# *CHAPTER 1*

## GENERAL INTRODUCTION AND REVIEW OF THE PREVIOUS WORKS

## 1.1. Introduction:

The aim of the dielectric investigation in this thesis is to provide the reader a very simplified and significant approach to grasp the dielectric relaxation phenomena in both pure polar liquid and polar liquid molecules in non-polar solvent under low and high frequency electric fields. In order to reach the goal, the central idea of the work is concentrated to measure both the macroscopic and microscopic entities like relative permittivity $\varepsilon$ and dipole moment $\mu$ respectively of the molecule. The electric dipole moment $\mu$ is not only significant as a reflection of the electronic structure of the molecules. But it is of prime importance in our understanding of molecular interactions. It also partly controls the transition between solid, liquid and gaseous states of a substance. The electric behaviour of dielectric molecule has wide applications in different fields. Scientists are mainly interested to predict shape, size, structure, molecular interactions and change of phase of the polar molecules. Technologists, on the other hand, find its important applications in the field of electrical engineering.

## 1.2. Dielectric Relaxation :

Dielectric relaxation phenomena are related to some form of disorder present in the system under study. There can be no relaxation in a perfectly ordered system, because nothing can relax from perfection. In the case of polar liquid molecules, even if for a perfectly ordered spatial array of dipoles, their orientation distribution would need to be random for the isotropic behaviour in the electric field.

If a dielectropolar substance is placed under the application of the alternating electric field, the molecule becomes polarised. There exist various types of polarisations. Each type of polarisation takes some finite time to respond the applied alternating electric field. Thus there is a considerable lag in the attainment of the equilibrium. This lag in response to the alternation of the applied electric field is commonly known as dielectric relaxation. When the external electric field is removed, all types of polarisation including the orientation polarisation decay exponentially with time. The time in which the orientation polarisation is reduced to 1/e times the initial value is called the relaxation time $\tau$ of a dielectropolar liquid molecule. In the case of static or low frequency electric field, all the polarisations are operative. When the frequency of the alternating electric field becomes high, all the polarisations are not able to attain the equilibrium before the applied electric field is reversed. The relaxation time $\tau$ is an important molecular parameter, which is usually used to determine dipole moment $\mu$ of a polar substance.

## 1.3. Relative Dielectric Permittivity :

Permittivity is a parameter of a dielectric medium. It arises in the calculation of force exerted on each of the electric charges placed in a medium. If two charges are placed in a homogeneous or isotropic dielectric medium, the forces on each of them is reduced by a dimensionless scalar factor $\varepsilon_r$ called the relative dielectric permittivity which is the ratio of the capacitances of the condenser when two charged plates of opposite signs are filled up with dielectric medium and vacuum respectively. Thus $\varepsilon_r$ is given by:

$$\varepsilon_r = \frac{C_m}{C_v}$$

where $C$'s are the capacitance of the condenser having dielectric medium and vacuum respectively. If the relative permittivity of the material is higher the greater is the polarisability of the molecule. So the polar molecule usually has higher permittivities than the non-polar one.

## 1.4. Dielectric Polarisation :

Under the application of the electric field $\vec{E}$ the centres of the positive and negative charges of each molecule of dielectric material are displaced in opposite directions. This sort of relative displacement of charges is called polarisation and the dielectric is said to be polarised.

In a homogeneous or isotropic dielectric, the dielectric polarisation $\vec{P}$ per unit electric field of $\vec{E}$ is called the molecular polarisability $\alpha$. The polarisability in a non-polar molecule arises from two effects. The displacement of the electrons relative to the nucleus in each atom is called the electronic polarisation and that of the atomic nuclei relative to one another is called the atomic polarisation. For a polar molecule the permanent dipole aligns along the applied electric field direction, although they have thermal motions, is called the orientation polarisation.

Therefore the total polarisability $\alpha_T$ of the molecule is:

$$\alpha_T = \alpha_e + \alpha_a + \alpha_o = \alpha_d + \alpha_o \qquad \text{....(1.1)}$$

where $\alpha_e$, $\alpha_a$ and $\alpha_o$ are the electronic, atomic and the orientation polarisabilities respectively. $\alpha_d$ is called the distortion polarisability. Each of three types of polarisabilities is obviously a function of frequency of the applied electric field. As the electric field alters and reverses its sign both their distortion and average orientation polarisations must change. When the frequency is higher, this affect the orientation polarisation which takes some time of the order of $10^{-12}$ to $10^{-10}$ sec to reach the equilibrium in the cases of liquids and solids. In such frequency the distortion polarisation takes much less time than the orientation polarisation to reach equilibrium.

## 1.5. Clausius–Mossotti Equation and Lorentz–Lorentz Formula :

When an electric field $\vec{E}$ is applied between two plates of the condenser, the field is modified to $\vec{E}_{loc}$ by a linear liquid dielectric. The total polarisation of the molecules is given by :

$$\vec{P} = n\alpha_d \vec{E}_{loc} \qquad \text{..... ( 1.2 )}$$

where '$n$' is the number of molecules per unit volume of the dielectric medium and $\alpha_d$ is the distortion polarisability of the non-polar dielectric.

Hence, the dielectric displacement vector $\vec{D}$ is :

$$\vec{D} = \varepsilon_r \vec{E} = \vec{E} + 4\pi\vec{P} \qquad \text{..... ( 1.3 )}$$

$$\varepsilon_r - 1 = \frac{4\pi n \alpha_d \vec{E}_{loc}}{\vec{E}} \qquad \text{..... ( 1.4 )}$$

For a simple cubic crystal or an isotropic liquid dielectric it can be shown that

$$\vec{E}_{loc} = \vec{E} + \frac{4}{3}\pi\vec{P} \qquad \text{..... ( 1.5 )}$$

From Eqs.(1.4) and (1.5) one gets,

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{4}{3}\pi n \alpha_d \qquad \text{..... ( 1.6 )}$$

Multiplying both sides by molar volume $M/\rho$ the above Eq.(1.6) becomes

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\frac{M}{\rho} = \frac{4}{3}\pi N \alpha_d \qquad \text{..... ( 1.7 )}$$

where $N$ is the Avogadro's number. The Eq.(1.7) is known as the Clausius–Mossotti equation [1.1-1.2].

The electronic polarisation occurs at frequencies corresponding to the electric transitions between different energy levels in the atom *i.e*, mostly at visible and ultra-violet frequencies. In such case the relative permittivity $\varepsilon_r$ is replaced by the square of the refractive index $n_D^2$ measured at that frequency according to Maxwell's electromagnetic theory. The above relation now becomes:

$$\frac{n_D^2 - 1}{n_D^2 + 2}\frac{M}{\rho} = \frac{4}{3}\pi N \alpha_e \qquad \text{..... ( 1.8 )}$$

and is called Lorentz–Lorentz formula [1.3-1.4].

## 1.6. Debye Equation Under Static Electric Field :

For a non-polar molecule the molecular polarisability $\alpha_d$ due to distortion polarisation does not depend on temperature while for a polar molecule the orientation polarisation of the molecule depends on temperature unlike distortion polarisation. The polar molecule also possesses a permanent dipole moment $\vec{\mu}_p$ which is randomly directed due to thermal agitation prevailing in the system such that net moment is zero.

Under the application of the electric field the permanent dipoles are forced to orient along the field direction and equilibrium is set up to yield the resulting orientation polarisation $\vec{P}_o$ which is inversely proportional to the absolute temperature $T$ K. It can be shown [1.5] that:

$$\vec{P}_o = \frac{n\mu_p{}^2 \vec{E}_{loc}}{3k_B T} = n\alpha_o \vec{E}_{loc} \qquad \text{.....(1.9)}$$

where $\alpha_o = \mu_p^2 / 3k_B T$ is defined as the effective orientation polarisability.

Thus the total polarisability in case of polar liquid molecule, is

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

$$\alpha_T = \alpha_d + \frac{\mu_p{}^2}{3k_B T} \qquad \text{.....(1.10)}$$

where $\alpha_d$ is the polarisability due to distortion polarisation. Hence the Clausius–Mossotti equation (1.7) becomes;

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\frac{M}{\rho} = \frac{4}{3}\pi N\left(\alpha_d + \frac{\mu_p{}^2}{3k_B T}\right) \qquad \text{.....(1.11)}$$

The Eq.(1.11) is the well known Debye equation [1.6] for a polar molecule which relates a macroscopic quantity like relative permittivity at the L.H.S of the equation to the microscopic quantity like polarisability at the R.H.S.

## 1.7. Onsager Equation :

The failure of Debye equation (1.11) to assume that the field due to molecules in the spherical region is equal to zero led Onsager [1.7] to develop the following model. The molecule is treated as a point dipole at the centre of a spherical cavity of molecular dimension in a continuous medium. The radius '$a$' of the cavity is defined by:

$$\frac{4}{3}\pi a^3 N_1 = 1 \qquad \text{.....( 1.12 )}$$

where $N_1$= no. of dipoles per unit volume. In case of spherical molecule Onsager neglected the short range dipolar interaction among the molecules unlike long range interaction. The internal field in the spherical cavity consists of the cavity field $\vec{G}$ and the reaction field $\vec{R}$ due to external applied electric field and the polarisation by the dipole respectively. The cavity field alone orients the molecule whereas the reaction field only increases their electric moment and always remains parallel to the dipole. A relation between relative permittivity and dipole moment of nearly non-spherical polar liquid molecule is obtained by Onsager [1.7] in a continuous medium of static permittivity $\varepsilon_o$ and refractive index $n_D$ by:

$$\frac{(\varepsilon_o - n_D^2)(2\varepsilon_o + n_D^2)}{\varepsilon_o (n_D^2 + 2)^2} = \frac{4\pi N \rho \mu^2}{9Mk_B T} \qquad \text{.....( 1.13 )}$$

This theory gives a successful account of the general behaviour of pure polar liquid. The validity of Onsager's equation is limited by the assumption that molecules are point dipoles and embeded in a sphere of isotropic polarisable material. In general real molecules are non-spherical and have anisotropic polarisabilities. They have quadrupole and higher moments which may be neglected at macroscopic distances. To take such effects into account a theory would need to contain a prohitively large parameter. Later on a large number of workers [1.8-1.11] modified Debye and Onsager equations to obtain $\mu$ of a highly non-spherical polar liquid molecules.

## 1.8. Debye's Diffusive Model of Relaxation Phenomena :

On the basis of Einstein's theory of the Brownian motion Debye [1.6] supposed that the rotation of a polar molecule under an alternating electric field is constantly interrupted by collisions with the neighbouring molecules. The collisions among molecules may produce a resistive couple proportional to the angular frequency $\omega$ of the dielectropolar molecule. This model is applicable only to liquid molecules and helped Debye to yield the frequency dependence of the permittivity of a polar molecule.

$$\frac{\varepsilon^* - n_D^2}{\varepsilon_o - n_D^2} = \frac{1}{1 + j\omega\tau} \qquad \text{.....( 1.14 )}$$

where $n_D$ is the refractive index and macroscopic relaxation time $\tau$ is related to microscopic relaxation time $\tau'$ by :

$$\tau = \frac{\varepsilon_o + 2}{n_D^2 + 2}\tau' \qquad \text{.....( 1.15 )}$$

## 1.9. Kirkwood Model of Relaxation Phenomena :

Kirkwood [1.12], however, imagined a specimen of the material containing a number of dipoles each of moment $\mu$ confined in a spherical volume. When such volume is situated in a uniform external electric field the moment of the specimen can be separated into two parts:

(i) The molecule somewhere within the specimen is fixed but the others take up all possible configurations and

(ii) The moment induced in a homogenous specimen of the fixed molecule, and the molecule itself plus local ordering of the molecules immediately round it.

The Kirkwood's equation for a dipolar liquid is given by :

$$\frac{(\varepsilon_o - 1)(2\varepsilon_o + 1)}{3\varepsilon_o} = \frac{4\pi N}{V}\left(\alpha + \frac{g\mu^2}{3k_B T}\right) \qquad \text{.....( 1.16 )}$$

where the correlation parameter $g$ is a measure of the local ordering in the material.

## 1.10. Fröhlich's Model :

Fröhlich, on the other hand, assumes a spherical region of microscopic dimensions in an infinite continuous medium. The spherical region is not assumed to be an exact sphere but modified slightly. Then the equation for non polarisable dipole is deduced by Fröhlich [1.13]:

$$\frac{(\varepsilon_o - 1)(2\varepsilon_o + 1)}{3\varepsilon_o} = \frac{4\pi N}{V}\frac{\langle m.\overline{m}\rangle}{3k_B T} \qquad \text{.....( 1.17 )}$$

where $< m.\overline{m} >$ is the weighted average of electric dipole moment $\overline{m}$.

## 1.11. The Barrier Model of Dielectric Relaxation :

The molecules are assumed to change the orientations of a polar molecule by a series of small steps. This model is applicable to polar-nonpolar liquid mixture. A molecule in solid, may, interact with its neighbors, creating a number of " equilibrium positions". This corresponds to a minimum potential energy separated by potential barriers. This type of process was first considered by Debye [1.6].

## 1.12. Bauer's Theoretical Model of Dielectric Relaxation :

Bauer's [1.14] model of dielectric relaxation is closely similar to Eyring's [1.15] reaction rate theory. It explicitly refers to dipole rotation. The orientational coordinate $(\theta,\phi)$ of a dipole in a system can be represented by a point on a unit sphere. The unit sphere can be divided into two

domains separated by a potential barrier of height $H$. The minimum potential energies of dipoles in two domains are 0 and $U$ respectively.

### 1.13. Real and Imaginary Parts of The Relative Permittivity :

Under static electric field there is no absorption of electric energy by the dielectric material and the dielectric displacement vector $\vec{D}$ is simply related to the applied electric field $\vec{E}$ by the relation $\vec{D} = \varepsilon\vec{E}$.

When the dielectric material is placed between the plates under an alternating electric field like $\vec{E} = \vec{E}_o \cos \omega t$ there is always a dissipation of energy due to absorption of electromagnetic waves. This is called "dielectric loss" over a broad band of frequencies. Molecular forces impeding the dipole rotation dominate if the direction of the applied electric field changes sufficiently fast. The dipoles become unable to follow the changes and the orientation of permanent dipoles no longer contributes to the dielectric relaxation at such frequencies. A phase difference between $\vec{D}$ and $\vec{E}$ develops, and energy is drawn from the electrical sources by the material which is due to

(i) electrical conduction

(ii) the relaxation effect due to permanent dipoles and

(iii) the resonance effect due to rotation or vibration of atoms, ions, or electrons of the dielectric material.

Thus it is useful to describe the relationship between $\vec{E}$ and $\vec{D}$ by

$$\vec{E} = \vec{E}_o e^{j\omega t} \quad \text{and} \quad \vec{D} = \vec{D}_o e^{j(\omega t - \delta)}$$

where $\delta$ is the phase difference and $\omega = 2\pi f$, $f$ being the frequency of the applied electric field. $j$ = complex number $=\sqrt{-1}$.

The dielectric response of a system is described by the complex representation of the relative permittivity $\varepsilon^*(\omega)$ at frequency $(\omega)$:

$$\varepsilon^*(\omega) = \frac{\vec{D}}{\vec{E}} = \frac{\vec{D}_o}{\vec{E}_o}(\cos\delta - j\sin\delta)$$

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \varepsilon''(\omega) \qquad \text{..... ( 1.18 )}$$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary parts of the complex relative permittivity $\varepsilon^*(\omega)$. In the low frequency, $\varepsilon''(\omega) \to 0$, $\varepsilon'(\omega) \to \varepsilon_o$. In the high frequency *i.e* infrared region $\varepsilon'(\omega) \to \varepsilon_\infty$.

Kramers and Krönig [1.16-1.17] developed the mutual transformation relation between the two parts, dispersion and absorption of the dielectric relaxation:

$$\varepsilon'(f)-\varepsilon_\infty=\frac{2}{\pi}\int_o^\infty\frac{f'\varepsilon''(f)}{f'^2-f^2}df' \quad ; \qquad \varepsilon''(f)=-\frac{2}{\pi}\int_o^\infty\frac{\varepsilon'(f')-\varepsilon_\infty}{f'^2-f^2}df \qquad .....(1.19)$$

The frequency $f$ must have been supplemented by a further frequency variable $f'$ over which integration is made.

## 1.14. Debye Equations Under High Frequency Electric Field :

The rotation of a dipolar molecule due to an applied alternating electric field is constantly interrupted by collisions with the neighbours. These collisions may be described by a resistive couple proportional to the angular velocity of the molecule. The dipole moment $\mu$ of the molecule on which the orienting couple acts is given in terms of complex relative permittivitiy $\varepsilon^*$ [1.6]

$$\frac{\varepsilon^*-1}{\varepsilon^*+2}\frac{M}{\rho}=\frac{4\pi N}{3}\left(\alpha_d+\frac{\mu^2}{3k_BT}\frac{1}{1+j\omega\tau'}\right) \qquad .....(1.20)$$

In the low frequency range Debye expression for the static permittivity is:

$$\frac{\varepsilon_o-1}{\varepsilon_o+2}\frac{M}{\rho}=\frac{4\pi N}{3}\left(\alpha_d+\frac{\mu^2}{3k_BT}\right) \qquad .....(1.21)$$

In the high frequency limit, *i.e* in the far infra red or visible region ($\varepsilon_\infty=n_D^2$) all types of distortion polarisation make full contribution except dipolar polarisation which is zero. In this region,:

$$\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\frac{M}{\rho}=\frac{4\pi N}{3}\alpha_d \qquad .....(1.22)$$

On substitution of Eqs.(1.21) and (1.22) in Eq.(1.20) it can be written as

$$\frac{\varepsilon^*-1}{\varepsilon^*+2}=\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}+\left(\frac{\varepsilon_o-1}{\varepsilon_o+2}-\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\right)\frac{1}{1+j\omega\tau'} \qquad .....(1.23)$$

The Eq.(1.23) can be rearranged to give

$$\frac{\varepsilon^*-\varepsilon_\infty}{\varepsilon_o-\varepsilon_\infty}=\frac{1}{1+j\omega\tau} \qquad .....(1.24)$$

Separating real and imaginary parts one can obtain

$$\varepsilon'=\varepsilon_\infty+\frac{\varepsilon_o-\varepsilon_\infty}{1+x^2} \qquad .....(1.25)$$

$$\varepsilon''=\frac{\varepsilon_o-\varepsilon_\infty}{1+x^2}x \qquad .....(1.26)$$

where $x = \omega\tau = \frac{\varepsilon_o + 2}{\varepsilon_\infty + 2}\omega\tau'$.

Eqs.(1.25) and (1.26) are known as Debye equations under *hf* electric field.

## 1.15. Murphy–Morgan Conductivity Relation :

Under the application of an alternating electric field $E=E_o e^{j\omega t}$ the conductivity of a dielectropolar liquid due to displacement current is:

$$\sigma = \frac{1}{E}\frac{dq}{dt} \qquad \text{.....( 1.27 )}$$

Again $D = 4\pi q = E + 4\pi P$ and $E = \frac{V}{d} = \frac{D}{\varepsilon}$, we have

$$\frac{dq}{dt} = \frac{1}{4\pi}\frac{dD}{dt} = \frac{\varepsilon}{4\pi d}\frac{dV}{dt} = I \text{ (say)}$$

where $V$ is the applied alternating potential $V=V_o e^{j\omega t}$. The expression for the displacement current $I$ is given by:

$$I = \frac{\varepsilon^*}{4\pi d}\frac{dV}{dt} \qquad \text{.....( 1.28 )}$$

Introducing $\varepsilon^*=\varepsilon'-j\varepsilon''$ and $V=V_o e^{j\omega t}$ in Eq.(1.28), the current $I$ can be written as according to Murphy and Morgan [1.18] :

$$I = \left(\frac{\omega\varepsilon''}{4\pi} + j\frac{\omega\varepsilon'}{4\pi}\right)E_o e^{j\omega t} \qquad \text{.....( 1.29 )}$$

When eq. (1.29) is compared to Ohm's law i.e. $I=\sigma^* E_o e^{j\omega t}$, one gets $\sigma^*$ where $\sigma^*$ is called the *hf* complex conductivity which is:

$$\sigma^* = \sigma' + j\sigma'' \qquad \text{.....( 1.30 )}$$

Thus, $\sigma'$ = the real part of *hf* complex conductivity $=\omega\varepsilon''/4\pi$ and $\sigma''$ = the imaginary part of *hf* complex conductivity $=\omega\varepsilon'/4\pi$

However, it was assumed that the conduction current due to free molecular ions and electrons in pure liquids or polar-nonpolar liquid mixtures is neglected.

The magnitude of the total *hf* conductivity $\sigma$ is given by :

$$\sigma = \frac{\omega}{4\pi}\left(\varepsilon'^2 + \varepsilon''^2\right)^{\frac{1}{2}} \qquad \text{.....( 1.31 )}$$

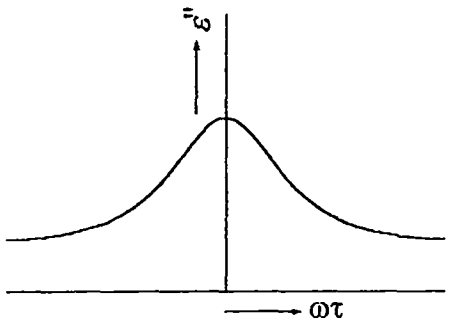


Figure 1.1: Variation of $\varepsilon''$ with $\omega\tau$

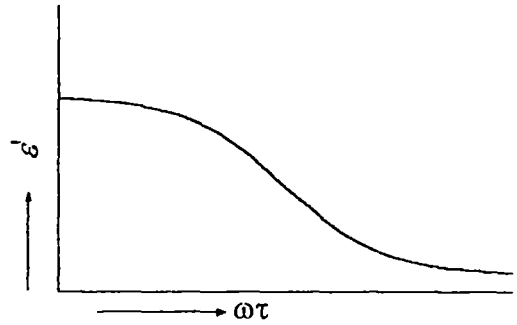


Figure 1.2: Variation of $\varepsilon'$ with $\omega\tau$

**1.16. Macroscopic and Microscopic Relaxation Time :**

The gradual increase of polarisation in a dielectric medium with time to its equilibrium value under the alternating electric field is described by the decay function $f(t)$ where

$$f(t) \propto e^{-t/\tau} \qquad \text{..... ( 1.32 )}$$

The relaxation time $\tau$ is independent of time but may depend on temperature. With a time dependant electric field $E(t)$, a field $E(u)$ which is applied during a time interval between $u$ and $u+du$; the corresponding electric displacement $D(t)$ is written as:

$$D(t) = \varepsilon_\infty E(t) + \int_{-\infty}^{t} E(u) f(t-u) du \qquad \text{..... ( 1.33 )}$$

On differentiating Eq.(1.33) with respect to time and multiplying both sides by $\tau$ one gets:

$$\tau \frac{dD(t)}{dt} = \varepsilon_\infty \tau \frac{dE(t)}{dt} + \tau f(o) E(t) - \int_{-\infty}^{t} E(u) f(t-u) du \qquad \text{..... ( 1.34 )}$$

Adding Eqs.(1.33) and (1.34) yields:

$$\tau \frac{d}{dt}(D - \varepsilon_\infty E) + (D - \varepsilon_\infty E) = \tau f(o) E \qquad \text{..... ( 1.35 )}$$

In a static electric field $D=\varepsilon_o E$

Hence from Eq.(1.35) we get

$$\tau f(o) = \varepsilon_o - \varepsilon_\infty \qquad \text{..... ( 1.36 )}$$

Therefore Eq.(1.35) becomes :

$$\tau \frac{d}{dt}(D - \varepsilon_\infty E) + (D - \varepsilon_\infty E) = (\varepsilon_o - \varepsilon_\infty) E \qquad \text{..... ( 1.37 )}$$

In the alternating electric field $E \propto e^{-j\omega t}$. The dielectric permittivity $\varepsilon^*$ is complex. Hence

$$\frac{dE}{dt} = -i\omega E, \qquad D = \varepsilon^* E, \qquad \frac{dD}{dt} = -i\omega\varepsilon E \qquad \text{..... ( 1.38 )}$$

Introducing this in Eq.(1.37) we get,

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + j\omega\tau} \qquad \text{..... ( 1.39 )}$$

Separating the real and imaginary parts one gets

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \frac{1}{1 + \omega^2\tau^2} \qquad \text{..... ( 1.40 )}$$

$$\frac{\varepsilon''}{\varepsilon_o - \varepsilon_\infty} = \frac{\omega\tau}{1 + \omega^2\tau^2} \qquad \text{..... ( 1.41 )}$$

Although the polarisation may show a characteristic exponential decay with characteristic time $\tau$, it does not follow that the orientation of an individual dipole decays with the same characteristic time. It is clear from (1.41) that $\varepsilon''$ has a maximum value for $\omega\tau = 1$ and approaches zero both for small and large values of $\omega\tau$ as shown in Fig.1.1. The variation of $\varepsilon'$ with $\omega\tau$ is shown in Fig.1.2. The Eqs.(1.40) and (1.41) differ from Debye Eqs.(1.25) and (1.26) which contain the quantity $\tau'(\varepsilon_o+2)/(\varepsilon_\infty+2)$ instead of $\tau$. Comparing the two equations a relation between macroscopic relaxation time $\tau$ and the microscopic relaxation time $\tau'$ is obtained by:

$$\tau = \frac{\varepsilon_o + 2}{\varepsilon_\infty + 2}\tau' \qquad \text{..... ( 1.42 )}$$

On eliminating the parameter $\omega\tau$ and rearranging Eqs.(1.40) and (1.41) one gets :

$$\left(\varepsilon' - \frac{\varepsilon_o + \varepsilon_\infty}{2}\right)^2 + \varepsilon''^2 = \left(\frac{\varepsilon_o - \varepsilon_\infty}{2}\right)^2 \qquad \text{..... ( 1.43 )}$$

A plot of $\varepsilon''$ is drawn against $\varepsilon'$ representing the semicircle of radius $(\varepsilon_o - \varepsilon_\infty)/2$ and the center lying on the abscissa at a distance $(\varepsilon_o+\varepsilon_\infty)/2$ from the origin as illustrated in Fig.1.3. This semi-circular arc intersecting the abscissa at $\varepsilon' = \varepsilon_\infty$ and $\varepsilon' = \varepsilon_o$, is known as Debye semi-circle [1.6].

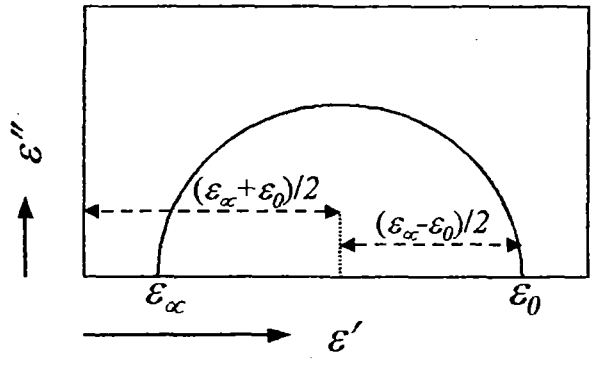


Figure 1.3: Variation of $\varepsilon''$ with $\varepsilon'$ for different angular frequency $\omega$ (Debye semi-circle)

Powles [1.19] and Glarum [1.20], however, found a relation between $\tau$ and $\tau'$ by introducing a factor of approximately 3/2 given by ;

$$\tau = \frac{3\varepsilon_o}{2\varepsilon_o + \varepsilon_\infty}\tau' \qquad \text{..... ( 1.44 )}$$

Another relation of macroscopic and microscopic relaxation time was given by O'Dwyer and Sack [1.21] :

$$\tau = \frac{(2\varepsilon_o^2 + 6\varepsilon_o^2\varepsilon_\infty + \varepsilon_\infty^2)}{3\varepsilon_o\varepsilon_\infty(2\varepsilon_o + \varepsilon_\infty)}\tau' \qquad \text{..... ( 1.45 )}$$

## 1.17. Distribution of Relaxation Times :

For a dielectropolar liquid mixtures or solutions, it is found that some dipoles relax with one characteristic rate, some with another. It is impossible to study the dielectric relaxation phenomena in terms of a single Debye equation or sum of two or three Debye terms. Cole–Cole [1.22] and Davidson–Cole [1.23-1.24] relations were found to be satisfied by experimental results. But the theoretical explanation behind them has not yet been given. For most of the liquids, the experimental curve deviates from the simple normal Debye curve. In addition to Debye semi-circular behaviour, a number of distributions of relaxation times were found for different liquid dielectrics. The circular arc of Cole-Cole [1.22] plot with center lying below the abscissa as shown in Fig.1.4 exhibits symmetric distribution of relaxation time. A skewed arc, on the other hand, proposed by Cole-Davidson [1.23-1.24] is obtained to indicate an asymmetric distribution of relaxation times as shown in Fig.1.5.

Debye equation can thus be written for such a distribution of relaxation time :

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_o - \varepsilon_\infty)\int_o^\infty \frac{G(\tau)d\tau}{1 + j\omega\tau} \qquad \text{..... ( 1.46 )}$$

Here, $G(\tau)d\tau$ is the distribution function for fraction of the molecules associated with relaxation times between $\tau$ and $\tau + d\tau$ such that the normalization condition for $G(\tau)$ is:

$$\int_o^\infty G(\tau)d\tau = 1 \qquad \text{..... ( 1.47 )}$$

Separating the real and imaginary parts of Eq.(1.46) one gets :

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_o - \varepsilon_\infty)\int_o^\infty \frac{G(\tau)d\tau}{1 + \omega^2\tau^2} \qquad \text{..... ( 1.48 )}$$

and

$$\varepsilon'' = (\varepsilon_o - \varepsilon_\infty)\int_o^\infty \frac{\omega\tau G(\tau)d\tau}{1 + \omega^2\tau^2}. \qquad \text{..... ( 1.49 )}$$

as Debye equations.

## 1.18. Cole–Cole Distribution :

The dielectric dispersion and absorption of many systems can not be described by a single relaxation time. For a large number of liquid dielectrics the experimental curve deviates from Debye curve of Fig.1.3. The broader dispersion and lower maximum loss are shown in Fig.1.4. Cole–Cole [1.22], on the other hand, found that the plot of $\varepsilon''$ against $\varepsilon'$ for a dielectric material at different frequencies in a complex plane having a distribution of relaxation time is generally a semi-circular arc intersecting the abscissa axis at two points $\varepsilon_\infty$ and $\varepsilon_o$. The center of semi-circle lies below the abscissa axis as found in Fig.1.4. The radius of the semi-circle makes an angle $\gamma\pi/2$ with $\varepsilon'$ axis where $\gamma$ is called the symmetric distribution parameter for $0 \leq \gamma \leq 1$. Cole and Cole modified the empirical formula of Debye by:

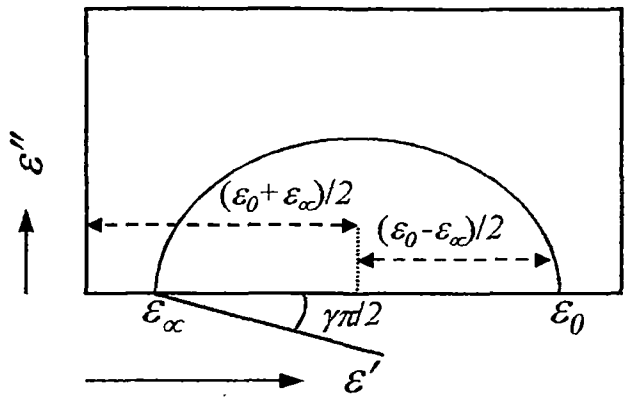

Figure 1.4: Cole-Cole Plot.

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + (j\omega\tau_s)^{1-\gamma}} \qquad \text{..... ( 1.50 )}$$

where $\tau_s$ = symmetric relaxation time.

## 1.19. Davidson–Cole Distribution :

A skewed arc was, however, obtained by Davidson and Cole [1.23-1.24] by plotting $\varepsilon''$ against $\varepsilon'$ in order to analyse asymmetrical relaxation spectra for certain dielectric materials like glycerol as sketched in Fig.1.5. The arc is obtained from a series of continuous relaxation mechanism of decreasing importance extending to the high frequency side of the main dispersion. The behaviour is represented by empirical relation:

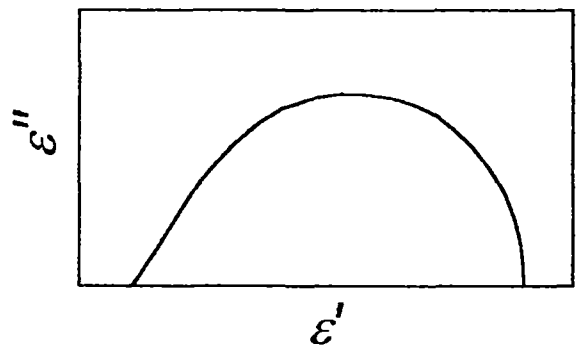

Figure 1.5: Davidson – Cole plot

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{(1 + j\omega\tau_{cs})^{\delta}} \qquad \text{..... ( 1.51 )}$$

where $\delta$ is asymmetric distribution parameter ( $0< \delta \leq 1$ ) related to characteristic relaxation time $\tau_{cs}$ of the polar molecule. This behaviour seems to be applicable in representing the behaviour of substance at low temperature. These were well discussed by Powles in recent years [1.25]. A curve is supposed to be made up of a number of Debye semi-circular arcs with multiple relaxation times. This is displayed in Fig.1.6 to understand the asymmetric relaxation behaviour.

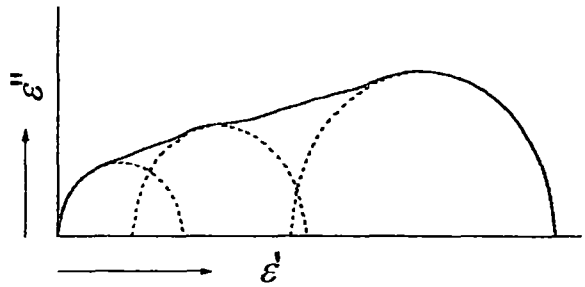


Figure 1.6: Plot of $\varepsilon''$ against $\varepsilon'$ for a number of Debye semicircular arc with multiple relaxation.

## 1.20. Havriliak–Negami (HN) Distribution :

Dielectric relaxation behaviour of some dipolar materials is not often explained by either Cole–Cole or Davidson–Cole distribution. The most widely used distribution for the phenomenological description of dielectric experiments is the Havriliak–Negami distribution [1.26] that describes an asymmetric and broadened profile as compared to the Debye curve. The expression of the complex relative permittivity is now :

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{[1+(j\omega\tau_{HN})^{1-\gamma}]^\delta} \qquad \text{..... ( 1.52 )}$$

Eq.(1.52) reduces to Cole–Cole distribution when $\delta = 1$ and Davidson–Cole when $\gamma = 0$. Since H–N distribution is the generalization of Cole–Cole and Davidson–Cole distribution it can explain the relaxation phenomena of a wider variety of materials with different values of $\gamma$ and $\delta$ parameters.

## 1.21. Kohlrausch–Williams–Watts (KWW) Distribution :

Under certain circumstances, the dielectric parameters are describable in the time domain by the well known stretched exponential or Kohlrausch–Williams–Watts (KWW) function [1.27-1.28] in terms of macroscopic decay function $\phi(t)$ by :

$$\phi(t) = \exp[-(t/\tau_{KWW})^\beta] \qquad \text{..... ( 1.53 )}$$

where $\tau_{KWW}$ is the effective relaxation time in time domain, $\beta$ is the shape parameter of the time relaxation function such that $0< \beta \leq 1$. In the frequency domain, the complex dielectric constant $\varepsilon^*$ is written for a pure Debye process as a function of angular frequency $\omega$ and temperature $T$. Hence

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the relationship between $\varepsilon^*(\omega,t)$ and $\phi(t,T)$ is given by one side Fourier or pure imaginary Laplace transformation of the form:

$$\frac{\varepsilon^*(\omega,T)-\varepsilon_\infty}{\varepsilon_o-\varepsilon_\infty}=\int_o^\infty\left(-\frac{d\phi}{dt}\right)\exp(-j\omega t)dt$$

$$=\pounds\left[\frac{\beta}{\tau_{KWW}}\left(\frac{t}{\tau_{KWW}}\right)^{-(1-\beta)}\exp\left\{-\left(\frac{t}{\tau_{KWW}}\right)^{\beta}\right\}\right] \qquad \text{..... ( 1.54 )}$$

where $\pounds$ is the Laplace transformation of $-d\phi(t)/dt$.

Eq.(1.54) gives the single exponential Debye like distribution for $\beta$ =1. KWW distribution has been widely used to describe the relaxation behaviour of glass forming liquids and complex polymeric systems.

## 1.22. Distribution Function of Relaxation Times :

The experimental results can satisfactorily be explained by Gaussian probability distribution function made by Wagner [1.29] and Yager [1.30] and is given by:

$$G(\tau)d\tau=\frac{b}{\sqrt{\pi}}\exp(-b^2y^2)dy \qquad \text{..... ( 1.55 )}$$

Here $b$ is the breadth of the distribution and $y$ is defined as:

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

where $\tau_o$ is the most probable relaxation time

In long chain polar molecules, like alcohols and polymers there are many possibilities of internal rotations, bending and twisting about the bond axis of the molecule each with a corresponding characteristic relaxation time. Kirkwood and Fuoss [1.31], on the other hand, defined a distribution function $G(\tau)$ in averaging to the macroscopic conditions of distribution of relaxation times for long chain polymeric dielectric molecules.

$$G(\tau)=\frac{1}{2\cosh y+2} \qquad \text{..... ( 1.56 )}$$

where $y$ =ln($\tau/\tau_o$).

The experimental results were not in accord with this formula. So Fuoss and Kirkwood [1.32] further suggested that the empirical relation should represent the experimental data:

$$\varepsilon''=\varepsilon''_m\sec h\left[\beta\ln\frac{\omega}{\omega_m}\right] \quad \text{for } 0<\beta<1 \qquad \text{..... ( 1.57 )}$$

where $\beta$ is a distribution parameter and $\omega_m$ is the angular frequency corresponding to the maximum value $\varepsilon_m''$ of $\varepsilon''$. The corresponding distribution function is given by:

$$G(\tau) = \frac{\beta}{\pi} \frac{\cos(\beta\pi/2)\cosh(\beta y)}{\cos^2(\beta\pi/2) + \sinh^2(\beta y)} \qquad \text{.....( 1.58 )}$$

where $y = \log(\omega/\omega_m)$.

Another distribution function of Cole–Cole [1.22] is given by:

$$G(\tau) = \frac{\sin\gamma\pi}{2\pi}\left[\cosh\{(1-\gamma)\ln(\tau/\tau_o)\} - \cos\gamma\pi\right]^{-1} \qquad \text{.....( 1.59 )}$$

The distribution function $F(y)$ based on Havriliak–Nigami [1.26] function is :

$$F(y) = \left(\frac{1}{\pi}\right) y^{(1-\gamma)\delta} (\sin\delta\theta)\left(y^{2(1-\gamma)} + 2y^{1-\gamma}\cos\pi(1-\gamma) + 1\right)^{-\frac{\delta}{2}} \qquad \text{.....( 1.60 )}$$

In this expression, $y = \tau/\tau_o$ and

$$\theta = \arctan\left[\frac{\sin\pi(1-\gamma)}{y^{1-\gamma} + \cos\pi(1-\gamma)}\right] \qquad \text{.....( 1.61)}$$

Fröhlich [1.13] derived the distribution function for a molecular mechanism which leads to a distribution of relaxation time between two limiting values $\tau_1$ and $\tau_2$ such that $\tau_2 > \tau_1$. The distribution function is:

$$G(\tau) = (\varepsilon_o - \varepsilon_\infty)\frac{k_B T}{V_o}\frac{1}{\tau} \qquad \text{if } \tau_1 \le \tau \le \tau_2$$

$$= 0 \qquad \text{if } \tau < \tau_1 \text{ and } \tau > \tau_2 \qquad \text{.....( 1.62 )}$$

Davidson and Cole [1.23-1.24] also gave another distribution function :

$$G(\tau) = \frac{\sin\beta\pi}{\tau\pi}\left(\frac{\tau}{\tau_o - \tau}\right)^{\beta} \qquad \text{for } 0 < \tau < \tau_o$$

$$= 0 \qquad \text{for } \tau > \tau_o \qquad \text{.....( 1.63 )}$$

Similar to that of Fröhlich, Higasi *et al* [1.33] gave another distribution function $y(\tau)$ for a number of *n*-alkyl bromides at different temperatures which may be represented by :

$$y(\tau) = \frac{1}{A\tau} \qquad \text{if } \tau_1 < \tau < \tau_2$$

$$= 0 \qquad \text{if } \tau < \tau_1 \text{ and } \tau > \tau_2 \qquad \text{.....( 1.64 )}$$

where $\tau_1$ is the relaxation time of the rotational orientation of the $CH_2Br$ group about its bond to the rest of the molecule, while upper limit $\tau_2$ is the relaxation time of the largest orienting unit, usually the molecule as a whole.

Matsumoto and Higasi [1.34] also suggested a more general distribution function $y(\tau)$ in order to explain the dielectric properties of some non rigid alkyl halides at lower temperature from the same principle which describes the dielectric properties of the same substance at higher temperature like:

$$y(\tau) = \frac{1}{A\tau^n} \qquad \text{if } \tau_1 < \tau < \tau_2$$

$$= 0 \qquad \text{if } \tau < \tau_1 \text{ and } \tau > \tau_2 \qquad \text{..... (1.65)}$$

and $0<n<\infty$.

### 1.23. Debye Equation in Solution:

In pure polar liquids, one polar molecule is surrounded by a large number of similar molecules and eventually polar-polar interaction occurs. In order to avoid the polar-polar interaction it is better to study the relaxation phenomena of dipolar liquids dissolved in non-polar solvents. In such case one polar unit is assumed to be far apart from the others and remains in the quasi-isolated state to eliminate polar-polar interactions almost completely.

Let a polar liquid ($j$) is dissolved in a non-polar solvent ($i$). Let $\alpha_i$ and $\alpha_j$ are the polarisabilities of solvent and solute of molecular weights $M_i$ and $M_j$ respectively. If the relative permittivitiy of the liquid mixture is $\varepsilon_{ij}$ then Debye equation [1.6] for polar-nonpolar liquid mixture is:

$$\frac{\varepsilon_{ij}-1}{\varepsilon_{ij}+2}\frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{4\pi N}{3}\left[\alpha_i f_i + \alpha_j f_j + \frac{\mu_s^2}{3k_B T} f_j\right]$$

$$= \frac{4\pi N \alpha_i}{3} + \frac{4\pi N}{3}\frac{\mu_s^2}{3k_B T} f_j \qquad \text{..... (1.66)}$$

Here $f_i$ and $f_j$ are the mole fractions of the solvent and solute defined by $f_i=n_i/(n_i+n_j)$; $f_j=n_j/(n_i+n_j)$, where $n_i$ and $n_j$ are the number of molecules per unit volume of the respective liquids and $\alpha_i=\alpha_j$

Eq.(1.66) is written as :

$$\frac{\varepsilon_{ij}-1}{\varepsilon_{ij}+2}V_{ij} = \frac{\varepsilon_i - 1}{\varepsilon_i + 2}V_i + \frac{4\pi N}{3}\frac{\mu_s^2}{3k_B T} f_j \qquad \text{..... (1.67)}$$

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

In case of neutral dielectrics $\varepsilon_{ij} = n_{Dij}^2$, where $n_{Dij}$ is the refractive index. The equation can be written as:

$$\frac{n_{Dij}^{\ 2}-1}{n_{Dij}^{\ 2}+2}V_{ij} = \frac{n_{Di}^{\ 2}-1}{n_{Di}^{\ 2}+2}V_i \qquad \text{..... ( 1.68 )}$$

Eqs.(1.67) and (1.68) can, however, be used to measure the dipole moment of any dipolar liquid treated as a solute in a solution.

From Eqs.(1.67) and (1.68) one gets :

$$\left(\frac{\varepsilon_{ij}-1}{\varepsilon_{ij}+2} - \frac{n_{Dij}^{\ 2}-1}{n_{Dij}^{\ 2}+2}\right) = \left(\frac{\varepsilon_i-1}{\varepsilon_i+2} - \frac{n_{Di}^{\ 2}-1}{n_{Di}^{\ 2}+2}\right)\frac{V_i}{V_{ij}} + \frac{4\pi N}{3}\frac{\mu_s^{\ 2}}{3k_BT}\frac{f_j}{V_{ij}} \qquad \text{..... ( 1.69 )}$$

Introducing molar concentration $c_j$ ie $c_j = f_j / V_{ij}$ and for extremely dilute solution $(V_i/V_{ij}) \rightarrow 1$ Eq.(1.69) is given by:

$$\left(\frac{\varepsilon_{ij}-1}{\varepsilon_{ij}+2} - \frac{n_{Dij}^{\ 2}-1}{n_{Dij}^{\ 2}+2}\right) = \left(\frac{\varepsilon_i-1}{\varepsilon_i+2} - \frac{n_{Di}^{\ 2}-1}{n_{Di}^{\ 2}+2}\right) + \frac{4\pi N}{3}\frac{\mu_s^{\ 2}}{3k_BT}c_j \qquad \text{..... ( 1.70 )}$$

The Eq.(1.70) is a simple, straightforward and useful one to determine $\mu_s$ of a dipolar liquid molecule at infinite dilution. It is the well-known Debye equation [1.6] for a polar-nonpolar liquid mixture.

## 1.24. Extrapolation Technique and Guggenheim Equation :

In order to measure $\mu_s$ of a dipolar liquid molecule at infinite dilution a large number of workers used the extrapolation technique of different dielectric relaxation parameters. The methods suggested by Hedestrand [1.35], Cohen Henrique [1.36] and Le Fevre [1.37] had some inherent uncertainties in the calculation of $\left(\partial\rho_{ij}/\partial x_j\right)_{x_j\rightarrow 0}$ and $\left(\partial n_{Dij}/\partial x_j\right)_{x_j\rightarrow 0}$ by graphical extrapolation technique.

Higasi [1.38] measured $\mu_s$ of different polar-nonpolar liquid mixtures from the empirical formula:

$$\mu_s = \beta\left(\frac{\Delta\varepsilon}{x_j}\right)^{1/2} \qquad \text{..... ( 1.71 )}$$

where $\Delta\varepsilon = \varepsilon_{ij} - \varepsilon_i$ and the constant $\beta$ depends upon the solvent used. Guggenheim [1.8], on the other hand, introduced a fictitious atomic polarisability to make the solution free from atomic polarisation. The simpler method suggested is to calculate $\mu_s$ in which the need for measuring densities of liquid mixtures was not necessary. The slope of the curve drawn through the experimental parameters of $\Delta$

where $\Delta = 3(\varepsilon_{ij} - n_{Dij}^2)/(\varepsilon_{ij} + 2)(n_{Dij}^2 + 2)$ against mole fraction $c_j$ gave $\mu_s$ of a dielectropolar liquid molecule dissolved in a non-polar solvent. The quantity $\Delta = [(\varepsilon_{ij} - n_{Dij}^2) - (\varepsilon_i - n_{Di}^2)]$ was found from the extrapolated value of $\Delta / c_j$ at infinite dilution to calculate $\mu_s$ from the relation :

$$\mu_s^{\ 2} = \frac{9k_BT}{4\pi N} \frac{3}{(\varepsilon_i + 2)(n_{Di}^{\ 2} + 2)} \left(\frac{\Delta}{c_j}\right)_{c_j \to 0} \qquad \text{.....( 1.72 )}$$

In the meantime many workers [1.39-1.41] suggested different modified formulations to calculate $\mu_s$ by smoothing the experimental data extrapolated to infinite dilution. Smith [1.39] following Guggenheim [1.8] subsequently introduced the idea of weight fraction $w_j$ instead of $c_j$ where,

$$c_j = \frac{\rho_{ij}}{M_j} w_j \qquad \text{.....( 1.73 )}$$

Guggenheim [1.42], later on, accepted the view of extrapolation technique of other workers [1.39-1.41] to modify the Eq.(1.72) for $\mu_s$ :

$$\mu_s^{\ 2} = \frac{9k_BT}{4\pi N} \frac{3}{(\varepsilon_i + 2)^2} \frac{M_j}{\rho_i} \left(\frac{\Delta}{w_j}\right)_{w_j \to 0} \qquad \text{.....( 1.74 )}$$

where

$$\left(\frac{\Delta}{w_j}\right)_{w_j \to 0} = \left[\left(\frac{\varepsilon_{ij} - \varepsilon_i}{w_j}\right)_{w_j \to 0} - \left(\frac{n_{Dij}^{\ 2} - n_{Di}^{\ 2}}{w_j}\right)_{w_j \to 0}\right] \qquad \text{.....( 1.75 )}$$

$M_j$ is the molecular weight of the dipolar liquid and $\rho_i$ is the density of the solvent.

Palit and Banerjee [1.43] made an analysis of the error involved in the Guggenheim–Smith approximate equation to find how far solution density measurement are necessary for calculation of $\mu_s$ of a polar molecule in a non-polar solvent. Botcher [1.44], however, calculated $\mu_s$ for a large number of polar-nonpolar liquid mixture using different extrapolation techniques and found different $\mu_s$'s. Later on, Krishna and Srivastava [1.45] used the following relation:

$$\mu_s = \beta \left(\frac{d\varepsilon_{ij}}{dx_j}\right)_{x_j \to 0}^{1/2} \qquad \text{.....( 1.76 )}$$

to calculate $\mu_s$ of some dielectropolar solute in liquid state.

Srivastava and Charandas [1.46] found the constant $\beta$ was different for different polar liquids. A question, therefore, arises regarding the validity of Higasi's method [1.38]. Prakash [1.47], however, showed that Eq.(1.76) is a special case of Debye equation (1.70) when $\varepsilon_{ij}$ is very

nearly equal to unity. Since $\varepsilon_{ij} \cong 1$ is not true for any polar-nonpolar liquid mixture, Higasi's [1.38] method can not be regarded as a universal one to compute $\mu_s$ at all concentrations of the polar liquid. The Eq.(1.72) was modified to calculate $\mu_s$ at $w_j \to 0$.

$$\mu_s^2 = \frac{27M_j k_B T}{4\pi N \rho_i}\left(\frac{\delta X_{ij}}{\delta w_j}\right)_{w_j=0} \qquad .....(1.77)$$

Here,

$$\left(\frac{\delta X_{ij}}{\delta w_j}\right)_{w_j=0} = \left[\frac{1}{(\varepsilon_i+2)^2}\left(\frac{\delta \varepsilon_{ij}}{\delta w_j}\right)_{w_j\to 0} - \frac{2n_{Di}}{(n_{Di}^2+2)^2}\left(\frac{\delta n_{Dij}}{\delta w_j}\right)_{w_j\to 0}\right] \qquad .....(1.78)$$

Eq.(1.77) is the famous Guggenheim Eq.(1.74) when $\varepsilon_i = n_{Di}^2$. Thus one can conclude that Guggenheim equation is a special case of Debye formula if $\varepsilon_i = n_{Di}^2$. Therefore one should know the extrapolated values at $w_j \to 0$ from the measured relaxation parameters of different $w_j$'s to estimate $\mu_s$'s of dipolar liquids. Le Fevre and Smyth [1.41] and Guggenheim [1.42] obtained two different values of $\mu_s$ i,e 0.91 D and 0.83 D for trimethyl amine in benzene at 25 $^0$C using different extrapolation technique. Therefore in order to calculate $\mu_s$ accurately one should choose what type of extrapolation technique is needed to be used.

Guha *et al* [1.48] and Ghosh and Acharyya [1.49] tried to develop the dielectric theory within the frame work of Debye model [1.6] by introducing a new concept of $w_j$ instead of $c_j$ where $c_j = \rho_{ij} w_j / M_j$ and $w_i + w_j = 1$. But the density of solution $\rho_{ij}$ is a function of $w_j$

$$\rho_{ij} = \frac{\rho_i}{1-\gamma w_j} \qquad .....(1.79)$$

where $\gamma = (1-\rho_i/\rho_j)$, $\rho_i$, and $\rho_j$ are the densities of solvent and solute used.

Here Eq.(1.70) can now be written as

$$\frac{\varepsilon_{ij} - n_{Dij}^2}{(\varepsilon_{ij}+2)(n_{Dij}^2+2)} = \frac{\varepsilon_i - n_{Di}^2}{(\varepsilon_i+2)(n_{Di}^2+2)} + \frac{4\pi N \mu_s^2 \rho_i}{27 k_B T M_j}\frac{w_j}{1-\gamma w_j}$$

$$X_{ij} = X_i + \frac{4\pi N \mu_s^2}{27 M_j k_B T}\rho_i (w_j + \gamma w_j^2 + .....) \qquad .....(1.80)$$

$$X_{ij} = a + b w_j + c w_j^2 \qquad .....(1.81)$$

where $X_{ij}$ and $X_i$ are the experimentally measured static or low frequency parameters and $\mu_s$ is the dipole moment of the polar liquid under static electric field.

The Eq.(1.81) is highly converging in nature in the low concentration region of the polar-nonpolar liquid mixture and $\mu_s$ can easily be calculated from the derived equation

$$\mu_s = \left( \frac{27 k_B T M_j b}{4\pi N \rho_i} \right)^{1/2} \qquad .....(1.82)$$

The theory mentioned above is applied for a large number of polar-nonpolar liquid mixtures [1.48-1.50] in order to calculate $\mu_s$.

Suryavanshi and Mehrotra [1.51], on the other hand, suggested the least squares extrapolation technique to calculate $\mu$ of a dipolar liquid from the Eq.(1.82) of Acharyya *et al* [1.48]. The results were in excellent agreement with the reported values. One may, therefore, conclude that the least squares extrapolation [1.44] is one of the accurate techniques to study the dielectric relaxation of polar-nonpolar liquid mixture.

## 1.25. Eyring's Rate Theory in Dielectric Relaxation :

Eyring [1.15] treated dipole rotation in analogy with chemical rate process. He considered the chemical reaction of the type $A+B \rightarrow C$. The reaction takes place in the following way: $A$ and $B$ first form an 'activated complex' $AB$. The activated complex must acquire a certain amount of electric energy to form it which will react to form $C$ later. When this model is applied to dipole rotation in angular coordinates, the two states '$A+B$' and '$C$' are considered to have two different equilibrium of the orientations of the dipole while the activated state $AB$ as the state in which the dipole has sufficient energy to pass from one equilibrium position to the other over a potential barrier as shown in Fig.1.7. Applying this theory to the case of dipole rotation, Eyring identified that a dipole requires sufficient energy to pass over the potential barrier from one equilibrium position to the other with relaxation time $\tau$ by :

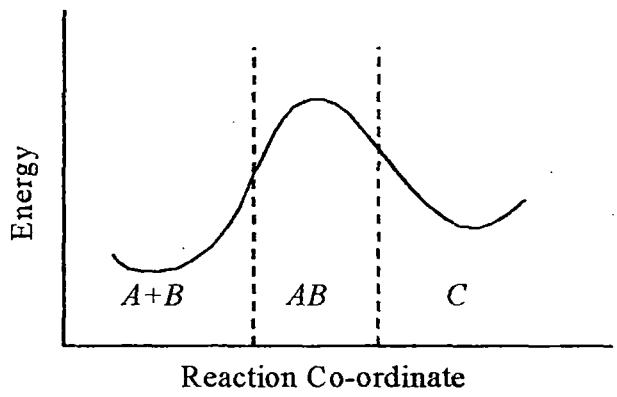


Figure 1.7: Variation of activation energy eith reaction co-ordinate

$$\tau = \frac{h}{k_B T} \exp(\Delta F_\tau / RT)$$

$$= \frac{h}{k_B T} \exp(-\Delta S_\tau / R) \exp(\Delta H_\tau / RT) \qquad .....(1.83)$$

where,

$\Delta F_\tau$= molar free energy of activation

$\Delta S_\tau$= molar entropy of activation

$\Delta H_\tau$= molar enthalpy of activation

Eyring has also obtained an expression for the viscosity flow of a dipolar liquid in terms of reaction rates as:

$$\eta = \frac{Nh}{V}\exp\left(-\Delta S_\eta / R\right)\exp\left(\Delta H_\eta / RT\right) \qquad .....(1.84)$$

where $V$ is the molar volume of the liquid. Eyring thus arrives at the equation :

$$\tau T \propto \eta V \qquad .....(1.85)$$

only if the enthalpies of activation are the same for both the processes.

Kauzmann [1.52] critically analysed Eyring's rate theory and gave a general theory of dielectric relaxation in terms of the frequency of discontinuous molecular reorientations called '*jumps*'. Assuming the relaxation process as a chemical reaction he defined the relaxation time $\tau = 1/k_o$ such that in this time the polarisation will fall to $1/e$ th of its initial value. Here $k_o$ is the rate constant for the activation of dipoles and is known as the dielectric relaxation rate. The reaction rate is:

$$k = K\frac{k_B T}{h}e^{\Delta S_\tau / R}e^{-\Delta E_\tau / RT} \qquad .....(1.86)$$

The main importance of the above formulations is that one can know the thermodynamics of the normal and the activated states from the observed reaction rate.

## 1.26. Brief Review of Relaxation Phenomena :

A large number of workers [1.1-1.4, 1.53-1.58] studied the relaxation phenomena of dipolar gases and liquids from dielectric polarisation. The observations are found in good agreement with the gas kinetic values except for substances having high dielectric constants [1.55-1.59] due to the presence of the substituent polar groups like –OH or $-NH_2$ in them. The anomalous behaviour of dispersion for liquids having –OH or $-NH_2$ groups was first observed by Drude [1.56] under relatively longer wavelength electric fields. Debye [1.6] explained this anomalous dispersion due to dielectric relaxation under *rf* electric field of the polar molecules. The radii of molecules of some ketones and glycerine were found to be smaller than the gas kinetic values as measured by Mizushima [1.60-1.61] based on Debye theory. The dipole moment $\mu$ for methyl, ethyl and amyl alcohols in benzene were measured by Stranathan [1.62] and found to be temperature independent in accordance with Debye theory. Rocard [1.63] modified Debye's theory by considering the influence

of moment of inertia of the molecules on the relaxation process. Fischer and Frank [1.64], however, measured $\varepsilon''$ under 4.3 metre wavelength electric field in order to estimate $\tau$ of aromatic halides. The shorter $\tau$'s were claimed for the rotation of $CH_2$–X group around their bond ring. But the theory could not explain the behaviour of alcohols for the strong interaction of –OH groups due to formation of hydrogen bonding. Budo [1.65] proposed the theory of dielectric relaxation considering the intra-molecular and inter-molecular rotations of the molecule. The analyses of dielectric relaxations of some non-spherical polar liquid molecules in non-polar solvent were made by Gross [1.66] to show the solvent effect under an isotropic electric field.

Onsagar [1.67] ,Plumley [1.68] and Pao [1.69] interpreted the origin of ionic conduction in dielectric liquids even in the purest hydrocarbons like hexane. Ryhel [1.70] and Eck [1.71] showed that ionic conduction occurs due to existence of ionic clusters in the liquids. Whiffen and Thompson [1.72] obtained relaxation time, dipole moment and different energy parameters of toluene, o-xylene, p-cymene chloroform etc. in non-polar solvent from –70 $^0$C to +80 $^0$C to predict the limitations of different rate processes in solutions. Jackson and Powles [1.73] estimated $\tau$ of polar molecules in benzene and paraffin only to show their dependence on the viscosity of solvents. The relaxation phenomena of polar liquid molecules under *rf* electric field were studied by Schallamach [1.74] in order to facilitate the rearrangement under single relaxation process. Macke and Reuter [1.75] measured relative permittivities of normal alcohols and phenols in benzene, carbon tetrachloride and cyclohexane at different temperatures to infer the molecular associations. The absorption of high frequency electric energy in dipolar aliphatic chlorides and alcohols were performed by Kremmling [1.76]. It was found difficult to sort out the effects of molecular association due to H-bond formation to change the shape of molecules. Further, the internal rotation, multiple relaxation times etc. could, however, be predicted.

Curties *et al* [1.77] observed that $\tau$'s were different in different solutions of pure polar or polar-nonpolar liquid mixtures of almost same viscosity. Methyl and ethyl alcoholic solutions of electrolytes have been studied by Lane and Saxton [1.78] who clearly established that the presence of ions reduces the permittivities of the media more markedly than that of water. Smyth *et al* [1.79] made a systematic studies on relaxation phenomena of some flexible polar molecules (alkyl halides) in liquid state in which dipole can reorient and play a significant role in the observed relaxation time. Jaffe and Lemay [1.80] concluded that dielectric liquids gave conduction current under breakdown voltage. The presence of positive ions is noticed by Green [1.81] in dielectric liquids due to dissociation of impurity molecules by external cosmic rays. Poley [1.82] estimated $\tau$ from measured $\varepsilon'$ and $\varepsilon''$ for mono substituted benzene. The increase of $\tau$ occurs with molecular size. Müller [1.83], however, calculated the low molecular radii in comparison to other methods. Dielectric measurements of relaxation parameters on pure normal propyl to decayl alcohols were

carried out by Garg and Smyth [1.84] to show three different $\tau$ 's which are associated with polymeric cluster formation by the strong H-bonding between OH-groups. The intermediate $\tau$'s were attributed to the rotation of free alcohol molecules.

Simultaneous determination of $\tau$ and $\mu$ of polar-nonpolar liquid mixtures was made by Gopalakrishna [1.85]. The advantage of this method is to know only the density of the pure solvent. Different molecular associations in saturated dielectric liquids were studied by Schellman [1.86]. Srivastava and Vershri [1.87] explained the variation of $\varepsilon'$ with concentration and temperature for binary polar mixtures of methyl and butyl alcohols with water.

Bergmann *et al* [1.88] gave a graphical method in complex plane to estimate $\tau_1$(smaller) and $\tau_2$(larger) that interpreted the intramolecular and molecular rotations of polar molecule respectively. Higasi *et al* [1.33] analysed the experimental data of liquid *n*-alkyl bromide in terms of distribution of $\tau$ 's between two limiting $\tau$ values.

The $\tau$'s of alkyl cyanides and alkythiols increase with the size of the molecules as observed by Krishnaji and Mansingh [1.89] from the dielectric relaxation measurement. Froster [1.90] explained the conduction in aliphatic hydrocarbons by the presence of impurities of trace polar or trapped electrons at the electrode surfaces. Experimental evidences showed electronic conduction in unsaturated hydrocarbons. Dielectric relaxation studies of ionic solutes in non-hydroxylic solutions [1.91-1.92] over a wide range of frequency established the simultaneous presence of conduction and dipole dispersion. Sinha *et al* [1.93-1.94] predicted the temperature dependence of $\tau$ and $\mu$ of polar molecule in non-polar solvent. The dependence of $\tau$ on $T$ is, however predicted. Temperature dependence of conductivity for organic liquids were studied by Adamezewski and Jachym [1.95]. Jayprakash [1.96] estimated $\tau$ of some spherical polar molecules in non-polar solvents in excellent agreement with Gopalakrishna [1.85]. Bhattacharyya *et al* [1.97] modified Bergmann equations [1.88] in order to obtain molecular and intra-molecular $\tau_2$ and $\tau_1$ of phenetole, aniline and orthochloro aniline. Non-rigid molecules having two $\tau$'s and average $\tau$ could, however, be obtained by Higasi *et al* [1.98] 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.

Lohneysen and Nageral [1.99] found the existence of natural charge carriers in liquids of two kinds of mobilities. The direct evidence of ionic conduction in polar dielectrics was found by Gaspared and Gosse [1.100] when the electrodes were membraned by teflon. The $\varepsilon'$ and $\varepsilon''$ of aliphatic alcohols in non-polar solvents at different concentrations under *hf* electric field were measured by various workers [1.101-1.103]. Other group of workers [1.104-1.113] measured relative permittivities $\varepsilon'$, $\varepsilon''$, $\varepsilon_o$ and $\varepsilon_\infty = n_D^2$ of some substituted toluidines, para-compounds,

diphenylene oxide, chloral, ethyltrichloroacetate, trifluoroethanol, trifluoroacetic acid and a large number of monosubstituted and disubstituted benzenes and anilines in different non-polar solvents at various $w_j$'s and $t^0$C under nearly 3 cm. wavelength electric field to estimate $\tau$, $\mu$ and thermodynamic energy parameters. The observed results were explained in terms of molecular associations of the polar liquid molecules. Rajyam *et al* [1.114] studied the dielectric dispersion of glycerol and diethylene glycol under *rf*, *mw* and *uhf* electric fields at 80$^0$C and confirmed the Davidson-Cole type of dispersion. Mulechi *et al* [1.115] 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.

A number of workers [1.116-1.120] estimated $\tau$ from the number density '$n$' of free ions, radius '$a$' of the rotating units for some straight chain alcohols, anilines, benzyl chlorides, acetone under *rf* electric field at different temperatures. $\tau$'s are observed to increase as the number of C-atom of dipolar molecules increases. The relaxation parameters from the *rf* conductivity $\sigma$ has been used to study the structure of liquids.

Dhull, Sharma and Gill [1.121-1.125] measured $\varepsilon'$ and $\varepsilon''$ of NMA, DMF, DMA in benzene, dioxane and carbon tetrachloride in order to obtain the different relaxation parameters. Acharyya and Chatterjee [1.126] and Acharyya *et al* [1.127] estimated $\tau$, $\mu$ and different energy parameters $\Delta H_\tau$, $\Delta S_\tau$ and $\Delta F_\tau$ of some interesting polar liquid molecules in benzene and carbon tetrachloride. *Hf* conductivity $\sigma$ in $\Omega^{-1}.cm^{-1}$ of a polar–nonpolar concentrated liquid mixture is liable to yield $\mu$ of dimer formation. Low concentration region $\sigma$ in $\Omega^{-1}.cm^{-1}$ gives $\mu$ for monomer formation. The estimated $\mu_{theo}$ 's from the available bond angles and bond moments reveal the structural conformations. $\varepsilon'$ and $\varepsilon''$ of *n*-butyl chloride, chlorobenzene and tertiary butyl alcohol in benzene were measured by Agarwal [1.128] at 32$^0$C under 9.96 GHz electric field to estimate $\tau$. It is observed that $\tau$ is influenced by structural conformation in the following manner $\tau_{linear} > \tau_{planer} > \tau_{spherical}$. The experimental and theoretical $\tau$ 's were found in agreement in case of thiophenone, acetone, benzophenone and their mixture in *mw* electric field over a wide range of temperature as observed by Madan [1.129]. Vyas and Vashisth [1.130] explained the variation of $tan\delta$ ($=\varepsilon''/\varepsilon'$) curve against weight fraction $w_j$ of solute in case of four aliphatic alcohols, their binary mixtures and the mixtures of alcohols with DMF and 2-fluoroaniline in benzene under 3 cm. wavelength electric field. The alcohols +DMF mixtures showed complex formations at a very low concentration. The study of alcohol+2-fluoro aniline, however, indicates dissociation effects. Gandhi and Sharma [1.131] determined $\tau_o$, $\tau_1$ and $\tau_2$, distribution parameters of isobutyl-methacrylate and allyl-

methacrylate and their mixtures in benzene. The observed results reveal the existence of intra-molecular and molecular rotations.

Murthy *et al* [1.132] however, modified the work of Acharyya *et al* [1.126] and gave a new dimension in the theoretical formulation of dielectric relaxation in which simultaneous determination of $\tau$ and $\mu$ of a polar-nonpolar liquid mixture can be obtained. Makosz [1.11] calculated $\mu$ of some ellipsoidal dipolar liquids in non-polar solvents at 25$^0$C from the formula derived from Onsager's equation. Sharma and Sharma [1.133] and Sharma *et al* [1.134] measured $\varepsilon_{ij}'$ and $\varepsilon_{ij}''$ of dilute solution of DMSO and DMF+DMSO mixture in benzene and carbon tetrachloride in the temperature region of 25$^0$C to 40$^0$C under 9.174 GHz electric field. $\tau$, $\mu$, $\Delta H_\tau$ and $\Delta S_\tau$ of dielectric relaxation and $\Delta H_\eta$, $\Delta S_\eta$ and $\Delta F_\eta$ for viscous flow were obtained.

A series of relaxation parameters were calculated by Saha and Acharyya [1.135-1.136] from the measured relative permittivities based on newly developed methodology. Higher and lower values of $\mu$ arise due to the monomer and dimer formations. $\mu_{theo}$'s from the available bond angles and bond moments of substituted polar groups attached to the parent molecules were estimated. The excellent agreement of $\mu_{theo}$'s with measured $hf\,\mu$ 's shed much light on the inductive, electromeric and mesomeric moments of polar groups. The concentration variation of the measured [1.108-1.112] $\varepsilon_{ij}'$, $\varepsilon_{ij}''$, $\varepsilon_{oij}$ and $\varepsilon_{\infty ij} = n_{Dij}^2$ of a large number of disubstituted benzenes, anilines and monosubstituted anilines in benzene and carbon tetrachloride under *hf* electric field were analysed by Saha *et al* [1.137] and Sit *et al* [1.138-1.139] to estimate $\tau_1$, $\tau_2$ and $\mu_1$ and $\mu_2$ due to the rotation of the flexible polar groups attached to the parent molecules and the whole molecules themselves. The dielectric relaxation phenomena of acetophenone, DMSO and their mixtures in benzene were done by Singh and Sharma [1.140] under 9.33 GHz electric field in the temperature range of 20$^0$C to 40$^0$C. Nonlinear behaviour of $\tau$ reveals the presence of solute-solvent and solute-solute molecular associations. Jangid *et al* [1.141] made extensive study on four pure nicotinades and their quartarnary mixtures. The sufficient information about intra-molecular and inter-molecular rotations was obtained in terms of solute-solvent (monomer) and solute-solute (dimer) formations. Measurement of $\varepsilon'$, $\varepsilon''$, and $tan\delta$ of polar liquids in non-polar solvents under different GHz electric fieled were made by a number of workers. The results are well explained by the rotation of –OH group about the whole molecular rotation. The molecular shapes, sizes and structures by H-bonding, and various molecular associations were interpreted by the dipole–dipole interactions.

Sengwa and Kaur [1.142] determined Kirkwood correlation factor '$g$', average $\tau_o$, $\Delta F_{\tau_o}$ of ortho-hydroxy benzaldehyde in benzene at different experimental temperatures under GHz electric field. Molecular associations hinder the intra-molecular rotations of –CHO and –OH groups in the compound to affect $\tau$. Temperature variation of dielectric relaxation of ethylene glycol–water

mixture was carried out by Saha and Ghosh [1.143] under 1 MHz electric field. High values of $\tau$ were explained by the polymeric cluster formation of molecular association. Formation of H-bonding between two polar molecules in non-polar solvent was investigated by Dash *et al* [1.144] in some alcohols. Thakur and Sharma [1.145] measured the thermodynamic energy parameters due to dielectric relaxation and viscous flow for acetonitrile and DMF in benzene to explain the solute-solvent molecular association.

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