

# **CHAPTER -1**

## **GENERAL INTRODUCTION AND BRIEF REVIEW OF PREVIOUS WORKS**

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### **1.1. Introduction**

At the beginning of the present century the subject matter of dielectrics was scattered in different journals of many countries and in various languages. This field becomes the centre of interest to the scientific community and technologists all over the world when Debye [1] published a comprehensive monograph : "Polar Molecules". Since then a large number of research workers [2-6] were engaged themselves to explore the different aspects of pure polar liquid molecule and polar - nonpolar liquid mixture. Series of monographs were gradually published one after the other starting from Fröhlich [7], Smyth [8] Hill [9] to Jonscher [10] to enhance the scientific content of this particular field of research. The structural and associational aspect of the complicated and nonspherical polar molecules could, however, be reached from the study of dielectric relaxation phenomena involved with the orientational polarisation.

### **1.2. Dielectric Polarisation**

When an isotropic nonpolar dielectric material is placed between two charged plates of a condenser, the positive nuclei of dielectric molecule are attracted by the negative plate while the negatively charged electrons by the positive plate. As a result an induced electric dipole is formed. This is known as induced polarisation due to distortion of the electric lines of force by the molecule as well as molecule itself by the electric field. The distortion polarisation is the sum of electronic and atomic polarisations. They occur both in the nonpolar and polar dielectrics, although the polar molecule has the molecular asymmetry. The asymmetric nature of molecules occur due to noncoincidence of centre of positive and negative charges. The centre of gravity of the positive and negative charges of the nonpolar molecule coincides in

absence of the applied electric field. The part of the polarisation on the other hand, for the permanent dipole of the molecule is called the orientational polarisation. In addition to distortion polarisation, the orientational polarisation takes place in case of polar molecules which are nonspherical in shape.

The induced electric dipole moment per unit volume or the polarisation charge per unit area of the nonpolar substance is commonly known as dielectric polarisation. It is a vector quantity parallel to the electric field. If we consider a unit charge in cylindrical cavity of small cross section with its axis in the direction of lines of force the actual force acting on this unit charge is called the electric field intensity  $\vec{E}$ . On the other hand, let a cavity is made in the space between two closely situated planes and perpendicular to electric lines of force, a unit charge between the planes is acted upon by the electric displacement vector  $\vec{D}$ . In Maxwell's electromagnetic theory it is assumed that

$$\vec{D} = \epsilon \vec{E} \quad (1.1)$$

where  $\epsilon$  = absolute permittivity of dielectric material =  $\epsilon_0 \epsilon_r$ ,  $\epsilon_0$  is called the permittivity of free space =  $\frac{1}{4\pi c^2 \times 10^{-7}} = 8.854 \times 10^{-12}$ . Farad metre<sup>-1</sup>.

where  $c$  is the velocity of light in vacuum and  $\epsilon_r$  is called the relative permittivity.

### 1.3. Static Relative Permittivity

If two charges of opposite signs are supposed to be placed on two separate conductors of a condenser having a homogeneous dielectric medium the forces on each of them is reduced by a factor  $\epsilon_r$  compared to when they are placed in vacuum.  $\epsilon_r$  being greater than unity is a scalar quantity called the static relative permittivity of the medium. Hence the capacitor filled with a dielectric material has a capacitance  $\epsilon_r$  times greater than a capacitor with the same electrodes in vacuum. Except for exceedingly high electric field unlike normally to be reached,  $\epsilon_r$  is independent of the magnitude of the applied electric field for all dielectric materials used in practice excluding ferroelectrics.

## 1.4. Static Dielectric Susceptibility

The introduction of a dielectric material between two charged plates reduces the electric field by a factor  $\epsilon_r$ . The medium produces a flux in Coulomb metre<sup>-2</sup> (C.m<sup>-2</sup>) known as polarisation  $\vec{P}$  which opposes the electric displacement vector  $\vec{D}$  produced by the capacitor. The reduction in electric field  $\vec{E}$  can be expressed by :

$$\vec{E} = \frac{\vec{D} - \vec{P}}{\epsilon_0} \quad (1.2)$$

$$\text{or } \frac{\vec{P}}{\epsilon_0 \vec{E}} = \frac{\vec{D}}{\epsilon_0 \vec{E}} - 1$$

$$\text{or } \frac{\vec{P}}{\epsilon_0 \vec{E}} = \epsilon_r - 1 \quad (1.3)$$

The dimensionless ratio of  $P$  to  $\epsilon_0 E$  is called the dielectric susceptibility  $\chi_e$  of the dielectric i.e.

$$\chi_e = \epsilon_r - 1 \quad (1.4)$$

represents the component of the static relative permittivity for the electrical response of the medium itself to the applied electric field.

## 1.5. Dipole Moment, Polarizability and Clausius–Mosotti Relation

When two charges of equal magnitude  $q$  but of opposite signs are separated by a distance  $d$ , they constitute what is known as electric dipole of moment  $\mu$  in Coulomb metre (C.m)

$$\mu = qd \quad (1.5)$$

In a dielectric material in which a polarisation  $\vec{P}$  exists, an elementary cuboid may be imagined of volume  $\delta V$  with two faces perpendicular to  $P$  of area  $\delta A$

separated by a distance  $\delta x$ . Its dipole moment is  $P \delta A \delta x$  or  $P \delta V$ . So the polarisation  $\vec{P}$  is defined as the dipole moment per unit volume of the dielectrics. This dipole moment is determined by the microscopic entity called the polarisability of the material.

When an isotropic dielectric is subjected to an external electric field  $\vec{E}$ , it causes the charge distribution within the dielectric to modify it into local field  $\vec{E}_1$ . In nonpolar dielectrics, the dipole moments  $\mu_a$  and  $\mu_e$  due to atomic and electronic polarisations are proportional to  $\vec{E}_1$  i.e.

$$\mu_a = \alpha_a E_1 \quad (1.6)$$

$$\mu_e = \alpha_e E_1 \quad (1.7)$$

where  $\alpha_a$  and  $\alpha_e$  are the proportionality constants called atomic and electronic polarisabilities. For a polar molecule having a permanent dipole moment  $\mu_p$  arising out of molecular orientational polarisation i.e.

$$\mu_p = \alpha_p E_1 \quad (1.8)$$

Now,  $\alpha_t = \alpha_a + \alpha_e + \alpha_p = \alpha_d + \alpha_p$ , is the total electric polarisability. Thus the polarisation  $\vec{P}$  is, however, obtained by multiplying  $\alpha$  with  $\vec{E}_1$  and number density  $n$  of molecules.

$$\vec{P} = n\alpha\vec{E}_1 \quad (1.9)$$

Substituting  $\vec{P}$  from Eq (1.3) in Eq (1.9) one obtains

$$\epsilon_r - 1 = \frac{n \alpha \vec{E}_1}{\epsilon_0 \vec{E}} \quad (1.10)$$

A classical calculation made by Lorentz [11] gives the expression for  $E_1$  where

$$\vec{E}_1 = \vec{E} + \frac{\vec{P}}{3\epsilon_0} \quad (1.11)$$

From Eqs. (1.10) and (1.11) one gets.

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{n\alpha}{3\epsilon_0} \quad (1.12)$$

Multiplying both sides by  $\frac{M}{\rho}$  we have

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \cdot \frac{M}{\rho} = \frac{N\alpha}{3\epsilon_0} \quad (1.13)$$

where  $nM/\rho = N =$  the Avogadro's number,  $M =$  molecular weight,  $\rho =$  mass density of the dielectric material.

Equation (1.13) is Clausius - Mosotti relation [12,13] which relates the macroscopic quantity  $\epsilon_r$  with the microscopic quantity  $\alpha$  for a material.

According to Maxwell's electromagnetic theory  $\epsilon_r = n_D^2$ , then Eq (1.13) becomes.

$$\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{\rho} = \frac{N\alpha}{3\epsilon_0} \quad (1.14)$$

which is Lorentz-Lorentz equation [14], for molar refraction. where  $n_D$  is the refractive index.

## 1.6. Debye Equation

The variable  $\frac{\epsilon_r - 1}{\epsilon_r + 2} \cdot \frac{M}{\rho}$  of Eq (1.13) does not vary with temperature. However, according to experimental observation  $\epsilon_r$  and  $\rho$  are temperature dependent quantities.  $\frac{\epsilon_r - 1}{\epsilon_r + 2} \cdot \frac{M}{\rho}$  was found to be independent of temperature for nonpolar dielectrics.

The variation of  $\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho}$  against  $\frac{1}{T}$  was, however, observed [1] for

some molecules called polar molecules. The charge distribution of such molecule is that even in absence of electric field it possesses a permanent dipole moment  $\mu_p$ . The permanent  $\mu$  of the molecule is randomly directed and hence the net moment is zero. The applied electric field tends to align  $\mu_p$  along the field direction whereas thermal motions tries to disorganise the orderly state so produced. The resulting orientational polarisation  $\vec{P}_o$  is inversely proportional to absolute temperature T K and except for exceedingly high electric field is directly proportional to  $\vec{E}_1$ .

$$\text{It can be shown [15] that } P_o = \frac{n\mu_p^2 \vec{E}_1}{3kT} \quad (1.15)$$

Now  $\vec{P}_o/n\vec{E}_1$  is defined as the orientational polarisability  $\alpha_p$  given by :

$$\alpha_p = \frac{\mu_p^2}{3kT}$$

Thus the total polarisability in case of polar dielectric is

$$\alpha_T = \alpha_a + \alpha_e + \frac{\mu_p^2}{3kT}$$

$$\alpha_T = \alpha_d + \frac{\mu_p^2}{3kT} \quad (1.16)$$

where  $\alpha_d$  is the polarisability due to fast polarisation. The Clausius - Mosotti equation (Eq. 1.13) becomes :

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{N}{3\epsilon_0} \left( \alpha_d + \frac{\mu_p^2}{3kT} \right) \quad (1.17)$$

This is known as Debye equation [1] for a dipolar gaseous molecule. It can be represented by a straight line between experimentally measured variables of

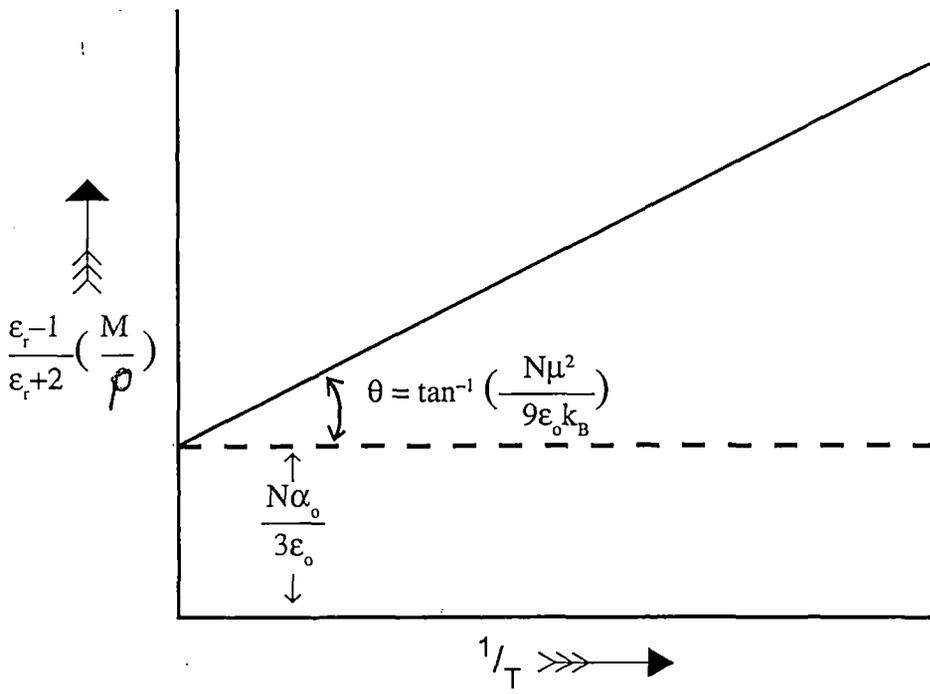


Figure 1.1

$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho}$  and  $\frac{1}{T}$  of Figure. 1.1., whose slope may yield  $\mu$  a of a dipolar gas molecule to arrive at the valuable information of the structural aspects of a molecule.

## 1.7. Dielectric Equation Based on Different Models

For almost spherical polar liquid molecule Onsager equation is applicable [2]. A relation between the relative permittivity and dipole moment is, however, obtained by considering the reaction field  $\vec{R}$  for the external applied electric field and the cavity field  $\vec{G}$ , in a continuous medium of static relative permittivity  $\epsilon$ .

$$\frac{(\epsilon_{oij} - n_{Dij}^2) \cdot (2 \epsilon_{oij} + n_{Dij}^2)}{\epsilon_{oij} (n_{Dij}^2 + 2)^2} = \frac{N\rho\mu^2}{9MkT\epsilon} \quad (1.18)$$

Later on, a large number of workers modified Debye and Onsager equations to obtain  $\mu$  of a highly nonspherical polar liquid molecule.

Kirkwood [3] pointed out the fact of hindered rotation of the polar molecule in a dielectric medium under polarisation. The effect of short range forces was considered to generalise Onsager equation [2]. The macroscopic relative permittivities of the medium are then connected by :

$$\frac{(\epsilon_{oij} - n_{Dij}^2) \cdot (2 \epsilon_{oij} + n_{Dij}^2)}{\epsilon_{oij} (n_{Dij}^2 + 2)^2} = \frac{N\rho\mu^2}{9MkT\epsilon} g \quad (1.19)$$

The correlation parameter “g” measures the hindered molecular rotation arising out of short range intermolecular forces. It can, however, be calculated from the knowledge of the structure of the liquid molecule. For normal liquids of nearly spherical shape and size “g” is equal to unity. But for highly nonspherical and associative liquids “g” values deviates significantly from unity.

Fröhlich and Sack [16] also extended Onsager equation to solids. They

applied it to the model having two equilibrium orientations for the molecules separated by an angle of  $180^\circ$ . The equation may be written as :

$$\frac{(\epsilon_{oij} - \epsilon_{\infty ij}) \cdot (2\epsilon_{oij} + \epsilon_{\infty ij})}{3 \epsilon_{oij}} = \left[ 1 + \frac{(\epsilon_{oij} - \epsilon_{\infty ij})^2}{3\epsilon_{oij} \epsilon_{\infty ij}} \right] \frac{\mu^2}{a^3 kT} \quad (1.20)$$

Where 'a' is the molecular radius. The equation (1.20) may be applied to highly viscous liquids as well as to solids. But for liquids of low viscosity it reduces to Onsager equation. The difficulties in Fröhlich equation are associated with the evaluation of interaction of the sample with the surrounding medium. Thus there exists experimental limitation in determining the required parameters involved in various equations presented. For nonassociative dipolar liquids where short range forces are absent one can use Onsager equation to analyse the experimental data to estimate  $\mu$ .

## 1.8 Dielectric Dispersion

When an alternating electric field is applied to a dielectric material electronic, atomic and orientational polarisations operate effectively. The inertia of sub microscopic entities increases with the frequency and thereby ceases to operate. The frequency range over which all the polarisations is dropping is known as dispersion. The springlike nature of the forces involved in electronic and atomic polarisations tend to disappear with the frequency of the applied electric field. The dropping out of the orientational polarisation is, however, accompanied by relaxation process which involves with a relaxation time over a much wider range of frequencies. When the frequency of the impressed electric field exceeds a certain critical value, the permanent dipoles of molecules can not follow the exact alternation of the applied electric field. The measurable lag is commonly known as dielectric relaxation and the relaxation time  $\tau$  is defined as the lag in response of the polar molecule with the forces to which it is

subjected. Thus when the electric field is switched off all the polarisations decay exponentially with time. The time in which the polarisation is reduced to  $1/e$  times its initial value is called relaxation time  $\tau$  [17]. Typically the mid frequency  $f_0$  is  $10^{15}$  Hz for electronic polarisation and  $10^{12}$  Hz for atomic polarisation. But the orientational polarisation has a wide range of  $f_0$  lying between  $10^4$  to  $10^9$  Hz [18] depending on the nature of the material and temperature.

Each region of dispersion is associated with an energy loss i.e. absorption of energy per second per unit volume. It has a peak at  $f_0$ . The existence of energy loss means that electric displacement vector  $\vec{D}$  instead of being inphase with  $\vec{E}$  lags by a phase angle  $\delta$ . Thus it is evident from Eq (1.1) that  $\epsilon_r^*$  is a complex quantity given by :

$$\epsilon_r^* = \epsilon_r' - j\epsilon_r'' \quad (1.21)$$

$$\epsilon_r''/\epsilon_r' = \tan \delta \quad (1.22)$$

$\epsilon_r''$  and  $\tan \delta$  are known as the dielectric loss factor and loss tangent respectively.

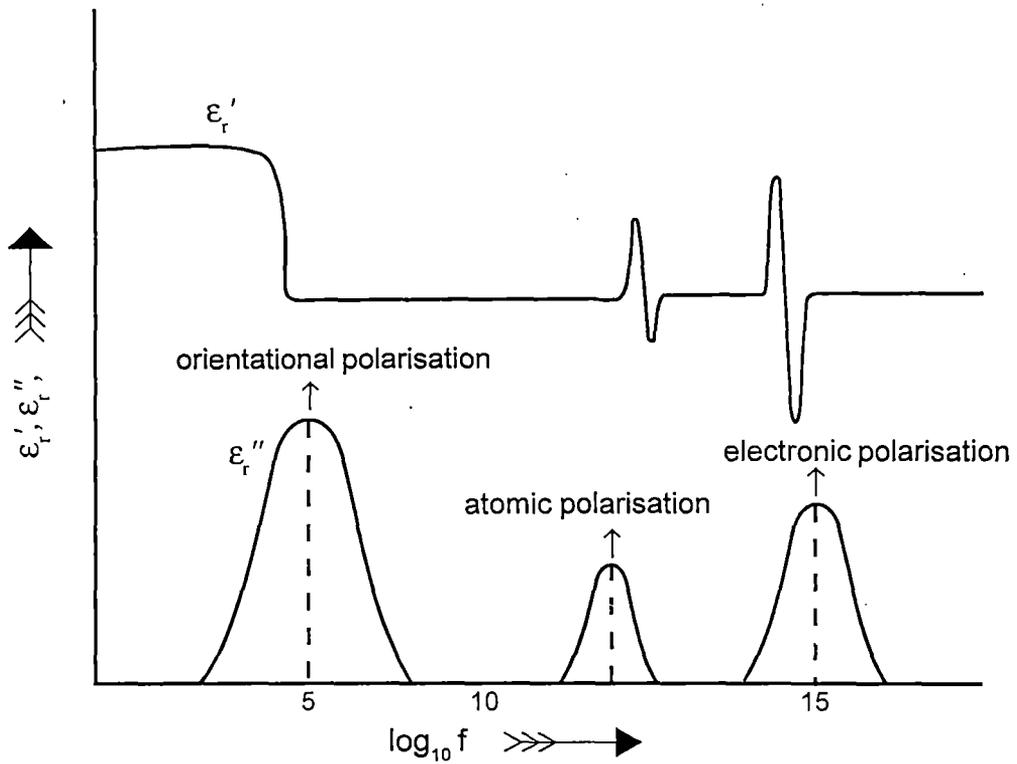
Also the real  $\chi_e'$  and imaginary  $\chi_e''$  parts of hf complex susceptibility  $\chi_e^*$  are related to complex relative permittivity  $\epsilon_r^*$  by :

$$\chi_e = \chi_e' - j\chi_e'' \quad (1.23)$$

$$\chi_e' = \epsilon_r' - 1 \quad (1.24)$$

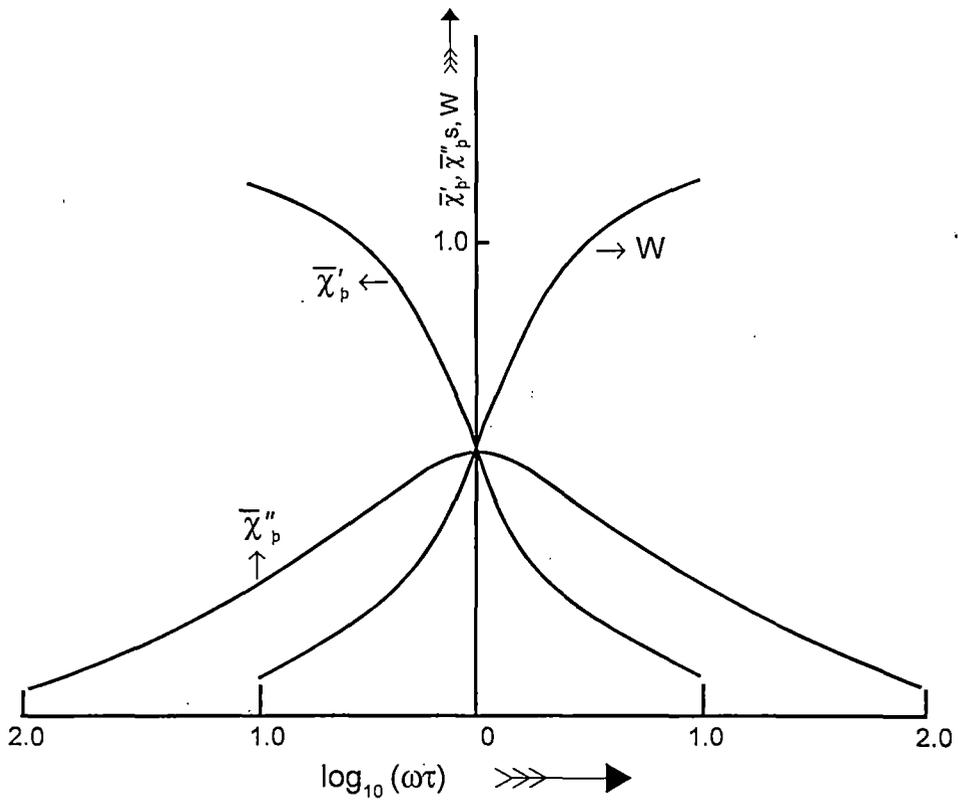
$$\chi_e'' = \epsilon_r'' \quad (1.25)$$

When the measured  $\epsilon_r'$  and  $\epsilon_r''$  are plotted against frequency 'f' of the applied alternating electric field the observed variations are shown in Figure 1.2. The resulting curves exhibit sharp resonance of  $\epsilon_r''$  at a particular frequency  $f_0$ . It indicates the regions for electronic, atomic and orientational polarisations (Figure 1.2). Almost similar behaviour of the molecular orientational polarisation process is observed in the plot of  $\bar{\chi}_p'' = (\chi''/\chi_{ps})$  against  $\log_{10}(\omega\tau)$  as seen in Figure 1.3[18].  $\chi_{ps}$  is the static orientational susceptibility and  $\omega (=2\pi f)$



**Figure 1.2**

(Variation of  $\epsilon'$ , and  $\epsilon''$ , with frequency  $f$ . Abscissa is  $\log_{10} f$ , where  $f$  is expressed in hertz)



**Figure 1.3**

Plot of  $\bar{\chi}'_p = \chi'/\chi_{ps}$ ,  $\bar{\chi}''_p = \chi''/\chi_{ps}$ , and  $W = W_\tau/\epsilon_0\chi_{ps}E^2$  for Debye behaviour ( $\chi_{ps}$  is the static orientational susceptibility)

is the angular frequency of the applied electric field. The frequency variation of  $\epsilon'_r$  and  $\epsilon''_r$  are not independent. The drop in  $\epsilon'_r$  from beginning to end of a dispersion region namely  $\Delta\epsilon'_r$  is called the strength of the dispersion and is governed by Kramers - Kronig [18] relation :

$$\Delta\epsilon'_r = \frac{2}{\pi} \int_{-\infty}^{+\infty} \epsilon'_r d(\ln f) \quad (1.26)$$

In practice, the integral is truncated to avoid the inclusion of area attributable to other mechanism.

At optical frequencies it is usual practice to characterize the material by its complex refractive index  $n^*_D$  given by :

$$n^*_D = n_D - jk \quad (1.27)$$

where  $n_D$  is the real part of refractive index and  $k$  is the absorption coefficient  $n^*_D$  is related to  $\epsilon_r$  by  $\epsilon_r = n^2_D$ . So from Eq (1.21) we have :

$$n^*_D = n^2_D - k^2 \quad (1.28)$$

$$\epsilon''_r = 2n_D.k \quad (1.29)$$

The use of the above relationship allows one to locate the value of  $\epsilon_r$  at high frequencies. For the optical measurements  $k$  is very low and hence one gets  $\epsilon_r \simeq n^2_D$ .

## 1.9. Representation of Permittivity in the Complex Plane

### A. Debye Behaviour

The variation of  $\epsilon_r^*$  with angular frequency  $\omega$  is [1] :

$$\frac{\epsilon_r^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{1 + j\omega\tau} \quad (1.30)$$

where  $\epsilon_\infty$  and  $\epsilon_s$  are the relative permittivities at much higher and lower

frequencies respectively than  $\varepsilon_r^*$  in the dispersion regions arising out of relaxation of permanent dipoles. Equating the real and imaginary parts of Eq.(1.30) one gets.

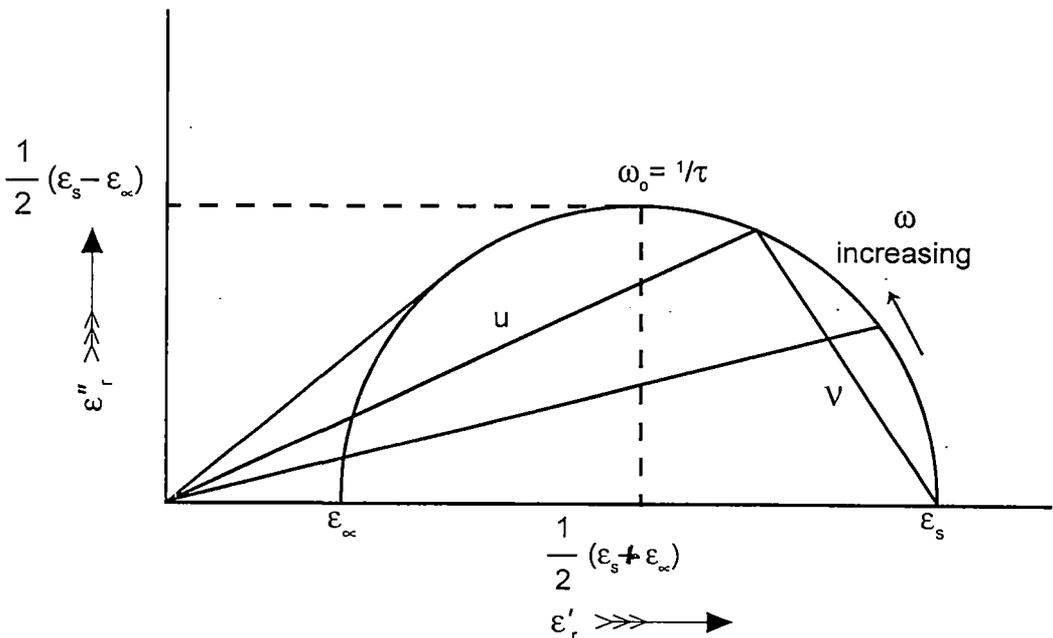
$$\frac{\varepsilon_r' - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + \omega^2\tau^2} \quad (1.31)$$

$$\frac{\varepsilon_r''}{\varepsilon_s - \varepsilon_\infty} = \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (1.32)$$

On eliminating the parameter  $\omega\tau$  and rearranging it is obtained :

$$\left(\varepsilon_r' - \frac{\varepsilon_s + \varepsilon_\infty}{2}\right)^2 + \varepsilon_r''^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2 \quad (1.33)$$

This is a parametric equation of a circle. If  $\varepsilon_r''$  be plotted against  $\varepsilon_r'$  a semicircular arc of radius  $\left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2$  results in the Figure 1.4 with its centre at  $\{\frac{1}{2}(\varepsilon_s + \varepsilon_\infty), 0\}$



**Figure 1.4**

(Plot of  $\varepsilon_r''$  versus  $\varepsilon_r'$  for Debye behaviour)

on the  $\epsilon_r'$  axis, making intercept of  $\epsilon_s$  and  $\epsilon_\infty$  in the lower and higher  $\omega$ . The loss factor has its maximum value when  $\omega_0 = 1/\tau$  and on the semicircle the frequency  $\omega$  is given by

$$\frac{\omega}{\omega_0} = \frac{v}{u} \quad (1.34)$$

where  $u$  and  $v$  are the distances of the point from the intercept of the semicircle with  $\epsilon_r'$  axis as shown in Figure 1.4.

The value  $\epsilon_r''$  gives a semicircle when plotted against  $\epsilon_r'$ . It indicates that the data conform to the Debye theory. Results of permittivity measurements when are analysed in this way for many simple liquids, the experimental points do not always lie on the expected Debye semicircle. The method has the disadvantage that the frequency, which is the independent variable, is very difficult to be known accurately.

### B. The Cole - Cole arc

The universally well known contribution of Cole -Cole [19] to the study of dielectric relaxation are found to satisfy materials including long chain alcohols and polymers. The measured permittivities at different frequencies follow the empirical equation :

$$\frac{\epsilon_r^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{1 + (j\omega\tau)^{1-\gamma}} \quad (1.35)$$

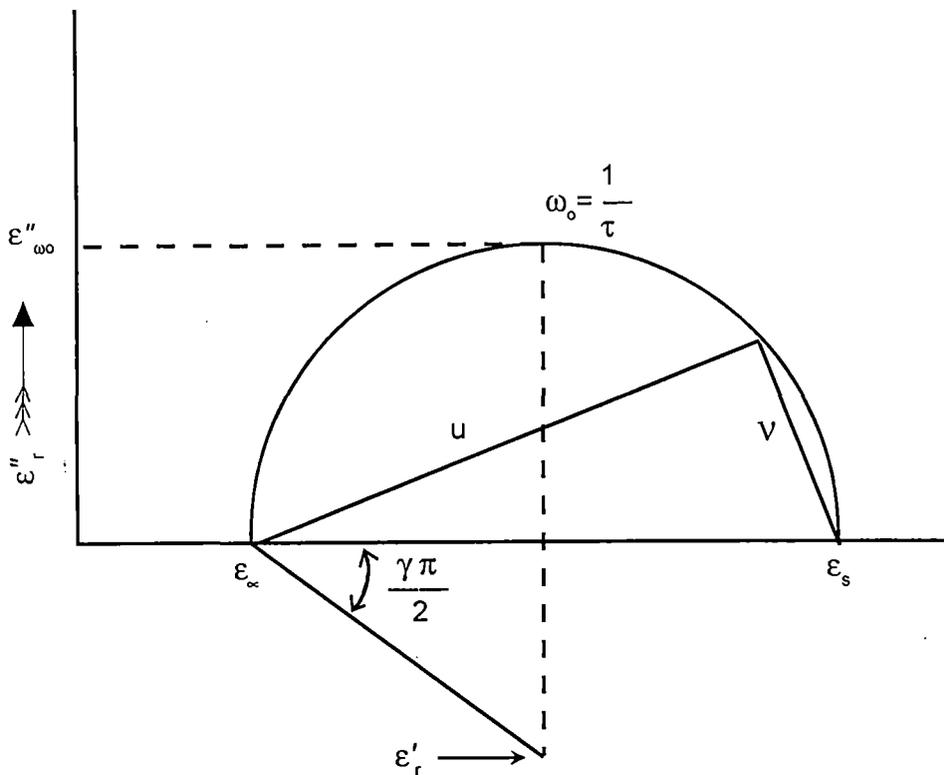
where  $0 \leq \gamma < 1$ . When  $\epsilon_r''$  be plotted against  $\epsilon_r'$  a circular arc results in with its centre at  $\{1/2 (\epsilon_s + \epsilon_\infty), -1/2 (\epsilon_s - \epsilon_\infty) \tan \pi\gamma/2\}$  and radius  $1/2 (\epsilon_s - \epsilon_\infty) \text{Sec } \pi\gamma/2$ . The physical significance of this plot as shown in Figure 1.5 is that  $\tau$  can be obtained by using.

$$\omega\tau = \left(\frac{v}{u}\right)^{1-\gamma} \quad (1.36)$$

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**Figure 1.5**

(Cole - Cole Plot)

Where  $u$  and  $v$  are distances of the point from the intercept on the  $\epsilon'_r$  axis. The value of  $\gamma$  found experimentally, show a tendency to increase with increasing number of internal degrees of freedom in the molecules and with decreasing temperature. In the limit  $\gamma = 0$  the Cole - Cole arc reduces to the Debye semi circle.

### C. The Cole - Davidson arc

The Cole-Cole symmetrical arc results in for certain materials like glycerol into a skewed arc by Cole and Davidson [20,21]. They suggested that behaviour of this kind could be represented by the equation

$$\frac{\epsilon'_r - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{(1 + j\omega\tau)^\delta} \quad (1.37)$$

Where  $\delta$  is a constant,  $0 < \delta \leq 1$

When  $\epsilon_r''$ 's are plotted against  $\epsilon_r'$  in Figure 1.6 it represents the skewed arc. The  $\epsilon_r'$  axis of the skewed arc cuts at an acute angle  $\pi\delta/2$  to yield  $\epsilon_r' = \epsilon_\infty$  at right angles and  $\epsilon_r' = \epsilon_s$  at the high and low frequencies ends respectively. The maximum value of  $\epsilon_r'$  occurs at angular frequency

$$\omega_m = \frac{1}{\tau} \tan \frac{\pi}{2(1+\delta)} \quad (1.38)$$

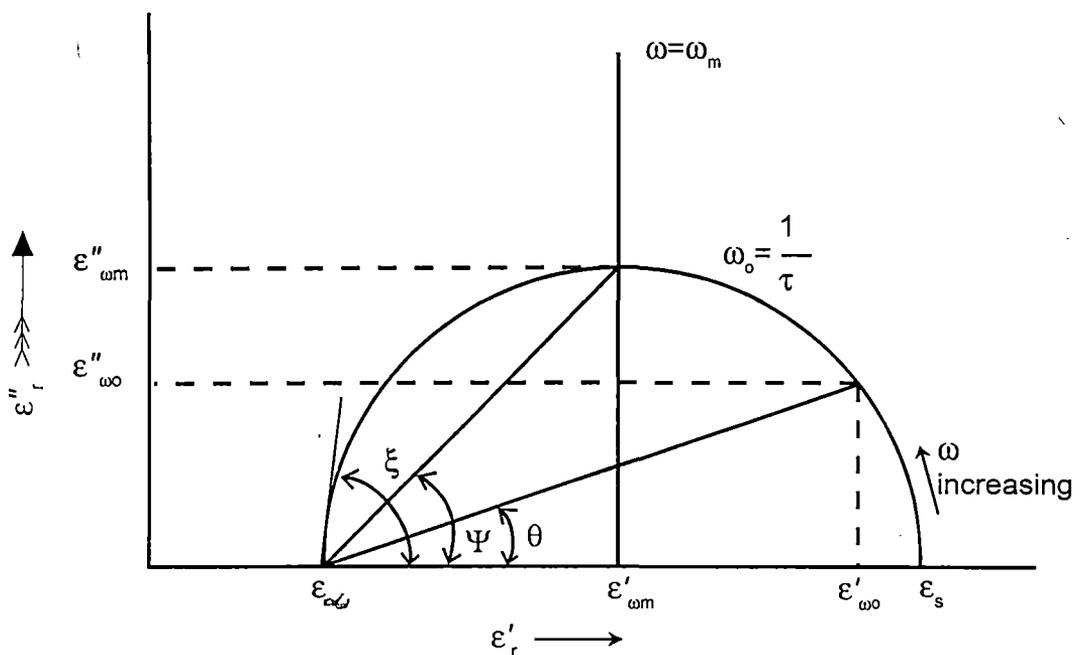


Figure 1.6

Cole-Davidson plot  $\xi = \frac{\pi}{2} \delta$ ;  $\psi = \frac{\pi}{2} \delta/(1+\delta)$ ,  $\theta = \frac{\pi}{4} \delta$ .

The physical significance of this plot is that  $\tau$  can be estimated by using Eq. (1.38) with the knowledge of  $\omega_m$  and  $\delta$ . Also Eq. (1.38) seems to be very successful in representing the behaviour of substances at low temperature. As the temperature increases  $\delta$  tends to 1 showing Debye semicircular arc.

## 1.10. Relaxation Time and Distribution Function

Many experimental results of dipolar liquids were found to satisfy Cole-Cole and Cole-Davidson plots almost quantitatively. The left hand side of both Eqs. (1.35) and (1.37) are associated with two physical constraints [22] and hence it is very difficult to draw any concrete physical conclusion from them. In addition to the semicircular and skewed arc plots a number of circular arc plots could, however, be observed for multiple relaxation times. For this reason the original Debye equations (1.31) and (1.32) can be considered.

$$\frac{\epsilon_r' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \int_0^{\infty} \frac{G(\tau) d\tau}{1 + \omega^2 \tau^2} \quad (1.39)$$

$$\frac{\epsilon_r''}{\epsilon_s - \epsilon_\infty} = \int_0^{\infty} \frac{G(\tau) d\tau}{1 + \omega^2 \tau^2} \quad (1.40)$$

Where  $G(\tau)$  is the distribution function of relaxation times which satisfies the normalisation condition

$$\int_0^{\infty} G(\tau) d\tau = 1 \quad (1.41)$$

$G(\tau)d\tau$  is the fraction of the group of dipoles at a given instant having individual relaxation time in a range  $d\tau$ .

A large number of workers suggested the distribution functions. Wagner [23] and Yager [24] applied the Gaussian error distribution function to observe some of the experimental data satisfactorily i.e.

$$G(\tau) d\tau = b\pi^{-1/2} \exp(-b^2 y^2) dy \quad (1.42)$$

Where 'b' is a constant which determines the breadth of distribution and

$$y = \ln(\tau/\tau_0)$$

where  $\tau_0$  is the most probable relaxation time.

In long chain polar molecules such as alcohols and polymers there are many possibilities of internal rotations bending and twisting each with characteristic relaxation time. In averaging to the macroscopic condition a distribution of relaxation time is observed by Kirkwood and Fous [25].

$$G(\tau) = \frac{1}{2 \cosh y + 2} \quad (1.43)$$

where  $y = \ln(\tau/\tau_0)$

This Eq. (1.43) failed to explain experimental results in most cases. Fous and Kirkwood [26] further observed that the experimental data should be represented by another empirical relation :

$$\epsilon'' = \epsilon_m'' \operatorname{sech}(\beta \ln \omega/\omega_m) \quad (1.44)$$

where  $\beta$  is a distribution parameter.  $\omega_m$  is the angular frequency corresponding to the maximum value of  $\epsilon_m''$  of  $\epsilon''$ . The distribution function is

$$G(\tau) = \frac{\beta}{\pi} \frac{\cos(\beta\pi/2) \cosh(\beta y)}{\cos^2(\beta\pi/2) + \sinh^2(\beta y)} \quad (1.45)$$

A useful empirical relation developed by Cole and Cole [19]. It is given by:

$$G(\tau) d\tau = \frac{1}{2\pi} \frac{\sin \alpha\pi}{\cosh(1-\alpha)\ln(\tau_0/\tau) - \cos \alpha\pi} \quad (1.46)$$

Where  $\alpha$  is a distribution parameter which measures the width of distribution.

Fröhlich [7] derived the distribution function as :

$$G(\tau) = (\epsilon_0 - \epsilon_\infty) \frac{kT}{V_0} \frac{1}{\tau} \text{ if } \tau_0 \leq \tau \leq \tau_1 \quad (1.47)$$

$$\tau_1 = \tau_0 \exp(V_0/kT)$$

$$G(\tau) = 0 \text{ if } \tau < \tau_0 \text{ and } \tau > \tau_1$$

$V_0$  is the width of potential barrier.

A more general form of distribution function has recently been described by Matsumoto and Higasi [27] as

$$G(\tau) = \frac{1}{A\tau^n} \text{ where } 0 < n < \infty \text{ if } \tau_1 < \tau < \tau_2$$

but  $G(\tau) = 0$  if  $\tau < \tau_1$  and  $\tau > \tau_2$  (1.48)

### 1.11. Double Relaxations Due to Molecular and Intramolecular Rotations

For a number of non interacting Debye type dispersions Budo [28] assumed that Debye equation (1.30) can be put into the form :

$$\frac{\epsilon_r^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \sum \frac{c_k}{1 + j\omega\tau_k} \quad (1.49)$$

Where  $c_k$  is the relative contribution for the  $k$ th type of relaxation process, such that  $\sum c_k = 1$ .

For almost all dipolar molecules the relaxation process is involved with two separate broad dispersions of relaxation times  $\tau_1$  and  $\tau_2$ . The relative contributions  $c_1$  and  $c_2$  due to  $\tau_1$  and  $\tau_2$  towards relaxation can also be estimated. Eq. (1.49) is written as

$$\frac{\epsilon_r' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad (1.50)$$

$$\frac{\epsilon_r''}{\epsilon_s - \epsilon_\infty} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (1.51)$$

such that  $c_1 + c_2 = 1$

Bergmann et al [29] used a graphical method to obtain  $\tau_1$  and  $\tau_2$  from Eqs (1.50) and (1.51). The above equations are :

$$Y = c_1 Y_1 + c_2 Y_2 \quad (1.52)$$

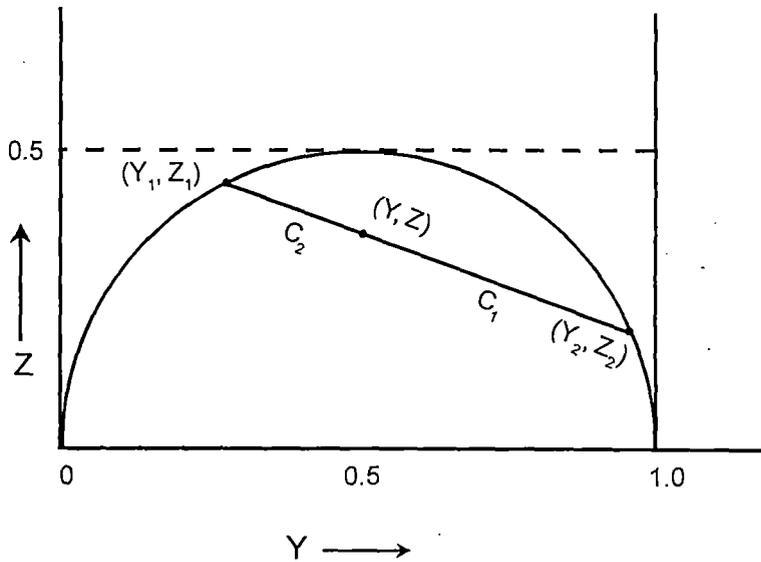
$$Z = c_1 Z_1 + c_2 Z_2 \quad (1.53)$$

where

$$Y = \frac{\epsilon_r''}{\epsilon_s - \epsilon_\infty}, \quad Y_1 = \frac{\omega\tau_1}{1 + \omega^2\tau_1^2}, \quad Z_1 = \frac{1}{1 + \omega^2\tau_1^2}$$

$$Z = \frac{\epsilon_r' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty}, \quad Y_2 = \frac{\omega\tau_2}{1 + \omega^2\tau_2^2}, \quad Z_2 = \frac{1}{1 + \omega^2\tau_2^2}$$

with reference to Figure 1.7.  $Z$  is plotted against  $Y$  for different experimental frequencies  $\omega$  of the applied electric field. An experimental point  $(Y, Z)$  lies on a chord between the points  $(Y_1, Z_1)$  and  $(Y_2, Z_2)$  on the normalised Debye semicircle of Figure 1.7. The selected point divides the chord in the ratio  $c_1/c_2$ . When this ratio is known, the analysis is made by drawing a chord through the experimental points  $(Y, Z)$  such that it is divided in that ratio. The consistent values of  $\tau_1, \tau_2$  and  $c_1, c_2$  are then estimated.



**Figure 1.7**

(Plot of normalised semi circle)

Bhattacharyya et al [30] subsequently simplified the above procedure to calculate  $\tau_1$  and  $\tau_2$  when the relative permittivities were measured at two different frequencies of the applied electric field. Let  $X_1 = \omega\tau_1$ ,  $X_2 = \omega\tau_2$ ,  $\xi = 1/(1+X^2)$  and  $\eta = X/(1+X^2)$ . Eqs. (1.52) and (1.53) becomes :

$$a = c_1 \xi_1 + c_2 \xi_2 \quad (1.54)$$

$$b = c_1 \eta_1 + c_2 \eta_2 \quad (1.55)$$

where  $a = \frac{\epsilon_r' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty}$  and  $b = \frac{\epsilon_r''}{\epsilon_s - \epsilon_\infty}$

From Eqs. (1.54) and (1.55) one obtains

$$c_1 = \frac{(b - aX_2)(1 + X_1^2)}{X_1 - X_2} \quad (1.56)$$

$$c_2 = \frac{(aX_1 - b)(1 + X_2^2)}{X_1 - X_2} \quad (1.57)$$

such that  $X_1 > X_2$

Since  $c_1 + c_2 = 1$  Eqs. (1.56) and (1.57) are solved to get :

$$\frac{1 - a}{b} = (X_1 + X_2) - \frac{a}{b} X_1 X_2 \quad (1.58)$$

to yield  $\tau_1$  and  $\tau_2$ , provided the data are measured at two different known frequencies of the electric field. The  $c_1$  and  $c_2$  can be estimated from Eqs (1.56) and (1.57) respectively.

Higasi et al [31] made a analysis to estimate  $\tau_1$  and  $\tau_2$  of polar liquid molecules in nonpolar solvents graphically under single frequency electric field. Saha et al [32] and Sit et al [33] put forward an analytical method based on single frequency measurement of relative permittivities  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  of polar-nonpolar liquid mixtures of different weight fractions  $w_j$ 's at a given temperature

to get  $\tau_1$ ,  $\tau_2$  and  $c_1$ ,  $c_2$  respectively. Earlier investigation had been made on different long chained molecules like alcohols in nonpolar solvents [34,35] to see the double relaxation phenomena at three different electric field frequencies in terms of relative permittivities. Recently Ghosh et al [36] has derived a formulation in terms of dielectric orientational susceptibilities to obtain  $\tau_1$  and  $\tau_2$  as presented in chapter 2.

## 1.12. Dielectric Loss and High Frequency Conductivity

The dielectric absorption measures the energy dissipation in a dielectric medium due to dielectric relaxation. This is of smaller magnitude and related to dc conductivity of the medium. The effect of Joule's heat arises from the conductivity associated with the loss factor  $\epsilon''$ .

In an ideal dielectric, there is actually no free-ion conduction still Joule heat is produced in dielectric by the drift of electrons or free ions under the applied alternating electric field. Let a potential  $V$  is established between the parallel plates of a condenser having dielectric material of complex dielectric constant  $\epsilon^*$  and  $d$  is the distance of separation between the plates of surface area  $A$ . A charge  $q$  per unit area appears on each plate. An electric displacement  $D$  is then created in the dielectric material. The current density  $i$  is then given by

$$i = \frac{dq}{dt} \quad (1.59)$$

In SI unit,  $q = D$  and  $D = \epsilon_r^* \epsilon_0 E$

Where  $E = \frac{V}{d}$  = intensity of applied electric field and  $\epsilon_0$  = permittivity of

free space =  $8.854 \times 10^{-12} \text{ Fm}^{-1}$

$$\text{or } i = \frac{d}{dt} (\epsilon_r^* \epsilon_0 E) = \epsilon_r^* \epsilon_0 \frac{d}{dt} \left( \frac{V}{d} \right)$$

under the alternating electric field potential  $V = V_0 e^{j\omega t}$  (1.60)

the above equation is :

$$i = \frac{\epsilon_r^* \epsilon_0}{d} \frac{d}{dt} (V_0 e^{j\omega t})$$

$$= j\omega \epsilon_r^* \epsilon_0 E \quad (1.61)$$

The current density  $i$  in terms of hf complex conductivity  $\sigma^*$  is :

$$i = \sigma^* E \quad (1.62)$$

From Eqs (1.61) and (1.62) one gets

$$\sigma^* = j\omega \epsilon_r^* \epsilon_0 \quad (1.63)$$

Murphy and Morgan [37], however, deduced  $\sigma^*$  :

$$\sigma^* = \sigma' + j\sigma'' \quad (1.64)$$

From Eqs. (1.63) and (1.64) one obtains

$$\sigma' + j\sigma'' = \omega \epsilon_0 \epsilon_r'' + j\omega \epsilon_0 \epsilon_r'$$

$$\text{since } \epsilon_r^* = \epsilon_r' - j\epsilon_r''$$

where  $\sigma' = \omega \epsilon_0 \epsilon_r''$  and  $\sigma'' = \omega \epsilon_0 \epsilon_r'$  are the real and imaginary parts of hf complex conductivity  $\sigma^*$ .

### 1.13. Relaxation Mechanism of Polar Solute in Nonpolar Solvent under High Frequency Electric Field

If  $\alpha_i$  and  $\alpha_j$  be the polarisabilities of a nonpolar and polar molecule of molecular weights  $M_i$  and  $M_j$  respectively the Eq (1.17) becomes :

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{N}{3\epsilon_0} f_i \alpha_i + \frac{N}{3\epsilon_0} f_j \alpha_j \quad (1.65)$$

$$\frac{\epsilon_s - 1}{\epsilon_s + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{N}{3\epsilon_0} f_i \alpha_i + \frac{N}{3\epsilon_0} f_j \alpha_j + \frac{N \mu_j^2 f_j}{9\epsilon_0 kT} \quad (1.66)$$

where  $\epsilon_\infty$  and  $\epsilon_s$  are the dielectric constants of the solution at infinite frequency and static electric fields respectively. The mole fractions  $f_i$  and  $f_j$  of the components are

$$f_i = \frac{n_i}{n_i + n_j} \quad \text{and} \quad f_j = \frac{n_j}{n_i + n_j}$$

$n_i$  and  $n_j$  are the number of solvent and solute molecules per unit volume of the solution. From Eqs (1.65) and (1.66) one obtains :

$$\epsilon_s - \epsilon_\infty = \frac{N c_j \mu_j^2}{27 \epsilon_0 kT} (\epsilon_s + 2) (\epsilon_\infty + 2) \quad (1.67)$$

$c_j$  is the concentration of the solute molecule in moles /c.c. Using  $(\epsilon_s - \epsilon_\infty)$  from Eq. (1.32) one gets.

$$\epsilon_r'' = \frac{N c_j \mu_j^2}{27 \epsilon_0 kT} (\epsilon_s + 2) (\epsilon_\infty + 2) \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (1.68)$$

In dilute polar-nonpolar liquid mixture, it is assumed that  $\epsilon_s \simeq \epsilon_\infty \simeq \epsilon_r'$

$$\epsilon_r'' = \frac{N c_j \mu_j^2}{27 \epsilon_0 kT} (\epsilon_r' + 2)^2 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (1.69)$$

$\epsilon_r''$  in Eq (1.69) depends linearly on  $c_j$ . At infinite dilution of  $c_j = 0$ ,  $\epsilon_r'$  may be replaced by  $\epsilon_i$ , the relative permittivity of the solvent used.

$$\epsilon_r'' = \frac{N c_j \mu_j^2}{27 \epsilon_0 kT} (\epsilon_i + 2)^2 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (1.70)$$

The Eq. (1.70) with  $\sigma' = \omega \epsilon_0 \epsilon_r''$  becomes

$$\sigma' = \frac{Nc_j \mu_j^2 (\epsilon_i + 2)^2 \omega^2 \tau}{27kT(1 + \omega^2 \tau^2)} \quad (1.71)$$

The Eq (1.71) may be used to estimate  $hf \mu_j$  in order to arrive at the structural aspects of a dielectropolar liquid molecule.

From Eq (1.31) it can be written as :

$$\epsilon_r' = \epsilon_\infty + \left( \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \right) \quad (1.72)$$

Multiplying both sides by  $\omega \epsilon_0$  and introducing the term  $\sigma'' = \omega \epsilon_0 \epsilon_r'$  and  $\sigma' = \omega \epsilon_0 \epsilon_r''$ , the Eq (1.72) with the help of Eq(1.32) becomes :

$$\sigma'' = \sigma_\infty + \left( \frac{1}{\omega \tau} \right) \cdot \sigma' \quad (1.73)$$

The Eq (1.73) is linear between the variables  $\sigma''$  and  $\sigma'$ . The slope  $1/\omega\tau$  may conveniently be used [38] to estimate  $\tau$  of a polar unit.

#### 1.14. Relaxation Mechanism of Polar - Nonpolar Liquid Mixture from Debye Equation under Low Frequency Electric Field :

The Eq. (1.17) is applied to estimate static  $\mu_s$  under static or low frequency electric field. For a mixture of two liquids : one of the  $i$  th type (nonpolar) and the other of the  $j$  th type (polar) Eq. (1.17) is :

$$\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} \frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{N}{3\epsilon_0} (\alpha_i f_i + \alpha_j f_j + \frac{\mu_s^2}{3kT} f_j) \quad (1.74)$$

$\epsilon_{ij}$  is the relative permittivity of solution. As  $\alpha_i = \alpha_j$  Eq. (1.74) reduces to :

$$\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} V_{ij} = \frac{N\alpha_i}{3\epsilon_0} + \frac{N}{3\epsilon_0} \frac{\mu_s^2}{3kT} f_j$$

$$\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} V_{ij} = \frac{\epsilon_i - 1}{\epsilon_i + 2} V_i + \frac{N\mu_s^2}{9\epsilon_0 kT} f_j \quad (1.75)$$

where  $V_{ij}$  and  $V_i$  are the specific volumes of the solution and solvent respectively.

As  $\epsilon = n_D^2$  where  $n_D$  is the refractive index, Eq (1.75) for a neutral dielectrics is :

$$\frac{n_{Dij}^2 - 1}{n_{Dij}^2 + 2} V_{ij} = \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} V_i \quad (1.76)$$

From Eqs (1.75) and (1.76) one gets :

$$\left( \frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} - \frac{n_{Dij}^2 - 1}{n_{Dij}^2 + 2} \right) = \left( \frac{\epsilon_i - 1}{\epsilon_i + 2} - \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) \frac{V_i}{V_{ij}} + \frac{N}{3\epsilon_0} \frac{\mu_s^2}{3kT} \frac{f_j}{V_{ij}}$$

$f_j/V_{ij} = c_j$  is the molar concentration per unit volume. Since  $V_i/V_{ij} \rightarrow 1$  at infinite dilution, the above equation becomes :

$$\left( \frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} - \frac{n_{Dij}^2 - 1}{n_{Dij}^2 + 2} \right) = \left( \frac{\epsilon_i - 1}{\epsilon_i + 2} - \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) + \frac{N\mu_s^2}{9\epsilon_0 kT} c_j \quad (1.77)$$

which is Debye equation for polar-nonpolar liquid mixture. At extremely low concentration of  $c_j = 0$  Eq. (1.77) is used to compute  $\mu_s$ . The disadvantage of this method is that it could not be applied for a concentrated solution. The different parameters like  $\epsilon_{ij}$ ,  $n_{Dij}$ ,  $\rho_{ij}$  were to be determined at infinite dilution by extrapolation technique.

## 1.15. Extrapolation Technique and Guggenheim Equation

The extrapolation technique was usually made to smooth out the curve through the experimentally measured relaxation parameters. The errors involved in the measurement were estimated by Hedestrand [39], Cohen Henrique [40] and others [41, 42]. They suggested various types of extrapolation to obtain the desired parameters including polarisation at infinite dilution. But all the methods are not free from inherent difficulties to locate the exact magnitudes of the quantities required to be measured. The difficulty arises to get  $(\delta\rho_{ij}/\delta f_j)f_j \rightarrow 0$  and  $(\delta n_{Dij}^2/\delta f_j)f_j \rightarrow 0$  from the graphical extrapolation. Böttcher [42], however, compared the results obtained from different extrapolation methods to compute  $\mu_s$ . A marked difference was, however, noticed in a solution of phenol in benzene to calculate  $\mu_s$  by different extrapolation techniques.

Higasi [43] put forward an empirical formula for the easy determination of  $\mu_s$ :

$$\mu_s = \beta (\Delta\varepsilon/f_j)^{1/2} \quad (1.78)$$

where the constant  $\beta$  depends entirely on the solvents used. As for example  $\beta = (0.90 \pm 0.10) D$  in  $C_6H_6$ . Krishna and Srivastava [44] used the following relation:

$$\mu_s = \beta (d\varepsilon_{ij}/df_j)^{1/2} \quad (1.79)$$

to compute  $\mu_s$  of some polar solutes in liquid state. Here  $(d\varepsilon_{ij}/df_j)$  is the slope of  $\varepsilon_{ij}$  vs.  $f_j$  curve. It is observed that Eq. (1.79) is valid in the straight part of  $\varepsilon_{ij}-f_j$  curve. Here,  $\beta = 0.828 D$ .

Again, Srivastava and Chandra [45] obtained different values of  $\beta$  for different solutes. A question, therefore arises for the validity of Higasi's method. Jaiprakash [46], however, showed that Eq (1.79) is a special case of Eq (1.77) when  $\varepsilon_{ij} \simeq 1$ . But no such polar-nonpolar liquid mixture is available for which  $\varepsilon_{ij} \simeq 1$ . Higasi's method is thus not a universal one to locate  $\mu_s$  at all concentrations.

Guggenheim [47] however, introduced fictitious atomic polarisability  $\gamma'_{ja}$  of the polar molecule. It was, further, assumed that  $\gamma'_{ja}$  is equal to atomic polarisability  $\gamma_{ja}$  so that they cancel each other to make the solution free from atomic polarisation. From Eq. (1.77) a curve might be drawn with  $3(\epsilon_{ij} - n_{Dij}^2) / (\epsilon_{ij} + 2)(n_{Dij}^2 + 2)$  against  $c_j$ . The slope of the curve was used to obtain  $\mu_s$ . Writing  $\Delta = (\epsilon_{ij} - n_{Dij}^2) - (\epsilon_i - n_{Di}^2)$  in Eq. (1.77) one obtains.

$$\mu_s^2 = \frac{9\epsilon_0 kT}{N} \cdot \frac{3}{(\epsilon_i + 2)(n_{Di}^2 + 2)} \cdot \frac{\Delta}{c_j} \quad (1.80)$$

taking  $\epsilon_i = n_{Di}^2$  [48,49]. Smith [50], however, introduced the concept of weight fraction  $w_j$  in place of  $c_j$

$$c_j = \rho_{ij} w_j / M_j \quad (1.81)$$

Guggenheim [51] also accepted Eq (1.81) to formulate the equation

$$\mu_s^2 = \frac{9\epsilon_0 kT}{N} \cdot \frac{3}{(\epsilon_i + 2)^2} \cdot \frac{M_j}{\rho_i} \left( -\frac{\Delta}{w_j} \right) \quad (1.82)$$

where

$$\frac{\Delta}{w_j} = \left[ \left( \frac{\delta\epsilon_{ij}}{\delta w_j} \right) w_j \rightarrow 0 - 2n_{Di} \left( \frac{\delta n_{Di}^2}{\delta w_j} \right) w_j \rightarrow 0 \right] \quad (1.83)$$

In Eq (1.82),  $M_j$  is the molecular weight of a polar liquid and  $\rho_i$  is the density of the nonpolar solvent. The  $\epsilon_{ij} - w_j$  and  $n_{Di}^2 - w_j$  curves are extrapolated at  $w_j \rightarrow 0$  to estimate  $\mu_s$  from Eqs (1.82) and (1.83). Hence a large number of data of  $\epsilon_{ij}$  and  $n_{Dij}^2$  for different  $w_j$ 's for a given solute-solvent mixture were experimentally measured. Jaiprakash [46] later on deduced

$$\mu_s^2 = \frac{27\epsilon_0 M_j kT}{N\rho_i} \left( -\frac{\delta X_{ij}}{\delta w_j} \right) w_j \rightarrow 0 \quad (1.84)$$

where

$$\left(\frac{\delta X_{ij}}{\delta w_j}\right)_{w_j \rightarrow 0} = \left[ \frac{1}{(\epsilon_i + 2)^2} \left(\frac{\delta \epsilon_{ij}}{\delta w_j}\right)_{w_j \rightarrow 0} - \frac{2n_{Di}}{(n_{Di}^2 + 2)} \left(\frac{\delta n_{Di}}{\delta w_j}\right)_{w_j \rightarrow 0} \right]$$

from Eq (1.80) to obtain  $\mu_s$ . The Eq (1.84) reduces to Guggenheim equation Eq. (1.82) when  $\epsilon_i = n_{Di}^2$ . Guggenheim equation is thus a special case of Debye equation (1.77). The Eq (1.84) is valid for low concentrated solution of polar liquid of low  $\mu_s$  in non-polar solvent. The evaluation of  $\mu_s$  depends on the theory of extrapolation of  $\epsilon_{ij}$ ,  $n_{Dij}$ ,  $\rho_{ij}$ , of polar-nonpolar liquid mixture with  $w_j$ 's of solute at any given temperature. For trimethyl amine in benzene Lefevre and Smyth [41] applied the technique of ratio of finite differences, and Guggenheim [51], on the other hand, used his personal judgement on the measured parameters against  $w_j$ 's to obtain  $\mu_s$ 's of 0.91D and 0.83D respectively. Such affairs often put the experimentalists to choose as to what method of extrapolation is needed to get accurate  $\mu_s$  of a dipolar liquid in a given solvent.

Recently, Ghosh et al [52], extended the theory of polar-nonpolar liquid mixture based on Debye and Smyth model as Guggenheim equation is derived from Debye's equation. This theoretical development has been described in Chapter 2.

### 1.16. Gopalakrishna's Method to Estimate $\tau$ and $\mu$

Debyes' equation (Eq (1.30) for complex dielectric constant  $\epsilon_{ij}^*$  of a polar non-polar liquid mixture is :

$$\frac{\epsilon_{ij}^* - 1}{\epsilon_{ij}^* + 2} = \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} + \frac{n\mu^2}{9\epsilon_0 kT} \frac{1}{1 + j\omega\tau} \quad (1.85)$$

Equating the real and imaginary parts from both sides of Eq (1.85) one gets :

$$\frac{\epsilon_{ij}''^2 + \epsilon_{ij}' + \epsilon_{ij}''^2 - 2}{(\epsilon_{ij}' + 2)^2 + \epsilon_{ij}''^2} = \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} + \frac{n\mu^2}{9\epsilon_0 kT} \frac{1}{1 + \omega^2\tau^2} \quad (1.86)$$

$$\frac{3\varepsilon_{ij}''}{(\varepsilon_{ij}' + 2)^2 + \varepsilon_{ij}''^2} = \frac{n\mu^2}{9\varepsilon_0 kT} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (1.87)$$

writing  $(\varepsilon_{\infty ij} - 1) / (\varepsilon_{\infty ij} + 2) = P$ ,  $\frac{\varepsilon_{ij}''^2 + \varepsilon_{ij}' + \varepsilon_{ij}''^2 - 2}{(\varepsilon_{ij}' + 2)^2 + \varepsilon_{ij}''^2} = x$

and  $3\varepsilon_{ij}'' / \{(\varepsilon_{ij}' + 2)^2 + \varepsilon_{ij}''^2\} = y$ , the above Eqs (1.86) and (1.87) can be put into a form :

$$x = P + \left(\frac{1}{\omega\tau}\right) \cdot y \quad (1.88)$$

which is a straight line between x and y whose slope  $(1/\omega\tau)$  may be used [53] to get  $\tau$  of a dipolar solute.

Since  $n = \frac{N\rho_{ij}}{M_j} w_j$ , the number of dipoles per unit volume, Eq (1.86) reduces to

$$x = P + K\rho_{ij} \cdot w_j \quad (1.89)$$

where  $K = \frac{N\mu^2}{9\varepsilon_0 kTM_j} \cdot \frac{1}{1 + \omega^2\tau^2}$ .

The Eq (1.89) is evidently a linear equation between the variables x and  $w_j$ . The slope  $K\rho_{ij}$  may be used [53] to estimate  $\mu_j$  of a dipolar liquid molecule under hf electric field.

### 1.17. Eyring's Rate Theory

According to Eyring [54] the dipole rotation is like a chemical rate process in which the dipole rotates from one equilibrium position to the other. The process requires an activation energy sufficient to overcome the energy barrier separating two mean equilibrium positions. The average time required for single rotation involved is known as relaxation time  $\tau$  given by :

$$\tau = \frac{h}{kT} e^{(\Delta F_{\tau}/RT)} \quad (1.90)$$

where  $\Delta F_{\tau}$  is the free energy of activation. From thermodynamics one gets

$$\Delta F_{\tau} = \Delta H_{\tau} - T\Delta S_{\tau} \quad (1.91)$$

where  $\Delta H_{\tau}$  and  $\Delta S_{\tau}$  are enthalpy and entropy of activation due to dielectric relaxation. So from Eqs (1.90) and (1.91) it is shown that

$$\ln(\tau T) = \ln A' + \frac{\Delta H_{\tau}}{R} \cdot \frac{1}{T} \quad (1.92)$$

where  $A' = \frac{h}{k} e^{(-\Delta S_{\tau}/R)}$  (1.93)

( $h/k$ ) is the ratio of Plancks' constant to Boltzmann constant and  $R$  is gramme molar gas constant.  $\Delta H_{\tau}$  is obtained from the slope of linear equation of  $\ln(\tau T)$  against  $1/T$ . With  $\Delta H_{\tau}$  and known  $\tau$ ,  $\Delta S_{\tau}$  and  $\Delta F_{\tau}$  could, however, be estimated from Eqs (1.93) and (1.91) respectively.

Like dielectric relaxation, the viscous flow of the liquid may be considered as a rate process. Viscous flow is, however, involved with the translational as well as rotational motions of the molecules, with an activation energy to pass over a potential barrier. We can write from Eyring's [54] rate theory :

$$\eta = \frac{hV}{N} e^{(\Delta F_{\eta}/RT)} \quad (1.94)$$

where  $\eta$  and  $V$  are the coefficient of viscosity and the molar volume of the liquid respectively.  $\Delta F_{\eta}$ , the free energy of activation for viscous flow is :

$$\Delta F_{\eta} = \Delta H_{\eta} - T\Delta S_{\eta} \quad (1.95)$$

The Eq. (1.94) with the help of Eq. (1.95) becomes

$$\eta = \frac{hV}{N} e^{-(\Delta S_{\eta}/R)} \cdot e^{(\Delta H_{\eta}/RT)} \quad (1.96)$$

$$\ln\eta = \ln B + \frac{\Delta H_{\eta}}{R} \cdot \frac{1}{T} \quad (1.97)$$

$\Delta H_{\eta}$  can be obtained from the slope of the linear variation of  $\ln\eta$  with  $1/T$  of Eq.(1.97). The corresponding  $\Delta S_{\eta}$  and  $\Delta F_{\eta}$  from Eqs. (1.96) and (1.95) could readily be obtained.

The approximate linearity of  $\ln(\tau T)$  against  $1/T$  of Eq (1.92) has been used in this thesis in many chapters to estimate the thermodynamic energy parameters of dipolar solutes in nonpolar solvents. Such study provides the information about molecular association in addition to stability or unstability of the molecules.

### 1.18. Relaxation Time and its Relationship with Viscosity

The torque acting on a dipolar molecule in a nonpolar solvent under electric field [1] is counter balanced by frictional force. This force is proportional to angular velocity of the polar molecule. The torque is given by:

$$M = \xi \frac{dv}{dt} \quad (1.98)$$

where  $\xi$  is a frictional coefficient depending on the surrounding medium.

The dipole may be assumed [1] a sphere of radius 'a' immersed in a medium of internal viscosity  $\eta_{int}$ . The frictional coefficient is according to Stokes' formula :

$$\xi = 8\pi\eta_{int} a^3 \quad (1.99)$$

The dipole in liquid state behaves as Brownian particle obeying a relation between  $\tau$  and  $\xi$  :

$$\tau = \frac{\xi}{2kT} \quad (1.100)$$

From Eqs (1.99) and (1.100) it leads

$$\tau = \frac{4\pi a^3}{kT} \cdot \eta_{int} \quad (1.101)$$

Debye [1] further considered the macroscopic viscosity  $\eta$  in place of  $\eta_{int}$  of the medium. So Eq (1.101) becomes :

$$\tau = \frac{4\pi a^3}{kT} \cdot \eta \quad (1.102)$$

From measured  $\tau$  and  $\eta$  at a certain temperature  $T$ , the size of the rotating unit may be estimated from Eq. (1.102) to arrive at the structural concept of a dipolar liquid molecule.

The Eq (1.102) was modified by Perrin [55] for ellipsoidal dipolar molecule. Thus  $\mu$  has components  $\mu_a$ ,  $\mu_b$  and  $\mu_c$  along three principal axes  $a$ ,  $b$ ,  $c$  of the ellipsoid. The Eq (1.17) becomes.

$$\frac{\epsilon_r^* - 1}{\epsilon_r^* + 2} \cdot \frac{M}{\rho} = \frac{N}{3\epsilon_0} \left[ \alpha + \frac{1}{3kT} \left\{ \frac{\mu_a^2}{1+j\omega\tau_a} + \frac{\mu_b^2}{1+j\omega\tau_b} + \frac{\mu_c^2}{1+j\omega\tau_c} \right\} \right] \quad (1.103)$$

where  $\tau_a$ ,  $\tau_b$ ,  $\tau_c$  are the relaxation times of the dipole along the three axes. Moreover, the dipole may act along one of the ellipsoidal axes. In such case  $\tau$  is given by Fischer and Frank [56].

$$\tau = \frac{4\pi abc f}{kT} \eta_{int} \quad (1.104)$$

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

## 1.19. Dielectric Relaxation of Polar Liquid Molecules in Nonpolar Solvent under Radio Frequency Electric Field

Under a radio frequency (rf) electric field  $E = E_0 e^{j\omega t}$  heat developed in a polar-nonpolar liquid mixture is due to combined effect of dielectric loss and joule heating. But rf conductivity often provides an information of conduction current in polar dielectrics.

Sen and Ghosh [57,58] subsequently put forward a theory of rf conductivity based on the assumption of existence of free ions in polar dielectrics. The conduction current due to free ions plays a prominent role to yield conductivity rather than the displacement current as suggested by Murphy and Morgan [37] in hf electric field. From Murphy - Morgan [37] relation hf conductivity  $\sigma'$  is written as :

$$\sigma' = \frac{1}{4\pi} \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \cdot \omega^2 \tau \quad (1.105)$$

using  $\tau = 4\pi\eta a^3 / kT$  from Eq (1.102) we have :

$$\sigma' = \frac{\epsilon_s - \epsilon_\infty}{kT} \cdot \omega^2 a^3 \eta \quad (1.106)$$

The factors  $(\epsilon_s - \epsilon_\infty)$  and  $\eta/T$  decrease with temperature and  $\sigma'$ , therefore, should decrease with temperature. But the experimental results show that the rf conductivity, increases with temperature like electrolyte. The conductivity in electrolytes is mainly due to free ions and Walden's rule is valid. This rule states that the product of equivalent conductance at infinite dilution and the viscosity of the solvent is approximately constant. A similar relation is observed in case of polar dielectric liquids where  $\sigma'\eta = \text{constant}$ .

## 1.20. A Brief Review of the Previous Works

From 1850 to 1904, a large number of workers [12,13, 59-61] inferred the structural aspects of dipolar gases and liquids from dielectric polarisation study. The observations are found in good agreement of gas kinetic values.

The radii of alcohols, ketones and glycerins were determined by Mizushima [62,63] from the Debye theory. The radii were found to be smaller than the gas kinetic value maintaining the same order. Stranthan [64] estimated  $\mu$  for methyl, ethyl and amyl alcohols in benzene from the intercepts of molar volume against concentration curve.  $\mu$ 's were found to be independent of temperature in accordance with Debye theory. Debye [1] explained the anomalous dispersion pointed out by Drude [61], under rf electric field by the polarity of the molecules.  $\epsilon''$ 's under 4.3 meter wavelength electric field were measured by Fischer and Frank [56] to estimate  $\tau_j$  of aromatic halides. The shorter  $\tau_j$ 's were claimed for the rotation of  $\text{CH}_2 - \text{X}$  group around their bond ring. But the theory could not explain the behaviour of alcohols for the strong interaction of  $-\text{OH}$  groups due to formation of hydrogen bonding. Goss [65] analysed the dielectric polarisation of some polar-nonpolar liquid mixtures to show the solvent effect under anisotropic electric field for non-spherical polar molecules. The study further showed the induction effect related to the dielectric constant of the liquids.

Onsager [66], Plumley [67] and Pao [68] interpreted the origin of conduction in dielectric liquids. Even the purest hydrocarbons such as hexane contain a small number of ions. Ryhel [69] and Eck [70] showed that ionic conduction occurs due to existence of ionic cluster in the liquids. Whiffen and Thomson [71] obtained  $\tau_j$  of toluene, o-xylene, p-cyanine to predict the size of the molecules. Jackson and Powles [72] estimated  $\tau_j$  of polar molecules in  $\text{C}_6\text{H}_6$  and paraffin. The observation showed that  $\tau_j$ 's depends on the viscosity of solvents. Schallamach [73] studied the relaxation phenomena in polar molecules under rf electric field. The molecular rearrangement takes place in liquid state under single relaxation process. Mecke and Reuter [74] measured

permittivities of normal alcohols, and phenols in  $C_6H_6$ ,  $CCl_4$  and cyclohexane at  $20^\circ C$  and  $40^\circ C$ . The molecular associations are inferred from their measured  $\mu$ 's. The dielectric absorption measurement of aliphatic chlorides and alcohols were performed by Kremmling [75]. It was found difficult to sort out the effects of molecular association and H-bond formation onto change in shape of molecules. Further, the internal rotation, multiple relaxation times etc. could, however, be predicted.

Jaffe and Lemay [76] concluded that dielectric liquids gave conduction current under breakdown voltage. The presence of positive ions are noticed by Green [77] in dielectric liquids due to dissociation of impurity molecules by external cosmic rays.  $\tau$ 's were found by Curties et al [78] in different solutions and in pure liquids although they have same viscosity.  $\tau_j$ 's were estimated by Poley [79] from  $\epsilon''$ 's measurement for monosubstituted benzenes. The increase of  $\tau_j$  occurs with molecular size. Müller [80], however, calculated the low molecular radii in comparison to other methods. Dielectric measurements on pure normal propyl to decyl alcohols were carried out by Garg and Smyth [81] to show three different  $\tau_j$ 's for three distinct dispersive regions. The larger  $\tau_j$ 's are associated with polymeric clusters formation by the strong H-bonding between -OH groups. The intermediate  $\tau_j$ 's were attributed to the rotation of free alcohol molecules. A significant contribution to obtain  $\tau_j$  and  $\mu_j$  of polar liquid in nonpolar solvent under GHz electric field was made by Gopalakrishna [53]. The main advantage of this method is to know the density of the pure solvent. Schellman [82] studied the associations in saturated dielectric liquids. Srivastava and Vershri [83] explained the variation of  $\epsilon'$  of binary polar mixtures with concentration  $c$  and temperature  $TK$  by :

$$\epsilon' = \left(1 + \frac{m}{T}\right) + \left(p + \frac{q}{T^{1/2}}\right) c + zc^2$$

where  $p$ ,  $q$ ,  $l$ ,  $m$  and  $z$  are constants. The relation was tested for mixtures of water-methyl and water-butyl alcohols.

Hart and Mungali [84] observed the conduction current in chlorobenzene after distillation. Higasi et al [85] analysed the experimental data of n-alkyl bromide in liquid state in terms of distribution of  $\tau$ 's between two Fröhlich's [7] limiting  $\tau$ 's. The lower  $\tau_j$  signifies the internal rotation of  $-\text{CH}_2\text{Br}$  group while larger  $\tau$ 's for whole molecular rotation. Bergmann et al [29] estimated  $\tau_1$  (smaller) and  $\tau_2$  (larger) by employing a graphical method in complex plane for diphenyl ether, anisol, and o-dimethoxy benzene. The results are interpreted as the intramolecular and molecular rotations of polar molecules respectively. Krishnaji and Mansingh [86] studied the dielectric relaxation process of alkyl cyanides and alkythiols. The  $\tau_j$ 's increase with the size of the molecules. Froster [87] explained the conduction in aliphatic hydrocarbons by the presence of impurities of trace polar or trapped electrons at the electrode surfaces. Experimental evidence thus showed the electronic nature of conduction in unsaturated hydrocarbons. Sinha et al [88,89] predicted the temperature dependence of  $\tau$  and  $\mu$  of some polar molecules in nonpolar solvent. The viscosity dependence of  $\tau_j$  on T is  $\tau_j T / \eta^\gamma = \text{constant}$  is, however, predicted.  $\gamma$  is the ratio of enthalpies of activation of dielectric relaxation and viscous flow. Barbenza [90] studied the dielectric behaviour of methyl alcohol in the temperature range of  $5^\circ\text{C}$  to  $55^\circ\text{C}$  under the electric fields of wavelengths 5cm to 15cm. The results were explained by single relaxation process. The measurements showed activation energy of 3.4 K cal / mole from rate process [54]. Adamczewski and Jachym [91] concluded that conductivity of organic liquids is a function of temperature. Very low values of  $\sigma$  were also found in nonpolar liquids. Jaiprakash [92] estimated  $\tau_j$  of five almost spherical polar molecules in nonpolar solvent in good agreement with Gopalakrishna's method [53]. Bhattacharyya et al [30] analysed phenetole, aniline and orthochloro aniline in terms of molecular and intramolecular  $\tau_2$  and  $\tau_1$  from the equation of Bergmann et al. [29].

Non-rigid molecules having two  $\tau$ 's and average  $\tau$  could, however, be obtained by Higasi et al [31] based on single frequency measurement technique.

A crude estimation of  $\tau_1$  and  $\tau_2$  can be had with a suitable equation derived from Debye model. The existence of natural charge carriers in liquids of two kinds of mobilities  $\mu^+$  and  $\mu^-$  was, however, tested by Loheneysen and Nageral [93]. The direct evidence of ionic conduction in polar dielectrics was found by Gaspared and Gosse [94] when the electrodes were membraned by teflon.

Crossley et al [95] and Glasser et al [96] measured concentration variation of  $\epsilon'$  and  $\epsilon''$  of aliphatic alcohols in n-heptane at 25°C under hf electric fields of different wave lengths. The lower  $\tau_j$ 's are due to rotation of -OH groups, the intermediate  $\tau_j$ 's for the monomer or small multimers formed by polar chain, while the shortest  $\tau_j$ 's in low frequency are associated with H-bonded structure. The  $\epsilon'$  and  $\epsilon''$  of methanol, ethanol, 2-propanol, 1-butanol, 3-methyl-1 butanol in  $C_6H_6$  for different  $w_j$  under X-band electric field was measured by Purohit and Sharma [97]. The marked increase of  $\tan \delta$  curves against  $w_j$ 's in the region  $0.03 \leq w_j \leq 0.04$  showed the formation of dimers except for 1-butanol. A similar observation on  $\tan \delta$  vs.  $w_j$  curve, was, however, carried out by Vyas and Vashisth [98] in case of four aliphatic alcohols and their binary mixtures and the mixtures of alcohols with DMF and 2-fluoroaniline in benzene for different  $w_j$  under 3 cm wave length electric field at 30°C. The alcohols + DMF mixtures showed complex formations at a very low concentration. The study of alcohol + 2 fluoro-aniline, however, indicates dissociation effects.

The relaxation parameters of Trifluoroethanol and Trifluoro acetic acid in dilute benzene solution was studied by Purohit et al [99]. The results could, however, be explained by strong H-bonding in the compounds. Hydrogen bonding plays a vital role in n-butylamine - n-butanol and in n-propylamine - n propanol mixtures as observed by Tripathy et al [100]. A number of workers [101-106] estimated  $\tau$  from the number density 'n' of free ions, radius 'a' of rotating units, activation energy  $\Delta E_\tau$  and thermodynamic energy parameters  $\Delta H_\tau$ ,  $\Delta S_\tau$ ,  $\Delta F_\tau$  for some straight chain alcohols, anilines, benzyl chloride, acetone under rf electric field at different temperatures.  $\tau_j$ 's are observed to increase with the number of

C-atom of dipolar molecules.  $\Delta E_\tau$  increases with the size of the molecules. The ratio of activation energies for electronic conduction and viscous flow is greater than unity for associative liquids while reverse is true for non associative liquids. The different  $\Delta F_\tau$  signifies the breaking of the cluster of molecules. It is greatly affected by the addition of impurity such as water. The relaxation parameters from the rf conductivity  $\sigma$  has been used to study the structure of liquids. Other group of workers, [107-111] measured relative permittivities  $\epsilon'$  and  $\epsilon''$  of some substituted toluidines, para compounds, diphenylene oxide, chloral and ethyl trichloro acetate in benzene, dioxane, n-heptane at various  $w_j$ 's and  $t^\circ\text{C}$  under nearly 3cm wavelength electric field to estimate  $\tau_j$ ,  $\mu_j$  and thermodynamic energy parameters. The observed results were explained in terms of molecular associations of the polar liquid molecules. Rajyam et al [112] studied the dielectric dispersion of glycerol and diethylene glycol under rf, mw and uhf electric fields at  $80^\circ\text{C}$  and confirmed the Cole-Davidson type of dispersion [20,21]. Mulechi et al [113] observed the self association of tertiary butyl alcohol and developed a method for simultaneous determination of three independent values of free energy of self association from experimental data.

Acharyya and Chatterjee [114] and Acharyya et al [115] estimated relaxation parameters  $\tau_j$ ,  $\mu_j$ ,  $\Delta H_\tau$ ,  $\Delta S_\tau$ ,  $\Delta F_\tau$  of some interesting polar liquid molecules in  $\text{C}_6\text{H}_6$  and  $\text{CCl}_4$ . High concentration  $\sigma$  data of a polar-nonpolar liquid mixture is liable to yield  $\mu_j$  of dimer formation.  $\sigma$  in low concentration region behaves linearly with  $w_j$  and gives  $\mu_j$  due to monomer formation. They also estimated  $\mu_{\text{theo}}$ 's to study the structural conformations. Agarwal [116] measured  $\epsilon'$  and  $\epsilon''$  of n-butyl chloride, chlorobenzene and tertiary butyl alcohol in  $\text{C}_6\text{H}_6$  at  $32^\circ\text{C}$  under 9.96 GHz electric field to estimate  $\tau_j$ . It is observed that  $\tau_j$  is influenced by structural configuration in the following manner :

$$\tau_{\text{linear}} > \tau_{\text{planer}} > \tau_{\text{spherical}}$$

Madan [117] studied the dielectric absorption of thiophene, acetone, benzophenone and their mixtures in mw electric field over a wide range of

temperatures. The experimental and theoretical  $\tau_j$ 's were found to agree within the experimental error. Gandhi and Sharma [118] determined  $\tau_0$ ,  $\tau_1$  and  $\tau_2$ , distribution parameters of isobutyl - methacrylate and allyl-methacrylate and their mixtures in  $C_6H_6$ . The observed results reveal the intramolecular and molecular rotations.

Guided by the work of Acharyya et al [115], Murthy et al [38] added a new dimension in the theoretical formulations by which simultaneous determination of  $\tau_j$  and  $\mu_j$  of a polar liquid in nonpolar solvent can be made. Makosz [119] calculated  $\mu$  of some ellipsoidal shaped dipolar liquids in nonpolar solvents at 25°C from the formula derived from Onsager's equation. Sharma and Sharma [120], Sharma et al [121] estimated  $\epsilon'$  and  $\epsilon''$  of dilute solutions of dimethyl sulphoxide (DMSO) in  $C_6H_6$ ,  $CCl_4$  and of DMF + DMSO mixtures in  $C_6H_6$  in temperature range of 25°C to 40°C under 9.174 GHz electric field to estimate  $\tau_j$ ,  $\mu_j$ ,  $\Delta H_\tau$ ,  $\Delta S_\tau$ ,  $\Delta F_\tau$  of dielectric relaxation and  $\Delta H_\eta$ ,  $\Delta S_\eta$  and  $\Delta F_\eta$  for viscous flow. The monomer structure i.e. the solute-solvent association of DMSO in solutions have been inferred. The solute-solute formation between DMF and DMSO increases with the enrichment of DMF in DMSO to a maximum value around 17 mole % of DMSO at all temperatures. A similar study on acetophenone and DMSO and their mixtures in  $C_6H_6$  was done by Singh and Sharma [122] under 9.33 GHz electric field in the temperature range of 20°C to 40°C. Non linear behaviour of  $\tau$  reveals the presence of solute-solvent and solute-solute molecular associations.

Saha and Acharyya [123] estimated the same parameters of NMA, DMF, DMA in  $C_6H_6$ , dioxane and  $CCl_4$  by using the measured values of  $\epsilon'$  and  $\epsilon''$  [124-128] in a newly developed methodology. The ternary mixtures of DMF +  $CH_3OH$ , DMF + acetonitrile, DMF + acetone in  $C_6H_6$  were studied by them [129]. Higher and lower values of  $\mu_j$ 's arise for the monomer or dimer formations. The high or low concentration  $\sigma_{ij}$ 's with  $w_j$ 's, although  $\sigma_{ij}$ 's behave linearly with lower  $w_j$ 's yield  $\mu_j$ 's for dimer or monomer formations.  $\mu_{jk}$ 's of polar-polar

mixture (jk) in solutions decreases with  $t^{\circ}\text{C}$  which is supported by solute-solute molecular association.  $\mu_{\text{theo}}$ 's from the available bond angles and bond moments of substituent polar groups attached to the parent molecules were estimated in agreement with measured hf  $\mu_j$ 's to shed much light on the inductive and mesomeric moments of polar groups. Puranik et al. [130] measured static  $\epsilon_0$  and hf dielectric constants  $\epsilon_{\infty}$  and activation energies of ethanol and ethelene glycol (EG) from 10 MHz to 10 GHz at different temperatures. Activation energy of EG is found to be larger than that of ethanol indicating molecular association due to strong H-bonding in polyhydric alcohols.

Saha et al [32] used the concentration variation of the measured  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{\text{oiij}}$ ,  $\epsilon_{\infty ij} = n_{\text{Dij}}^2$  of some disubstituted anilines and benzenes in  $\text{C}_6\text{H}_6$  and  $\text{CCl}_4$  under nearly 3 cm wave length electric field at  $35^{\circ}\text{C}$  [131-133] to estimate  $\tau_1$ ,  $\tau_2$  and  $\mu_1$ ,  $\mu_2$  due to rotation of flexible polar groups attached to the parent molecules and whole molecules themselves. The results are explained on the basis of polarity, size of the molecules and solvent environment around the solute molecules. Difference between  $\mu_{\text{theo}}$ 's and experimental  $\mu$ 's might be due to non consideration of inductive and mesomeric effects of the substituent polar groups of the molecules. The values of  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{\text{oiij}}$  and  $\epsilon_{\infty ij}$  measured by Srivastava and Chandra [134] of monosubstituted anilines at different  $\omega_j$ 's at  $35^{\circ}\text{C}$  in  $\text{C}_6\text{H}_6$  under electric field frequencies of 2.02, 3.86 and 22.06 GHz were used by Sit et al [33] to detect the mono or double relaxation phenomena in them. Elsayed et al [135] estimated the  $\Delta H_{\tau}$ ,  $\Delta S_{\tau}$ ,  $\Delta F_{\tau}$  from the temperature variation of  $\tau_j$ 's of solid and liquid phase of Ag Sb Te<sub>2</sub> under  $10^6$  Hz electric field. The strength of dielectric dispersion  $\Delta\epsilon'$  was observed to be proportional to number of dipoles per unit volume.  $\tau_j$ 's decrease with temperature due to increase of thermal agitations to weaken the intermolecular forces. The dielectric relaxation studies of four pure nicotines and their quartarnary mixtures were made by Jangid et al [136] to draw the sufficient information about intramolecular and intermolecular interactions of solute-solvent (monomer) and solute-solute (dimer) formations.  $\epsilon'$ ,  $\epsilon''$  and  $\tan \delta$  of  $\text{CH}_3\text{OH}$ , methyl acetate, methyl formate,

ethyl formate and acetone in  $C_6H_6$  under 10.3 GHz electric field measured at 308 K by Varadarajan and Rajagopal [137] established the rotation of — OH group about the whole molecule. They [138] observed dipole-dipole interaction and molecular association of five monoalcohols in benzene.

The measured  $\epsilon'$ ,  $\epsilon''$ ,  $n_D^2$  of  $CH_3OH$  + ketone, methanol + nitrile under 5.70, 9.70 and 32.97 GHz electric fields are used [139] to obtain  $\tau$  and  $\mu$ . The molecular shapes, sizes and structures are explained by H-bonding. Vyas and Rana [140] measured  $\epsilon'$  and  $\epsilon''$  of chlorobenzene, nitrobenzene, orthochloro aniline and their mixtures under 9.1 GHz, 10 KHz and optical frequency at 30°C to estimate  $\tau$  and thermodynamic energy parameters. The study indicates solute-solvent and solute-solute molecular associations. Sengwa and Kaur [141] determined Kirkwood correlation factor  $g$ , average  $\tau_0$ ,  $\Delta F_{\tau_0}$  of orthohydroxybenzaldehyde in  $C_6H_6$  at 10°, 20°, 30°C under 9.83 GHz electric field. Both inter and intramolecular associations about their respective bonds decreases by — CHO and — OH group rotations. The high  $\tau_2$  corresponds to group rotation. Molecular associations hinder the intramolecular rotations of — CHO and — OH groups in this compound to affect  $\tau$ . Temperature variation of dielectric relaxation studies of ethylene glycol (EG) — water ( $H_2O$ ) mixture were carried out by Saha and Ghosh [142] under 1 MHz electric field. High values of  $\tau_{jk}$  of EG —  $H_2O$  mixture is inferred from polymeric cluster formation by molecular association. Dash et al [143] investigated micro-level molecular dynamics of 1-propanol, 1-butanol, 1-octanol, methyl isobutyl ketones etc in terms of complex formations by H-bonding between two polar molecules in nonpolar solvent. The increase in  $\rightarrow O-H$  bond length due to enhancement of the bond moment  $\Delta\mu$  may be analysed. The temperature variation of  $\tau_j$ 's were used by Thakur and Sharma [144] to measure the thermodynamic energy parameters of dielectric relaxation and viscous flow of acetonitrile and DMF in  $C_6H_6$  under 9.40 GHz electric field in order to arrive at the solute-solvent molecular associations.

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