t} \quad \text{.....(1.7.43)}$$

Remembering $\omega^2\tau^2 \ll 1$ from (1.7.37),(1.7.42) & (1.7.43)

Thus

$$i_{(\text{total})} = \frac{1}{4\pi}\left[\left(\varepsilon_0 - \varepsilon_\infty\right)\omega^2\tau + \frac{n e^2}{6\pi a\eta}\right] E_0\, e^{j\omega t} \quad \text{.....(1.7.44)}$$

$$K' = \frac{1}{4\pi}\left(\varepsilon_0 - \varepsilon_\infty\right)\omega^2\tau + \frac{n e^2}{6\pi a\eta} \quad \text{.....(1.7.45)}$$

$$K' = A + \frac{B}{\eta} \qquad \ldots\ldots (1.7.46)$$

where $A = \frac{1}{4\pi}\left(\varepsilon_0 - \varepsilon_\infty\right)\omega^2\tau = \pi f^2\left(\varepsilon_0 - \varepsilon_\infty\right)\tau$

and $B = \frac{ne^2}{6\pi a}$ where $\omega = 2\pi f$

It is thus observed that in K' against $\frac{1}{\eta}$ curve, 'A' is the intercept made by the straight line with K' axis and is a function of frequency while 'B' denotes the slope of the curve. The above theoretical deduction can explain very satisfactorily the observed experimental results with regard to dependence of radio frequency conductivity on viscosity as well as the variation of 'A' on frequency and enables us to calculate the number of ions per c.c. of the polar dielectric. The experimental results by Sen and Ghosh (1974) also shows that there is a similarity between equation (1.7.46) and Walden's rule.

1.8: A BRIEF REVIEW OF THE EARLY WORK.

a) Dielectric dispersion and absorption and some related studies in some organic polar dielectric liquids.

The first quantative relation to unveil the nature of the liquid dielectrics in presence of an external electric field was put forward by Mossotti in (1850) and Clausius in (1879). Lorentz (1892) von-Helmholtz in (1892) and Drude (1904) independently explained the anamolous dispersion of refractive index of dielectric liquids at optical frequencies. Similar anamalous dispersion of dielectric constant at very high frequency electric field was also discovered by Drude in (1904).

But most of the earlier works were centered round the studies of applicability of Debye equation in the determination of 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 non-polar solvents. This type of work in pure liquid state are rather fewer in comparison with those in dilute solution of non-polar solvent due to various forces (London force, dipole induced dipole forces and dipole-dipole forces) acting among the molecules in liquid state.

In general the liquid system, in which the high frequency absorption has been observed may be classified broadly in two categories:

i) solution of polar rigid and non rigid molecules in nonpolar solvents.

ii) pure polar liquids.

The first quantitative verification of Debye theory was attempted by Mizushima. He carried out the investigation on dielectric dispersion (1926) in 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 alcohol in benzene solution. He found that the zero concentration (mol. vol. Vs concn. curve at diff. temp.) intersepts for methyl, ethyl propyl and amyl alcohol lead to the values of electric moment of molecules which are essentially independent of temperature, this 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 anamalous dispersion at radio frequency range is the polarity of their molecules.

Fischer (1939) measured the relaxation times of a number of liquid compounds in dilute solution and in pure liquid and found for the aliphatic chain molecules (ketones, monohalogenides, alcohols) the relative time increases in sequence alcohols, 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 liquid, but the general theory does not explains the behaviour of alcohols with their strong interaction of OH- groups.

Spengler (1941) showed relaxation time as a function of concentration with two liquids C_6H_6No and C_6H_5Cl. He pointed out that according to Debye's law, relaxation time (τ) varies with viscosity (η) holds for dilute solution where Brownian movement is a major factor in the arrangement of the dipole, with higher concentration the mutual action between the dipolses prepondarates and the ratio τ/η the reduced relaxation time decreases.

Whiffen and Thomson (1946) from the studies of some solvents obtained values of relaxation times which in low viscous medium arranged among themselves as regard magnitude in accordance with their sizes. But they obtained the (τ) values of any solute in different viscous media and found that the values only increased by 4-7 fold for an increase in viscosity of eighty fold.

Similiar results were obtained by Jackson and Powles (1946) from the measurement of (τ) values of benzophenon in benzene and paraffin solutions. Curtis et al (1952) observed although the viscosity of the liquid was same, value was different in solutions and in liquid state. Smyth (1954) also observed the samething. Muller (1956) from the measurement of dielectric loss at different frequencies calculated the critical wave length and (τ) values for a number of molecules such as nitrobenzene, chlorobanzene etc. at different viscous media. He found that the molecular radii calculated from Debye equation are too low compared to values determined by other methods. He also observed that the molecular radii becomes still lower the higher is the viscosity of the medium.

Sinha et al (1966) studied the influence of viscosity on relaxation time and their conclusion was that the macroscopic viscosity did not correctly represent the internal viscosity as required by Debye equation.

(1.8.1): Non rigid molecules in non-polar solvents:

Fischer and Frank (1939) using thermal method of measuring dielectric loss at 4.3 meter obtained relative values of relaxation times of some aromatic halides. The sharter relaxation times in larger molecules were explained by them as being associated with orientation of CH_2x group rotation around their bond to the ring. F.R. Goss (1940) analysed the dielectric polarization of certain binary mixtures of polar with non-polar liquids and showed that the solvent effect can be resolved into contributions depending on the anisotropy of the electric field 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) shown experimentally 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 law molecular weights.

Oster found (1946) the nature of molecular association for the solution of polar molecules in non-polar solvents using the Onsagar-Kirkwood theory of dielectric polarization. All the system ($COMe_2CCl_4$ $PhNO_2$-C_6H_{14}, Bu_2^0Bt-C_7H_{16}) show parallel association of dipoles in solution of higher concentration and in dilute solution dipoles are free.

Since after the development of Budo's theory of 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), Tay and Gossley (1972) analysed bromoalkanes - and ketones, interns of rotation of the molecules as a whole but in amines the NH_2 group rotation have been attributed to be responsible for dielectric relaxation.

It has been observed that while the molecular relaxation time is very sensitive to the viscosity of the medium and temperature, the group rotation is rather less sensitive of both viscosity and temperature.

(1.8.2): Pure liquid:

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 (1941) observed these values greatly different. They explain that the departures may be due to (a) association or interaction causing the molecules to act as a associated 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 from dielectric measurement obtained τ values for toluene, O-xylene, P-cyamine etc. in pure liquid state, which are in according to the size of the molecules. Hafelin (1946) determined permitivity 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). Graner (1948) showed that simple Debye theory does not hold for many insoluting liquids such as glycerine, phenolic resines and suggested an equation

$$\frac{1}{\varepsilon''} = B\left(x^{n} + 1/x^{n}\right) \text{ when } 0 < n < 1 ,$$

represents dielectric behaviour more correctly loss factor and

ε'' = loss factor and $x = \omega\tau$; τ = dipole relaxation time.

From dielectric loss measurement of some rigid molecules of mono substituted C_6H_6 in liquid state, Poley (1955) obtained the relaxation times which increases with the molecular sizes. Muller 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 investigations in substituted benzene and pyridine in the liquid state observed a regular increase in the (τ) values with 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 between two limits given by Frohlich (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 viscosities (η) has been experimentally determined by Bhanumati (1963) at different temperatures for a few liquids, such as α- chloronapthalenes, butyl-phthalate and iso-amylphthalate 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 of rotation but only rotational process was considered in dipole relaxation.

Krishnaji and Manshigh (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 ($\mu \simeq 1.5$ 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 $(\tau T) = \text{const.}\ \eta^{\gamma}$. 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 wt. factor as 0.2, while these values in dilute solution are about 8 to 0.8 respectively.

(1.8.3): Associated liquids and associated - associated liquids:

Molecular association may be expected to influence dielectric relaxation by modifying the structure of the liquid in the direction of greater or near range order as the molecular interaction become increasingly energetic and by providing variety of molecular forces, each of which might exhibit distinctive mechanism for absorption of energy from a external point.

The investigation of dielectric relaxation of alcohol, one of the first molecular system to be studied in this connection has continued to be persued actively in recent years.

Mecke and Reuter (1950) made precision measurements of permitivity on various solution of CH_3OH, C_2H_5OH, nC_4H_6OH, $nC_8H_{17}OH$, C_6H_5OH, $PC_6H_4(OH)\ CH_3$ 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 OH-group is usually not much more than half the value for the free unassociated molecules.

Davidson and Cole (1950) measured dielectric relaxation in glycerine. Kremmling (1951) 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, multipule relaxation times etc. cetyl alcohol showed hysterious effect below its melting point. Cole and Davidson brought the dispersion of n-propyl alcohol into region of audio and radio frequencies. In addition to the usual primary dispersion region two dispersion regions were found with small but significant contribution to the dielectric constant. The relaxation times for intermediate dispersion were 200 times smaller than those for primary ones. Haman (1953) et al made an extensive investigation on dielectric absorption and d.c. conductivity on n-primary alcohols in the frequency range down to 10^{-4}C/sec. by the use of D.C. Method. This results suggest that both absorption and d.c. conductivity depends on the presence of the hydrogen bonded chain. High frequency absorptions appears to be related with the secondary alcohols and it is the proton transition which accounts for D.C. conduction. The absorption at low frequencies is attributed to a Maxwell-Wagner type of mechanism. Brot (1956) made similiar conclusions from his measurements on straight chain alcohols $CH_3(CH_2)_nOH$ with n = 5 - 9 and 11. In 2nd. 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 orientation of the dipoles in the interior of the polymeric species.

Schellaman (1957) developed equations which take into account the association in liquids on dielectric saturation. Srivastava and Varshni also (1957) suggested equation for variation of dielectric constant of mixture of polar liquids (associated-associated) with concentration C and temperature T (deg. °K) : $\varepsilon = \left(l + \frac{m}{T}\right) + \left(p + q/T^{1/2}\right) \times C + Z C^2$

where l, m, p, q 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 the mechanism of proton mobility in water. V. Muralidhara Rao studied (1959) dielectric loss and dielectric constant of two liquid mixtures n-butyl alcohol + glycerol (both associated) and iso-butyl alcohol + n-propyl bormide (asso-nonassociated). Two picks were observed in both the cases in ε'' -freq. and ε'' -temperature curves. Schallamarch's(1948) suggestion was that the process of dielectric relaxation can not be directly connected with individual molecules but is an disturbance over an appricable region in the liquid does not appear to be vaid in the said mixture.

McDuffie 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 exhibit an assymetric distribution of relaxation times of the Davidson Cole form, (b) with the exception of hexanetriol 1,2,6 the distribution of relaxation times becomes narrower with increasing temperature. They concluded that the dielectric orientation is closely related to the structural breakup of the group and the structural breakup 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 expotential. 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 inferred for these mixtures rather than two individual distributions. They explained their experiemental findings in terms of the group concept of Schllamach 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 alcohols from 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} sec., 1.7 to 5 x 10^{-11} and 1.7 to 4 x 10^{-12} sec. respectively. The long relaxation times are associated with polymeric clustars 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 atrributed to the rotation of the free alcohol molecules.

Barbenza (1968) reported the dielectric properties of methyl alcohol (pure) in temperature range 5^{o} to $55^{o}C$ 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. (c) Rizk, I. Elanwar (1970) measured the frequency dependence of complex dielectric constant of glycerol - Iso propyl alcohol and glycerol-Iso butyl alcohol within the frequency band 10^{5} to 10^{7} c/sec. and the range of temperature - 19 to + $50^{o}C$. 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 expotentially with the molar 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-iso butyl 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 .004 to .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 .03 - .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 non-polar solvents from radio frequency conductivity measurements. They observed that the rate of break up of the cluster of molecules is affected with dilution in different non-polar solvents.

Deman, Vicq. and J.M.Vail (1972) studied Debye effect of ethylene glycol and its relaxation time distribution using X band and UHF band at a large number of thermal intervals and confirm the existance of a Cole - Davidson type relaxation time distribution. Deman, Vicq. C.H. and Hebd (1973) found the same effect in the case of glycerine between 0° to 180°C.

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

Brown and Parry Jones (1975) studied non-linear dielectric behaviour of lower alcohols (butanol, propanol, ethanol methanol) by applying short duration high field intensity pulses. The results obtained were compared with those of other workers. Ethanol in C_6H_6 demonstrate qualitatively same behaviour as higher alcohols in similiar non interacting solvent whilst previously the observed behaviour has been ascribed to a proton shift mechanism an alternative is suggested involving the opening up of cyclic non-polar multimers in the electric field to form a more polar species.

Rajyan, Ramasastry and Murthy (1977) studied dielectric dispersion of two pure liquid, glycol and diethylene glycol at radio frequency, ultra high frequency and microwave region at 30°C and confirmed the Cole-Devidson type of dispersion. Baba and Kamiyoshi (1979) studied the preposition of Hassion and Cole (1955) that the main dipole orientation of mono-alcohol is due to a switching mechanism instead of rotation of the molecule as whole or in part and put forward the experimental evidence for the same.

Ghosh and Sen (1980) calculated from r.f. conductivity measurement the relaxation time of methanol and ethanol dissolved in C_6H_6 at different concentration and at different frequencies of the measuring field and found for both the alcohols (τ) obtained from frequency variation is slightly lower than that obtained by concentration variation method. They also obtained (1980) from the similiar type of measurement on methyl alcohol, ethyl alcohol, aniline and benzyl chloride at different temperature, the relaxation time, the number of free ions/unit vol and the variation of activation energy with viscosity and frequency. The result proved the validity of the equation deduced by Sen and Ghosh (1974) and gave a quantative estimation of the imperfection in liquid polar dielectrics.

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

1.8: b). Electrical Conductivity of Organic Dielectric Liquids.

The earliest detailed investigation of conduction current in a liquid was done by Quincke in (1895). He used a static generator of 30 KV and employing an inter-electrode gap width of 1 to 3 mm. showed that the current depends upon voltage, gap width, and nature of the liquid. He concluded that the current is non-ohmic and probably electrolytic in ~~orgigin~~ 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) and (1908) studied the current, voltage characteristic of hexane when irradiated by gamma-rays and considered 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 succeeded 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 about 140 ions were produced per cm^3 per sec. Similiar 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 columns isolated from each other. The columns are the tracks of the photo-electrons ejected by γ-rays, and he concluded that for 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. 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 Drante (1940) interpreted their investigation to mean that the conductivity is due to thermionic emission from the cathode combined with Schottky-effect. That has been critised by Lepage and Dubridge (1940) and they observed that log I is a linear function of E and later concluded that the current is due to field enhanced thermionic emission and derived the following relation

$$J = A T^2 \exp\left[-\frac{\phi e}{RT} + \frac{1}{2.3\,RT}\left(\frac{e^3 E}{K'}\right)^{1/2}\right] \ldots\ldots (1.8.1)$$

where K' is the dielectric constant of the liquid. Plumley (1941) and Pao (1943) interpreted with experimental support that the potential dissociation theory originally proposed by Onsager (1934) for very weak electrolytes. According to their views there are even in purest hydrocarbon such as hexane, a very small number of ions exist resulting from the spontaneous dissociation of molecules. Ruhle (1943) developed the idea of induced conduction and Eck (1949) showed that variation of current strength with time can be represented by the equation,

$$\left(I - I_{\infty}\right) = \left(I_{0} - I_{\infty}\right) e^{-KT} \quad \ldots\ldots (1.8.2)$$

where I_0 is the initial current, I_{∞} is 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. Ruhle (1943), Goodwin and MacFadyen (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 obeys a field emission relation of the form

$$J = \left[A E^{2} \exp\left(\frac{-b}{E}\right)\right] \quad \ldots\ldots (1.8.3)$$

Jaffe and LeMay (1953) studied time dependent current in hexane for wide gap and low voltages and concluded that the current are ionic. The breakdown in dielectric liquid gives additional information concerning the conduction current in dielectric liquid. Goodwin and MacFadyen (1953) demonstrated that the time lag to break down is determined by pos~~s~~itive ion mobility. Green (1955) has studied the conduction and breakdown in hexane and assumed that pos~~s~~itive ions are always present in the liquid, because of external radiation or dissociation of impurity moleculles. When an external field is applied, these ions drift towards the cathode but a cathode surface layer impedes their immediate neutralization. The ions than set up a local field across the surface layer that t~~h~~end to produce electron emission. The size of the local field dependents upon the magnitude of the ionic current and the probability of neutralization of the ions. Standhammer 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. The mechanism by which these liquids conduct, has been subjected to only a few investigations and the only conclusion that has been reached is that, no long range order is necessary for conduction and higher conduction in molten form is due to higher mobility of the charge carrier. Hart and Mungall (1957) observed that the conduction current in chlorobenzene continued to decrease even after continuous distillation for as long as three months. From studies of drift mobility, LeBlance (1959) suggested that electrons exist in n-hexane in quasi trapped state. Forster (1962) studied the nature of conduction in pure hexane and in benzene and also at different concentrations in n-hexane in benzene mixture and obtained a relation.

$$\sigma_S = \sigma_H e^{CK} \qquad \ldots\ldots (1.8.4)$$

where σ_H is the conduction of n-hexane, K is the constant and C is the concentration. This relation suggests that conduction depends upon the probability that an electron will be transferred from one benzene molecule to another is a function of the number of molecules located between the electrodes and capable of sustaining the electron jump. So he reasonably 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. Again Forster (1964) showed that conduction in aliphatic 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 existence of electronic conduction. In addition to the hopping process, he suggested that at arbitrary temperatures a small but possibly potentially significant fraction of the molecules in a hydrocarbon liquid will be in the lowest excited state. The interaction of excited molecules is believed to lead to the formation of positive and negative ions. In the first process, the electron transfer step was visualised to occur by an overlap orbital constituting peripheral π -bonds on two adjacent molecules. He suggested an imperical relation for the activation energy of quasi-trapped mechanism $\varepsilon_a = 0.067P$. eV where P is the number of peripheral π -electrons. For nitrobenzene $P = 8$ which gives an activation energy of 0.54 eV. This is another confirmation of the electronic nature of the conduction current. In proposing the theory for conduction current in insoluting liquid, silver assumed (1965) a slow generation rate of carriers, regardless of generation mechanism, and the electrodes were non-injecting, only acting to balance the positive and negative charges. Further it was assumed that the electrodes did not block the discharge of ions reaching them. One consequence of Silver's theory is that the conductivity is a function of the electrode spacing and of the form

$$V = \left[A J^2 + B J L \right] \qquad \ldots\ldots (1.8.5)$$

where A and B are constants, V is the applied voltage, 'J' the current density and 'L' the gap length. This theory explained successfully the variation of conductivity with electrode spacing at various constant voltage in benzene, but in the case of nitrobenzene, material of the electrodes plays an important role (the cathode appears to be the likely an injector of electrons. Felsenthan and Vonne Cut (1967) concluded that the enhancement of conductivity in insulating liquid may be due to the presence of depressed conducting particles in the insulating liquid. Adamczewski (1965) and Adamczewski and Jachym (1968) (1969) 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 temperature. They further observed that among all the investigated organic compound which occur in liquid state, the lowest conductivity values are found in non-polar liquids. Gaspard and Gosse (1970) gave a clear evidence of ionic conduction in polar dielectrics. They used membrane electrodes and gave evidence for three distinct regions of conduction and in each case the conduction is ionic in nature. It is due to impurities at low and medium fields and injection of ions at high fields. They observed considerable erratic variation of current with time under electric field. Lohneysen and Nagerl (1971) also assumed the existence of natural charge carriers of two kinds having mobilities μ_1 and μ_2 for developing a satisfactory theory for time dependent current density.

Nicolau, Secareanu and Moisescu (1971) studied the electrical conductance of n-butyl, iso-butyl and amyl alcohol in the temperature range of 0-97°C. The variation of conductance with temperature for those aliphatic alcohols was explained in the light of intermolecular hydrogen bonding and concluded that intermolecular hydrogen bonding play an important role in the mechanism of electrical conduction. Miyairi, Leda and Kyoto (1978) investigated the influence of a space charge on electrical conduction in polytheylene terephalate film at high temperature and suggested that result may be attributed due to an ionic space charge accumulation in the vicinity of electrodes.

Sen and Ghosh (1974) and Ghosh and Sen (1980) determined the rf conductivity of some polar associating and non-associating dielectric liquids in different non-polar solvents at different temperatures. From the experimental datas they calculated the free ion number density, ionic mobility, activation energy for conductivity at various dilution in different nonpolar solvents and concluded that the dielectrics are far from being perfect.

1.9: Scope and object of the present work:

It is evident from the brief review of the previous works on electrical conduction on dielectric liquids that it become possible to obtain some definite information regarding the state, the degree of dessociation and the presence of free electrons and ions in liquids. The prevalent theories regarding the mechanism of electric conduction in liquids as presented by different authors have been discussed in detail and the models that have been built up to explain the electrical conductivity in liquids both polar and non-polar have helped us to gain some knowledge regarding the nature of the liquid state. The experimental results however definitely indicate that all dielectric liquids both polar and non-polar exhibit a finite conductivity. No general theory regarding the mechanism of conduction in the dielectric liquids has however been advanced so far. The main object of the present investigation is to obtain experimental data regarding the nature of electrical conduction in dielectric liquids and to present a consistant theory with the aid of the data thus obtained. From the review of literature in this field it is observed that almost all work on the electric conductivity of dielectric has been carried out in d.c. field and mostly on non-polar insulating liquids. It is thus thought worthwhile to carry out measurements in the radio frequency region because this type of measurements will provide us with data for both displacement and conduction current as well. In the present investigation the measurements have been particularly restricted to a number of polar molecules. It is thus proposed to undertake the following lines of investigation in the present work. The object of the present investigation are given below.

(3.0): To study the possibility of determining the natural ion number density exist in polar organic dielectric liquids and also the minimum number of ions/cc left after repeated distillation and electrostatic filtration of the liquids from the values of rf conductivity of the liquids. Further from the measurement of radio-frequency conductivity (K') and mobility (μ) of the liquids the time of dipole relaxation of polar liquids has been calculated. The relaxation time (τ_2) of liquids having free ions was calculated from the expression developed from Einstein - Stoke's relation $\tau_2 = \dfrac{2a^2 e}{3\mu KT}$ and the relaxation time (τ_1) for displacement current only was calculated from Debye relation $K' = \dfrac{1}{4\pi}\left(\varepsilon_0 - \varepsilon_\infty\right)\omega^2\tau$ respectively in order to show that the rotation of dipole is hindered by the interionic forces.

4.0: The dielectric loss (ε''), ($\tan\delta$), and time of relaxation (τ) for pure glycerol and ethylene glycol at 1 Mc/s and at various temperature may be obtained from RF conductivity measurement. From the results it may be possible to show that all the parameters are function of temperature. The variation of effective dielectric loss (ε''_{eff}) and tanδ with temperature and frequency may throw some light on the weak electrotytic nature of dielectric liquids in radio frequency field.

(5.0): The temperature dependence of time of relaxation (τ) and viscosity (η) of glycerol and ethylene glycol have been utilised for determining the thermodynamical parameters such as free energy of activation (ΔF_τ), heat of activation (ΔH_τ) and entropy of activation (ΔS_τ) for dipole orientation and (ΔF_η), (ΔH_η) and (ΔS_η) for viscons flow respectively. The values of activation energy may be used to obtain the information about various intermolecular interaction with polar dielectric medium. This experiment will further support the previous suggestion that the inner frictional co-efficient is better represented by (η^{γ}) where

$$\gamma = \frac{\Delta H_\tau}{\Delta H_\eta}$$

(6.0): The study of the intrinsic variation of HF conductivity at different temperatures for five different alcohols such as methyl alcohol, ethyl alcohol, Iso-propyl alcohol, n-butyl alcohol and Iso-amyl alcohol may suggest that the electrical conduction mechanism in hydrogen bonding liquid is possible due to proton transfer or due to proton jumping process.

(7.0): The activation energy for conductivity of some normal primary alcohol in benzene solution was computed from RF conductivity measurement at a frequency of 1 MH_z and at different temperatures. The values of activation energy for conductivity (We) are very close to the values of activation energy for dipole rotation ΔH_τ that is ratio $\frac{\Delta W_e}{\Delta H_\eta}$ =1 for all the alcohols. The close values of activation energy for conductivity and dipole orientation helps us to suggest that the height of the potential energy barrier to be surmounted in the case of dipole rotation is identical with that to be associated with conduction.

(8.0): The dielectric relaxation time of glycerol is approximately proportional to its viscosity, then a relatively large change in dielectric relaxation time should also be expected upon the additional of small quantity of water in pure glycerol which produces large change in its macroscopic viscosity. Therefore it has been thought to study the variation of time of relaxation of glycerol-water mixture at various concentrations and temperatures in order to get an idea about the smooth transition between average relaxation time of pure glycerol and water and the polymeric cluster formation by the molecular association through hydrogen bonding. Further the variation of thermodynamical parameter with concentration may help us to interpret that the rate of break up of cluster of molecules formation greatly affected by the addition of small amount of associating impurities.

(9.0): To study the nature of variation of dipole relaxation time of some aliphatic monohydric alcohol in non-polar solvent at different concentrations and temperatures and the variation of activation energies with dilution and with carbon atoms in order to support some of the basic assumptions made on the rate of breaking of hydrogen bonding of liquids with dilution and the dipole orientation at infinite dilution in non-polar solvent. The alcohol molecules are associated by hydrogen bridges in a temporary microcrystalline structure and the structures are not stable and at a given instant each of the structure has a finite length. At each instant some hydrogen bonds are raptured and others are formed. The dielectric relaxation process involves in the breaking and forming of hydrogen bonds with the orientation of displacement and the rate of breaking off is the determining factor for dipole relaxation time.

The experimental results and discussion of the works have been presented in chapter III to IX and a summary of the results are given in chapter X.

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