

CHAPTER 1

GENERAL INTRODUCTION AND BRIEF REVIEW OF THE PREVIOUS WORKS

1.1. Polarisation and Clausius Mossotti Relation

Dielectric materials are usually divided into two classes called nonpolar and polar dielectrics. The molecules having coincident and noncoincident centres of positive and negative charges are called nonpolar and polar dielectrics respectively.

When a nonpolar molecule is placed between two charged plates the centre of gravity of positive and negative charges get displaced in order to form an electric dipole. The phenomenon of producing induced dipole moment in nonpolar molecules is known as distortion polarisation. The distortion polarisation are of three types such as electronic, atomic and interfacial polarisation. Electronic polarisation arises due to the shift of centre of gravity of electron and nuclear particles. The displacement of the atoms or ions within the molecules causes change in interatomic or ionic distances which is known as atomic or ionic polarisation. Interfacial polarisation comes into play due to inhomogeneous constituents of materials which vary from layer to layer. All the above three polarisations are induced polarisation. Besides these, due to existence of dipolar nature of molecule which arises due to asymmetry of the molecules as in the case of polar molecules, the permanent polarisation is also present.

Therefore, total polarisation

$$P_t = P_i + P_p \quad \text{.....(1.1)}$$

where P_i = induced polarisation and P_p = Permanent polarisation.

If \vec{p} be the induced dipole moment on each dielectric molecule due to the external electric field \vec{E} which in its turn is modified called \vec{E}_{loc} , the local field or internal electric field within the dielectric.

Let $\vec{p} \propto \vec{E}_{loc}$ for a homogeneous or isotropic dielectric.

$$\text{or, } \vec{p} = \alpha \vec{E}_{loc} \quad \text{.....(1.2)}$$

where α is the proportionality constant called molecular polarisability. Now, in order to calculate \vec{E}_{loc} we assume that

$$\vec{E}_{loc} = \vec{F}_1 + \vec{F}_2 + \vec{F}_3 \quad \dots\dots\dots(1.3)$$

where \vec{F}_1 is the uniform electric field intensity at a point due to distribution of charges between condenser plates and $\vec{F}_1 = 4 \pi \sigma$, σ being charge density on the plates.

\vec{F}_2 is the electric field intensity produced due to polarisation of atoms or molecules as well as distortion of electrical lines of force.

$$\begin{aligned} \text{Thus } \vec{F}_2 &= \vec{F}'_2 + \vec{F}''_2 \quad \dots\dots\dots(1.4) \\ &= -4 \pi \vec{P} + \frac{4}{3} \pi \vec{P} \end{aligned}$$

where \vec{P} is the charge exerted at any point outside the sphere placed at the centre of the molecule under consideration.

$$\begin{aligned} \text{Now, } \vec{E}_{loc} &= \vec{F}_1 + \vec{F}'_2 + \vec{F}''_2 + \vec{F}_3 \\ &= 4 \pi \sigma + (-4 \pi \vec{P}) + \frac{4}{3} \pi \vec{P} + \vec{F}_3 \quad \dots\dots\dots(1.5) \end{aligned}$$

For homogeneous dielectric as well as for cubic crystal solids, $\vec{F}_3 = 0$

$$\begin{aligned} \text{So, } \vec{E}_{loc} &= 4 \pi \sigma - 4 \pi \vec{P} + \frac{4}{3} \pi \vec{P} \\ &= \vec{D} - 4 \pi \vec{P} + \frac{4}{3} \pi \vec{P} \\ &= \vec{E} + \frac{4}{3} \pi \vec{P} \quad \dots\dots\dots(1.6) \end{aligned}$$

Now, the dielectric displacement vector \vec{D} is $\vec{D} = \epsilon \vec{E}$ where $\epsilon =$ dielectric constant of the dielectric material.

So eq (1.2) can be written as

$$\vec{p} = \alpha \vec{E}_{loc} = \alpha \left(\vec{E} + \frac{4}{3} \pi \vec{P} \right)$$

$$\text{or, } \vec{P} = n \vec{p} = n \alpha \left(\vec{E} + \frac{4}{3} \pi \vec{P} \right) \quad \dots\dots\dots(1.7)$$

where n = number of molecules per unit volume. \vec{p} = dipole moment per unit volume = polarisation vector.

$$\text{Again, } \vec{D} = \vec{E} + 4\pi \vec{p} \text{ and } \vec{D} = \epsilon \vec{E}$$

$$\text{or, } \vec{p} = \frac{(\epsilon - 1) \vec{E}}{4\pi} \quad \dots\dots(1.8)$$

From eqs. (1.7) and (1.8) one can have.

$$\frac{(\epsilon - 1) M}{(\epsilon + 2) \rho} = \frac{4}{3} \pi N \alpha \quad \dots\dots(1.9)$$

Where M is the molecular weight, ρ is the density of the dielectric material and N = Avogadro's number respectively. The relation (1.9) is known as Clausius-Mossotti relation.

1.2. Debye Equation

When a polar dielectric is placed in an uniform electric field the permanent electric moment $\vec{\mu}$ associated with each polar molecule tends to orient along external field direction \vec{E} . The average dipole moment of each molecule be \bar{m} shown to be $\frac{\mu^2 E}{3 k T}$

$$\text{Since } \frac{\bar{m}}{E} = \alpha_o = \text{orientational polarisability} = \frac{\mu^2}{3 k T}$$

$$\text{Thus the total polarisability } \alpha_T = \alpha_d + \alpha_o = \alpha + \frac{\mu^2}{3 k T}$$

Equation (1.9) becomes

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4}{3} \pi N \left(\alpha + \frac{\mu^2}{3 k T} \right) \quad \dots\dots(1.10)$$

Equation (1.10) is known as Debye¹⁾ equation for polar dielectric when it is placed in an uniform electric field.

1.3. Onsager's Theory under Static Electric Field

Onsager²⁾ considered the polar liquid as a polarisable point dipole at the centre of a spherical cavity of molecular dimensions surrounded by an unpolarised medium. The field within the cavity consists of the cavity field \vec{G} , arising due to external charges. The cavity field \vec{R} arises due to polarisation of the environment medium by the field of dipoles.

The two fields are given by :

$$\vec{G} = \frac{3 \epsilon_0}{2 \epsilon_0 + 1} \vec{E} \quad \text{..... (1.11)}$$

$$\text{and } \vec{R} = \frac{2 (\epsilon_0 - 1)}{(2 \epsilon_0 + 1) a^3} \vec{\mu} \quad \text{.....(1.12)}$$

Where 'a' is the radius of the spherical cavity, ϵ_0 is the static dielectric constant of the surrounding medium, $\vec{\mu}$ is the dipole moment in the cavity under the uniform macroscopic field \vec{E} outside the cavity. Thus the total field acting upon a spherical polar molecule in a polarised dielectric medium is given by:

$$\vec{F} = \vec{G} + \vec{R} = \frac{3 \epsilon_0}{2 \epsilon_0 + 1} \vec{E} + \frac{2 (\epsilon_0 - 1)}{(2 \epsilon_0 + 1) a^3} \vec{\mu} \quad \text{.....(1.13)}$$

Onsager²⁾ equation for static dielectric constant in case of polar liquids is thus obtained in the following form:

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{\rho}{M} \left[\frac{3 \epsilon_0 (\epsilon_\infty + 2)}{(2 \epsilon_0 + \epsilon_\infty) (\epsilon_0 + 2)} \right] \frac{4 \pi N \mu^2}{9 k T} \quad \text{..... (1.14)}$$

This equation becomes Debye equation when the factor $\left[\frac{3 \epsilon_0 (\epsilon_\infty + 2)}{(2 \epsilon_0 + \epsilon_\infty) (\epsilon_0 + 2)} \right]$ approaches to unity as ϵ_0 tends to ϵ_∞ for infinitely dilute polar solute in a nonpolar solvent.

The approximate validity of Onsager's equation is found in case of large number of unassociated liquids, but the experimental results deviate largely from the theoretical ones

for associated liquids like water, alcohol and liquid ammonia. The discrepancies may be because of the following reasons:

- a) In associated liquids short range forces arise due to ordered array of neighbouring molecules which play an important role.
- b) Molecules should be spherical in form.
- c) The environment of the molecule is treated as homogeneous continuum and the local saturation effects are neglected

1.4. Kirkwood's Theory

The effect of the short range forces was first considered by Kirkwood³⁾. By taking into accounts the sum of the molecular dipole moment and the moment induced as a result of the hindered rotation in the spherical region surrounding the molecules, Kirkwood has derived following relation:

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{\rho}{M} \left[\frac{3 \epsilon_0 (\epsilon_\infty + 2)}{(2 \epsilon_0 + \epsilon_\infty) (\epsilon_0 + 2)} \right] \frac{4 \pi N \mu^2 g}{9 k T} \quad \dots\dots(1.15)$$

Where g is a correlation parameter which characterises the intermolecular interaction and short range forces. Kirkwood has pointed out that the departure of g from unity is a measure of hindered relative molecular rotation arising from short range intermolecular forces. Thus the unassociated liquids show the value of g approximately unity, while for associated liquids g 's are sufficiently apart from unity. Moreover, like Onsager's equation the Kirkwood's equation also contains the approximation involved in treating the polar molecules as spherical.

1.5. Fröhlich's Theory

Kirkwood Theory has been modified by Fröhlich⁴⁾ by considering a dipolar dielectric with a number of polarizable units of the same kind within a large spherical region. Each unit has various dipole moment $\vec{\mu}$ in different directions due to thermal fluctuation with a certain probability. The average moment $\vec{\mu}^*$ due to such unit within

the spherical region is different from $\vec{\mu}$ because of the short range interactions between the polarizable units and the deviation of the shape of the molecules from a sphere. An equation for low intensity field has been derived on above line as:

$$\epsilon_0 - 1 = \frac{3 \epsilon_0}{2 \epsilon_0 + 1} \frac{4 \pi N_0}{3} \frac{\vec{\mu} \vec{\mu}^*}{k T} \quad \dots\dots (1.16)$$

where N_0 = number of units per unit volume. The difficulties in Fröhlich's theory are associated with the evaluation of energy of the interaction of the sample with the surrounding medium.

However, as indicated above there are experimental limitations in determining the required parameters involved in various theories lead to Onsager's equation for unassociated liquids when short range forces are absent. So one can safely use Onsager's equation for analysing the experimental data to determine the dipole moment of a polar liquid.

1.6. The Dielectric Behaviour at High Frequencies

In the case of static or low frequency electric field the dielectric is in equilibrium with the applied electric field. When the frequency of the applied electric field exceeds a certain critical value, the permanent electric dipole can not follow the exact alternations of the electric field without measurable lag. The critical value of frequency depends on the chemical compositions, the structure of the dielectrics and on the temperature. In most of the cases this critical value is higher than $3 \times 10^6 \text{ Sec}^{-1}$. This lag is commonly referred to relaxation which is defined as the lag in the response of a system to change in the forces to which it is subjected.

The polarisation acquires a components out of phase with the field and the displacement current acquires a conductance component in phase with the field resulting in thermal dissipation of energy.

In such cases it is usual to relate the displacement vector \vec{D} and the electric field vector \vec{E} by a complex dielectric constant as:

$$\epsilon^* = \epsilon' - j \epsilon'' \quad \dots\dots(1.17)$$

where ϵ' is the real part of the dielectric constant and ϵ'' is the dielectric loss factor. So loss tangent $\tan \delta$ is given by:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad \dots\dots(1.18)$$

Debye¹⁾ was the first to give a relation between dielectric polarisation and the frequency of the alternating field by:

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \left[\frac{\epsilon_0 - 1}{\epsilon_\infty + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] \frac{1}{1 + j \omega \tau_0} \quad \dots\dots(1.19)$$

where τ_0 is the molecular relaxation time and ω is the angular frequency of the applied electric field. Solving the eqs (1.17) and (1.19) for ϵ^* and separating real and imaginary parts, one gets.

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + X^2} \quad \dots\dots(1.20)$$

$$\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 + X^2} X \quad \dots\dots (1.21)$$

where $X = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \omega \tau_0$

1.7. Macroscopic & Microscopic Relaxation Time

Fröhlich⁵⁾ has derived the Debye's equation by assuming that in the constant external field equilibrium is attained exponentially with time and has the decay function $f(t)$ as:

$$f(t) \propto e^{-t/\tau} \quad \dots\dots(1.22)$$

where τ is independent of time, but depends on temperature. With an electric field $E(t)$ which is dependent on time, a field $E(u)$ which is applied during a time interval between u and $u+du$ a corresponding electric displacement $D(t)$ can be written as:

$$D(t) = \epsilon_\infty E(t) + \int_{-\infty}^t E(u) f(t-u) du \quad \dots\dots(1.23)$$

The first term on the right hand side of above equation is the instantaneous displacement while the second term is absorptive term. The calculation of the Fröhlich finally leads to following relation:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j \omega \tau} \quad \dots\dots (1.24)$$

Separating the real and the imaginary parts one gets:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau^2} \quad \dots\dots(1.25)$$

and $\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau \quad \dots\dots(1.26)$

It is clear from (1.26) that ϵ'' 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 ϵ' with $\omega\tau$ is shown in Fig (1.2). The eqs (1.25) and (1.26) differ from the Debye eqs (1.20) and (1.21) only in that the Debye equation contains the quantity $\tau_0(\epsilon_0+2)/(\epsilon_\infty+2)$ instead of τ . Comparing, the two equations a relation between macroscopic relaxation time τ and the microscopic relaxation time τ_0 is obtained like.

$$\tau = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \tau_0 \quad \dots\dots(1.27)$$

Since Onsager's equation is an advancement over the Debye's equation, one can change Onsager's equation to be used for complex dielectric constant. For that μ^2 has to be replaced by $\frac{\mu^2}{1 + j \omega \tau_0}$ and ϵ_0 by ϵ^* . Thus the resulting expression is found to be quadratic in ϵ^* as:

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{\rho}{M} \left[\frac{3 \epsilon^* (\epsilon_\infty + 2)}{(2 \epsilon^* + \epsilon_\infty) (\epsilon^* + 2)} \right] \frac{4 \pi N}{9 k T} \frac{\mu^2}{1 + j \omega \tau_0} \quad \dots\dots(1.28)$$

Cole⁶⁾ has shown that the factor $\frac{3 \epsilon_0}{2 \epsilon_0 + \epsilon_\infty}$ can be put approximately equal to 3/2 for

higher values of ϵ_0 . Then the resulting expression is :

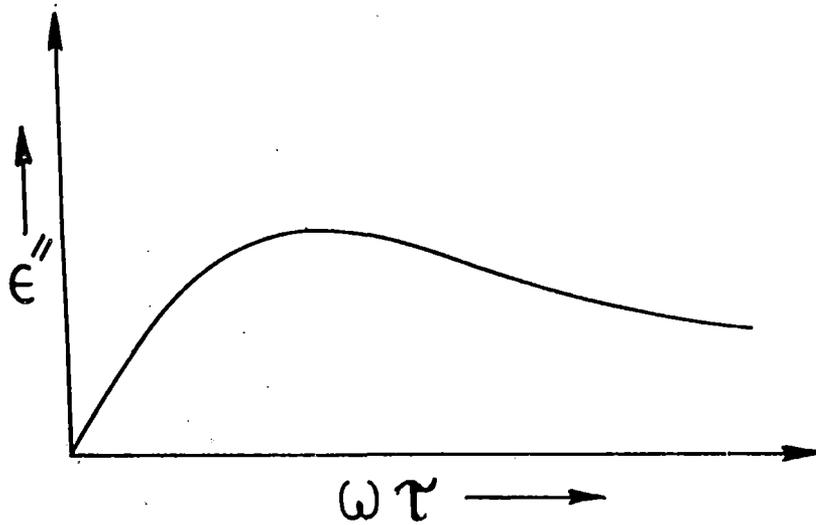


Figure 1.1 Variation of imaginary parts of dielectric constant with $\omega\tau$

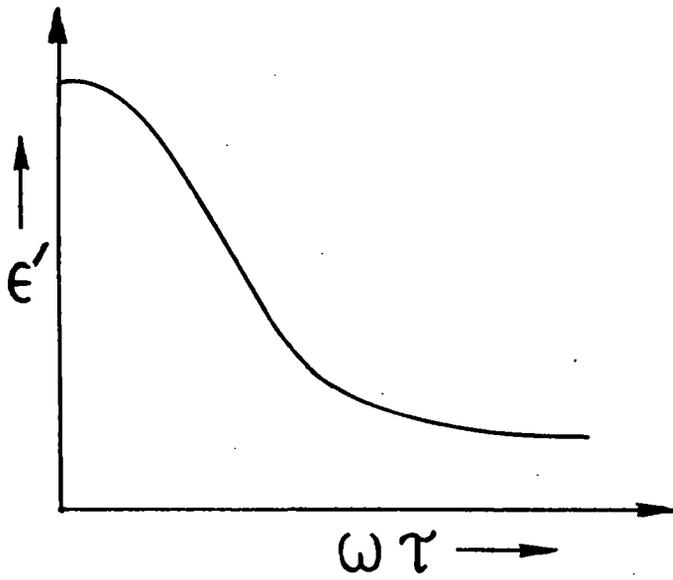


Figure 1.2 Variation of real parts of dielectric constant with $\omega\tau$

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + j\omega\tau_0} \quad \dots\dots(1.29)$$

which is similar to Fröhlich equation.

The above equation shows that the microscopic and macroscopic relaxation times are equal. Various workers⁷⁻⁹⁾ had roughly examined and modified the Onsager's equation, but none of them could give the satisfactory conclusion. O'Dwyer and Sack¹⁰⁾ had obtained a relation between macroscopic and microscopic relaxation times as a second order approximation

$$\tau_0 = \frac{3 \epsilon_\infty \epsilon_0 (2 \epsilon_0 + \epsilon_\infty)}{3 \epsilon_0^3 + \epsilon_\infty^3} \tau \quad \dots\dots(1.30)$$

Powles¹¹⁾ had also tried to solve the problems in a different way. He has defined a time dependent field \vec{H} , which reduces to cavity field \vec{G} in the static case, so that

$$\frac{\vec{H}}{\vec{E}} = \frac{3 \epsilon_\infty}{2 \epsilon_\infty + 1} + \left(\frac{3 \epsilon_0}{2 \epsilon_0 + 1} - \frac{3 \epsilon_\infty}{2 \epsilon_\infty + 1} \right) \frac{1}{1 + j \omega \tau} \quad \dots\dots(1.31)$$

Powles¹¹⁾ had shown that the comparison of eq (1.31) with that of Debye leads to a relation between τ and τ_0 like.

$$\tau = \frac{3 \epsilon_0}{2 \epsilon_0 + \epsilon_\infty} \tau_0 \quad \dots\dots(1.32)$$

1.8. Distribution of Relaxation Time

To check the validity of eqs (1.25) and (1.26), the experimental results are usually represented by plotting ϵ' and ϵ'' against logarithm of frequency or wavelength of the electric field. The curves obtained (ϵ' vs. $\log\omega$) and (ϵ'' vs. $\log\omega$) as shown in Figs (1.3) and (1.4) are called the dispersion and absorption curves respectively. Another method of examining the equations, proposed by Cole-Cole is to construct an Argand diagram or complex plane locus in which the imaginary part ϵ'' of complex dielectric constant ϵ^* is

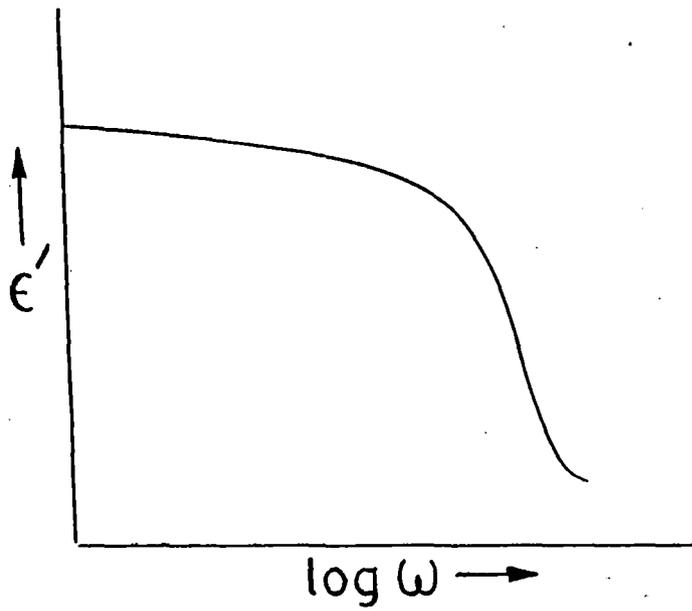


Figure 1.3 Frequency dependence of real part of dielectric constant

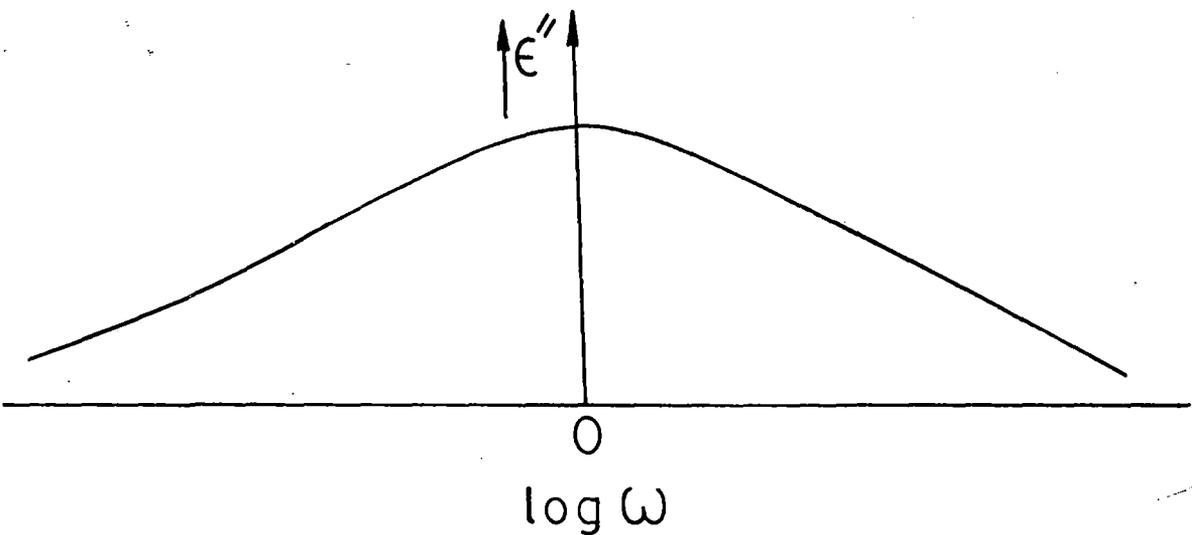


Figure 1.4 Frequency dependence of imaginary part of dielectric constant

plotted against ϵ' , the real part. Each point corresponds to one frequency. Combining the eqs (1.25) and (1.26) one gets:

$$\left(\epsilon' - \frac{\epsilon_0 + \epsilon_\infty}{2} \right)^2 + \epsilon''^2 = \left(\frac{\epsilon_0 - \epsilon_\infty}{2} \right)^2 \quad \dots\dots(1.33)$$

Thus by plotting ϵ'' against ϵ' , as shown in Fig (1.5), semicircle must be obtained with radius $\frac{\epsilon_0 - \epsilon_\infty}{2}$ and centre lying on the abscissa at a distance $\frac{\epsilon_0 + \epsilon_\infty}{2}$ from the origin.

The intersection points with the abscissa are given by $\epsilon' = \epsilon_\infty$ and $\epsilon' = \epsilon_0$. It has been found that only on exceptional cases the experimental results satisfy the above mentioned equation. Generally, the dispersion curve is found to be flatter and extends over a wide range of frequency while the absorption curve is broader and the maximum value of ϵ'' is smaller than the value given by $\epsilon_m'' = \frac{\epsilon_0 - \epsilon_\infty}{2}$. However, the curves are still symmetrical.

1.8 a) Cole-Cole Plot

Generally, the behaviour of a dielectric can not be described by single relaxation time. Cole-Cole¹²⁾ showed that if a dielectric system has a distribution of relaxation times, then the complex plane locus, obtained by plotting ϵ'' vs. ϵ' , is generally an arc of a circle intersecting the abscissa axis at the values ϵ_∞ and ϵ_0 and having its centre lying below the abscissa axis. The diameter drawn through the centre from ϵ_∞ makes an angle α $\pi/2$ with the ϵ' axis as shown in Fig (1.6). α is the symmetric distribution parameter determined from the plot. The empirical formula used by Cole-Cole can be represented as :

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + (j \omega \tau_0)^{1-\alpha}} \quad \dots\dots(1.34)$$

1.8b) Cole - Davidson Plot

Davidson and Cole¹³⁾ had obtained an skewed arc indicating an asymmetric distribution of relaxation times in Glycerol and Glycol. The variation of ϵ'' with ϵ' at low

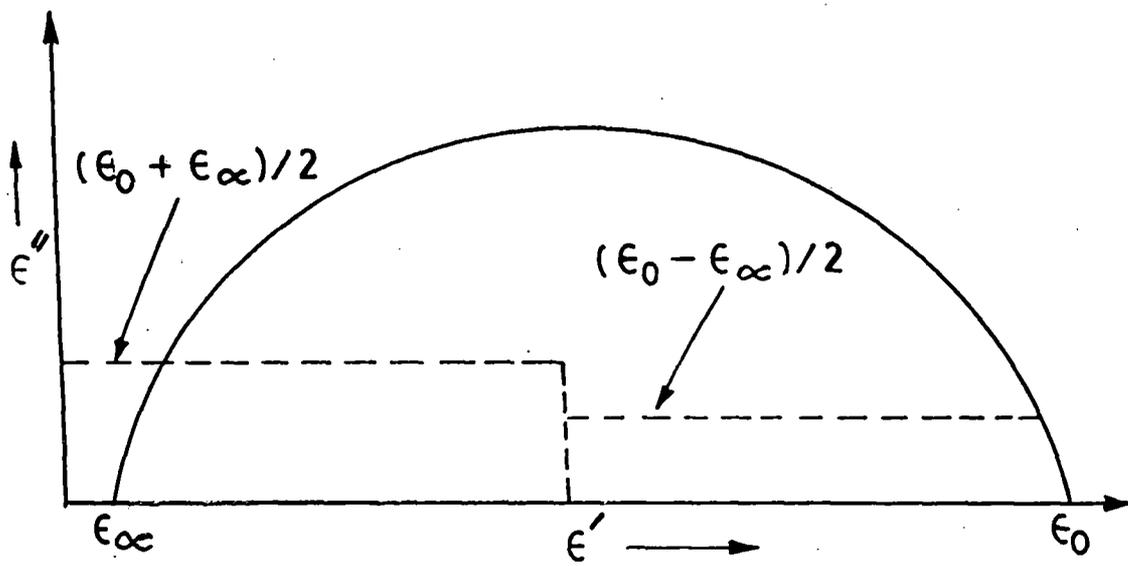


Figure 1.5 Plot of ϵ'' against ϵ' at different frequency

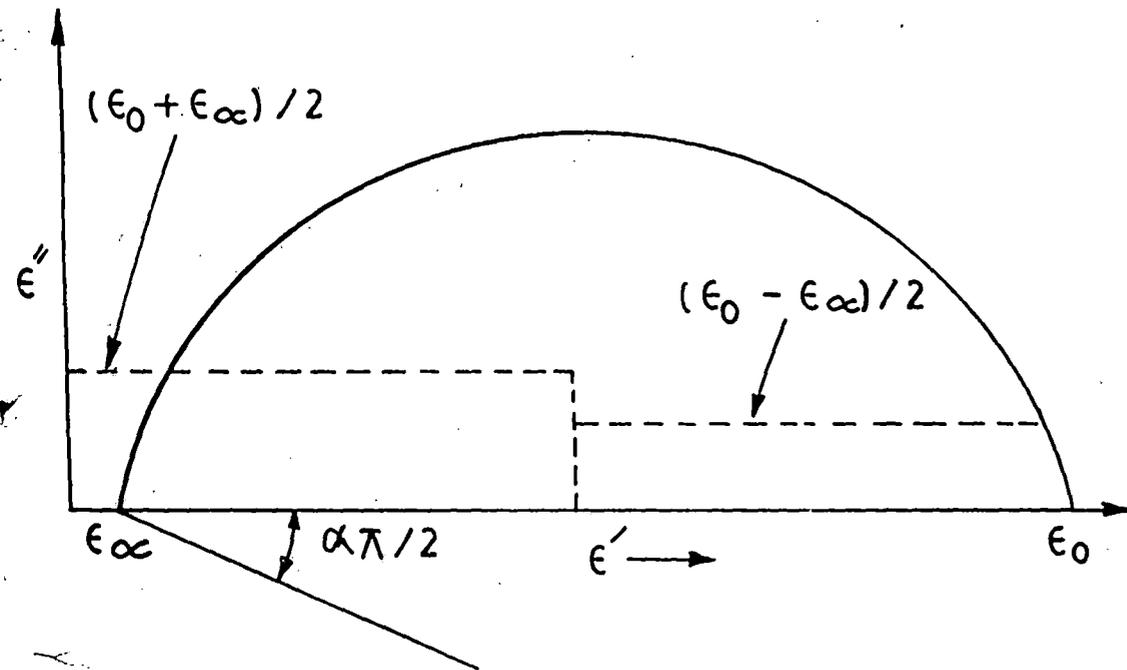


Figure 1.6

Cole-Cole plot of ϵ'' vs ϵ'

frequency end of this plot as seen in Fig (1.7) resembles with that found for a single relaxation time. At high frequency end, however, the locus approaches the X axis at an angle less than 90°. The corresponding form for complex dielectric constant ϵ^* and the asymmetric distribution parameter β can be written as:

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{(1 + j \omega \tau_0)^\beta} \quad \dots\dots(1.35)$$

It is obvious that the distribution is asymmetric having a low frequency cut off at τ_0 . β is a measure of the angle at which the complex plane locus intersects the ϵ' axis.

Although, many experimental results were found to satisfy the Cole-Cole and Cole-Davidson relation, but they have the disadvantage that a theoretical explanation has not yet been given.

The reason why in liquids the experimental curve deviates from the normal curve is that the model used in their derivations is too simple. The following three types of behaviours are generally obtained in variety of the systems in addition to semi-circular behaviour of Debye.

- i) A circular arc with centres lying below the abscissa shows, the symmetric distribution of relaxation time.
- ii) An skewed arc is obtained, indicating an asymmetric distribution of relaxation times.
- iii) A curve which can be supposed to be made up of a number of circular arc plots, showing multiple relaxation times.

For such a distribution of relaxation times, the Debye equation must be extended to:

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \int_0^\infty \frac{G(\tau)}{1 + j \omega \tau} d\tau \quad \dots\dots(1.36)$$

where $G(\tau)$ is the distribution function of the relaxation times. $G(\tau) d\tau$ is the fraction of the molecules associated at a given instant with relaxation times between τ and $\tau + d\tau$.

Thus $G(\tau)$ satisfies the normalisation condition:

$$\int_0^\infty G(\tau) d\tau = 1 \quad \dots\dots(1.37)$$

The original equation of Debye can be written as:

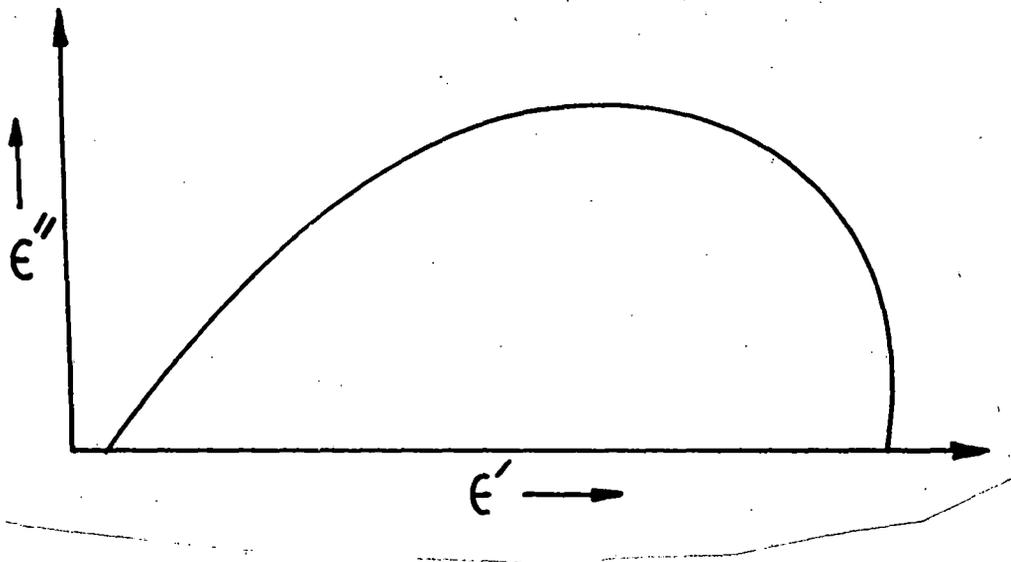


Figure 1.7

Cole - Davidson plot of ϵ'' vs ϵ'

$$\epsilon' = \epsilon_{\infty} + (\epsilon_0 - \epsilon_{\infty}) \int_0^{\infty} \frac{G(\tau) d\tau}{1 + \omega^2 \tau^2} \quad \text{.....(1.38)}$$

$$\text{and } \epsilon'' = (\epsilon_0 - \epsilon_{\infty}) \int_0^{\infty} \frac{\omega \tau G(\tau) d\tau}{1 + \omega^2 \tau^2} \quad \text{.....(1.39)}$$

1.9 Calculation of Distribution Function

A large number of relations connecting the distribution functions has been given by various workers. Wagner ¹⁴⁾ and Yager ¹⁵⁾ had shown that the Gaussian probability distribution is

$$G(\tau) d\tau = \frac{b}{\sqrt{\pi}} \exp(-b^2 y^2) dy \quad \text{.....(1.40)}$$

which can be used to explain the experimental results. Here b is a constant determining breadth of the distribution and y is

$$y = \ln(\tau/\tau_0) \quad \text{.....(1.41)}$$

where τ_0 is the most probable relaxation time. $G(\tau) d\tau$ gives the probability of finding a relaxation time τ such that $\ln(\tau/\tau_0)$ lies between y and $y + dy$.

In long chain polar molecules, such as polymers there are many possibilities of internal rotations, bending and twisting each with a corresponding characteristic relaxation time. In averaging to the macroscopic condition a distribution of relaxation times will result. For long chain polymers Kirkwood and Fouss ¹⁶⁾ derived:

$$G(\tau) = \frac{1}{2 \cosh y + 2} \quad \text{.....(1.42)}$$

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

This formula is not found in agreement with the experimental results. Fouss and Kirkwood ¹⁷⁾ further suggested that the experimental data should be represented by empirical relation:

$$\epsilon'' = \epsilon''_m \operatorname{sech} \left[\beta \ln \frac{\omega}{\omega_m} \right] \quad \text{.....(1.43)}$$

where β is a distribution parameter and ω_m is the angular frequency corresponding to the maximum value ϵ''_m of ϵ'' . The corresponding distribution function is given by.

$$G(\tau) = \frac{\beta}{\pi} \frac{\cos\left(\frac{\beta\pi}{2}\right) \cosh(\beta y)}{\cos^2\left(\frac{\beta\pi}{2}\right) + \sinh^2(\beta y)} \quad \dots\dots(1.44)$$

where $y = \log \frac{\omega}{\omega_m}$

Another distribution function of Cole-Cole eq (1.34) is given by:

$$G(\tau) = \frac{\sin \alpha \pi}{2 \pi} \left[\cosh \left\{ (1-\alpha) \ln \left(\frac{\tau}{\tau_0} \right) \right\} - \cos \alpha \pi \right]^{-1} \quad \dots\dots(1.45)$$

where α is known as the distribution parameter and is measured by the width of the distribution. Fröhlich⁵⁾ derived the distribution function for a molecular mechanism which leads to a distribution of relaxation time between two limiting values τ_0 and $\tau_1 = \tau_0 \exp(v_0/kT)$. The distribution function is:

$$G(\tau) = (\epsilon_0 - \epsilon_\infty) \frac{kT}{v_0} \frac{1}{\tau} \text{ if } \tau_0 \leq \tau \leq \tau_1 = \tau_0 \exp\left(\frac{v_0}{kT}\right)$$

$$G(\tau) = 0 \text{ if } \tau < \tau_0 \text{ and } \tau > \tau_1 \quad \dots\dots(1.46)$$

Davidson and Cole¹³⁾ showed that the molecules possess distribution of relaxation times given by

$$G(\tau) = \frac{\sin \beta \pi}{\pi} \left(\frac{\tau}{\tau_0 - \tau} \right)^\beta \text{ for } \tau < \tau_0$$

$$= 0 \text{ for } \tau > \tau_0 \quad \dots\dots(1.47)$$

where the interpretation of β and τ_0 have been given in eq (1.35).

Higasi et al¹⁸⁾ gave the distribution function $y(\tau)$ which is similar to that of Fröhlich like.

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

$$= 0 \text{ if } \tau < \tau_1 \text{ and } \tau > \tau_2 \quad \dots\dots(1.48)$$

A more general distribution function has been described by Matsumoto and Higasi¹⁹⁾ as:

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

$$\text{and } y(\tau) = 0 \text{ if } \tau < \tau_1 \text{ and } \tau > \tau_2 \quad \dots\dots(1.49)$$

1.10 Double Relaxation Phenomenon of Polar Molecules

If two distinct relaxation processes occur simultaneously, the mutually independent relaxation times τ_1 and τ_2 can be represented by following equations²⁰⁾:

$$\frac{\epsilon' - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{c_1}{1 + (\omega\tau_1)^2} + \frac{c_2}{1 + (\omega\tau_2)^2} \quad \text{.....(1.50)}$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_{\infty}} = c_1 \frac{\omega\tau_1}{1 + (\omega\tau_1)^2} + c_2 \frac{\omega\tau_2}{1 + (\omega\tau_2)^2} \quad \text{.....(1.51)}$$

where c_1 and c_2 are the relative weights of each relaxation term and $c_1 + c_2 = 1$. If the probabilities of occurrence of two processes are equal, then.

$$\frac{c_1}{c_2} = \frac{\mu_1^2}{\mu_2^2} \quad \text{.....(1.52)}$$

where μ_1, μ_2 are effective dipole moments which are relaxing.

1.11. High Frequency Conductivity

The conductivity K , due to displacement current of a dielectric material under alternating electric field $E = E_0 e^{j\omega t}$ is given by

$$K = \frac{1}{E} \frac{dq}{dt} \quad \text{.....(1.53)}$$

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

$$\frac{dq}{dt} = \frac{1}{4\pi} \frac{dD}{dt} = \frac{\epsilon}{4\pi d} \frac{dv}{dt} = I$$

Because of alternating nature of the electric field, The potential difference V is also given by

$$V = V_0 e^{j\omega t} \quad \text{.....(1.54)}$$

where V_0 is the amplitude. So the expression for the displacement current I is given by

$$I = \frac{dq}{dt} = \frac{\epsilon^*}{4\pi d} \frac{dV}{dt} \quad \dots\dots(1.55)$$

Substituting the values of ϵ^* and V from eqs (1.17) and (1.54) one gets

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

$$= \left(\frac{\omega\epsilon''}{4\pi} + j \frac{\omega\epsilon'}{4\pi} \right) E_0 e^{j\omega t} \quad \dots\dots(1.56)$$

According to Ohm's law we again write

$$I = K E_0 e^{j\omega t} \quad \dots\dots(1.57)$$

Comparing eqs (1.56) and (1.57) one gets

$$K = K' + jK'' \quad \dots\dots(1.58)$$

Thus $K' =$ the real part of the conductivity $= \frac{\omega\epsilon'}{4\pi}$ and $K'' =$ the imaginary part of conductivity $= \frac{\omega\epsilon''}{4\pi}$. The above equation is known as Murphy and Morgan²¹⁾ relation.

The magnitude of the total high frequency conductivity is, however, given by the relation:

$$K = \frac{\omega}{4\pi} \sqrt{\epsilon'^2 + \epsilon''^2} \quad \dots\dots (1.59)$$

By using the Debye's eqs (1.25) and (1.26), the expressions for conductivities are, therefore, be written as

$$K' = \frac{1}{4\pi} \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \omega^2\tau \quad \dots\dots(1.60)$$

and
$$K'' = \frac{\omega}{4\pi} \left[\epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + \omega^2\tau^2)} \right] \quad \dots\dots(1.61)$$

In the above considerations, it is assumed that there are no free ions or electrons in the dielectrics and the displacement current is the only factor to contribute to the total conductivity. When an electric field is set up across a dielectric, the total heat produced in the dielectric is not only due to dielectric loss, but due to Joule's heating also. So

conduction through polar dielectrics is due to the combined effect of the displacement current and the conduction current.

1.12. Dielectric Relaxation in Dilute Solution of Polar Molecules in Nonpolar Solvents under High Frequency Electric Field

When a trace amount of polar solute (j) is dissolved in a nonpolar solvent (i), the mixture becomes a dilute solution (ij) of polar nonpolar mixture.

Let n_i and n_j being the number of the i th and the j th molecules of molecular weights M_i and M_j are mixed per c.c to get a form of solution of certain concentration c_j . Then from Debye eq (1.10) we can write.

$$\frac{\epsilon_{0ij} - 1}{\epsilon_{0ij} + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{4}{3} \pi N (f_i \alpha_i + f_j \alpha_j + f_j \frac{\mu^2}{3 k T}) \quad \dots\dots(1.62)$$

and
$$\frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{4}{3} \pi N (f_i \alpha_i + f_j \alpha_j) \quad \dots\dots(1.63)$$

where $\epsilon_{\infty ij}$ and ϵ_{0ij} are the dielectric constants of the solution at infinite or optical frequency and the static dielectric constant respectively. f_i and f_j are the mole fractions of solvent and solute defined by:

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

respectively. α being the distortional polarisability of respective molecules. Now, rearranging eqs (1.62) and (1.63) one can write:

$$(\epsilon_{0ij} - \epsilon_{\infty ij}) = \frac{4 \pi N \mu_j^2}{27 k T} \cdot \frac{\rho_{ij} f_j}{f_i M_i + f_j M_j} (\epsilon_{0ij} + 2) (\epsilon_{\infty ij} + 2) \quad \dots\dots(1.64)$$

Again, c_j the concentration of solute molecules per unit volume is given by:

$$c_j = \frac{\rho_{ij} \omega_j}{M_j} \quad \dots\dots(1.65)$$

where ω_j = weight fraction of j th solute can be written as:

$$\omega_j = \frac{f_j M_j}{f_i M_i + f_j M_j} \quad \dots\dots(1.66)$$

So Debye eq (1.26) can now be written with the help of eq (1.65) as:

$$\epsilon''_{ij} = \frac{4 \pi N c_j \mu_j^2 (\epsilon_{\infty ij} + 2) (\epsilon_{0ij} + 2)}{27 k T} \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad \dots\dots(1.67)$$

In a dilute polar nonpolar mixture it is assumed that $\epsilon_{0ij} \approx \epsilon_{\infty ij} \approx \epsilon'_{ij}$. Thus eq (1.67)

becomes:

$$\epsilon''_{ij} = \left(\frac{\epsilon'_{ij} + 2}{3} \right)^2 \frac{4 \pi N \rho_{ij} \mu_j^2}{3 M_j k T} \left(\frac{\omega \tau}{1 + \omega^2 \tau^2} \right) \omega_j \quad \dots\dots(1.68)$$

The above equation reveals the linear behaviour of ϵ''_{ij} with ω_j for very dilute mixture of polar solute in nonpolar solvent. Now in case of infinite dilute solution i.e as $\omega_j \rightarrow 0$, $\epsilon'_{ij} \rightarrow \epsilon_{oi}$ and eq (1.68) becomes:

$$(\epsilon''_{ij})_{\omega_j \rightarrow 0} = \frac{4 \pi N \rho_{ij} \mu_j^2}{3 M_j k T} \left(\frac{\epsilon_{oi} + 2}{3} \right)^2 \left(\frac{\omega \tau}{1 + \omega^2 \tau^2} \right) \omega_j \quad \dots\dots(1.69)$$

The real part of hf conductivity is thus given by eqs (1.58) and (1.68) as:

$$\begin{aligned} K'_{ij} &= \frac{\omega}{4 \pi} \epsilon''_{ij} = \frac{\omega}{4 \pi} \frac{4 \pi N \rho_{ij} \mu_j^2}{3 M_j k T} \left(\frac{\epsilon'_{ij} + 2}{3} \right)^2 \left(\frac{\omega \tau}{1 + \omega^2 \tau^2} \right) \omega_j \\ &= \frac{N \rho_{ij} \mu_j^2}{3 M_j k T} \left(\frac{\epsilon'_{ij} + 2}{3} \right)^2 \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad \dots\dots(1.70) \end{aligned}$$

The K''_{ij} is, however, written with the help of eqs (1.58) and (1.25) as:

$$K''_{ij} = \frac{\omega}{4 \pi} \left(\epsilon_{\infty ij} + \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{1 + \omega^2 \tau^2} \right)$$

$$\begin{aligned}
&= \frac{\omega}{4\pi} \left[\epsilon_{\infty ij} + \frac{1}{\omega\tau} \frac{(\epsilon_{0ij} - \epsilon_{\infty ij})}{1 + \omega^2\tau^2} \cdot \omega\tau \right] \\
&= \frac{\omega}{4\pi} \left(\epsilon_{\infty ij} + \frac{1}{\omega\tau} \epsilon''_{ij} \right) \\
&= \frac{\omega}{4\pi} \epsilon_{\infty ij} + \frac{1}{\omega\tau} \frac{\omega}{4\pi} \epsilon''_{ij} \\
&= K_{\infty ij} + \frac{1}{\omega\tau} K'_{ij} \quad \text{.....(1.71)}
\end{aligned}$$

Since $\epsilon'_{ij} \gg \epsilon''_{ij}$, so imaginary part of conductivity of eq (1.71) can be written as total hf conductivity

$$K_{ij} = K_{\infty ij} + \frac{1}{\omega\tau} K'_{ij} \quad \text{.....(1.72)}$$

The eqs (1.70), (1.71) and (1.72) as presented in this chapter have been used in the present thesis to estimate relaxation time τ as well as dipole moment μ_j of a polar solute.

1.13. Eyring's Rate Theory

The study of dielectric relaxation mechanism from the stand point of chemical rate processes has been first pointed out by Eyring et al²²). According to this theory, the dielectric relaxation mechanism may be explained by treating the dipole orientation as a rate process in which the polar molecules rotate from one equilibrium position to another. This process of rotation requires an activation energy sufficient to overcome the energy barrier separating the two mean equilibrium positions. The average time required for single rotation is known as relaxation time τ_s , is given by:

$$\tau_s = \frac{h}{kT} \exp(\Delta F_{\tau} / RT) \quad \text{.....(1.73)}$$

where ΔF_{τ} is the free energy of activation. Now, from thermodynamics one can write.

$$\Delta F_{\tau} = \Delta H_{\tau} - T \Delta S_{\tau} \quad \text{.....(1.74)}$$

where ΔH_{τ} and ΔS_{τ} are the enthalpy and entropy of activation respectively. Eq (1.73) can now be written as:

$$\tau_s = \frac{h}{kT} \exp(-\Delta S_\tau / R) \exp(\Delta H_\tau / RT) \quad \dots\dots(1.75)$$

$$\text{or, } \ln(\tau_s T) = \ln A + \frac{\Delta H_\tau}{RT} \quad \dots\dots(1.76)$$

$$\text{where } A = \frac{h}{k} \exp(-\Delta S_\tau / R).$$

Thus ΔH_τ is calculated from the slope of linear relation of $\ln(\tau_s T)$ vs. $1/T$. Knowing ΔH_τ and τ one can easily calculate ΔS_τ and ΔF_τ by using eqs (1.75) and (1.74) respectively.

Like dielectric relaxation process; the viscous flow of the liquids may also be considered as rate process. Viscous flow is involved with the translational as well as rotational motion of molecules with an activation energy to pass over a potential barrier. If η is the co-efficient of viscosity of the medium then according to Eyring et al²²⁾ we can write:

$$\eta = \frac{hV}{N} \exp(\Delta F_\eta / RT) \quad \dots\dots(1.77)$$

where h is the Planck's constant, N is the Avogadro's number, V is the molar volume and ΔF_η is the free energy of activation for viscous flow given by:

$$\Delta F_\eta = \Delta H_\eta - T \Delta S_\eta \quad \dots\dots(1.78)$$

Again, η of eq (1.77) can be written with the help of eq (1.78) as:

$$\eta = \frac{hV}{N} \exp(-\Delta S_\eta / R) \exp(\Delta H_\eta / RT) \quad \dots\dots(1.79)$$

$$= A \exp(\Delta H_\eta / RT) \quad \dots\dots(1.80)$$

where ΔH_η and ΔS_η are the enthalpy and entropy of activation for viscous flow. ΔH_η can be calculated from the fitted linear equation of $\ln \eta$ with $1/T$ which is subsequently used to get ΔS_η and ΔF_η from eqs. (1.79) and (1.78) respectively.

The approximate linearity of $\ln(\tau_s T)$ against $1/T$ as presented in eq (1.76) has been used in this thesis in many places to estimate thermodynamic energy parameters of a polar solute in a nonpolar solvent to get an information of the molecular associations among the molecules under investigation.

1.14 A Brief Review of Early Works

The theory of the dielectric relaxation of polar liquids and polar nonpolar liquid mixtures goes back to the time when P Debye ¹⁾ published a monograph on polar molecules in the Year 1929. After Debye a significant improvement in this field till date is as follows:

The first quantitative verification of Debye theory was done by Mizushima ²³⁾. He measured the dispersion phenomena of some alcohols and ketones for a wide range of temperature in molecular radii as calculated by him were found to be almost of the right order in glycerin.

Fischer ²⁴⁾ measured the relaxation times of a number of liquid compounds in dilute solutions as well as in pure liquids. He observed that for long chain aliphatic alcohols τ is decreased in the sequence as halogenides, ketones and alcohols. The absolute value of τ can be evaluated by introducing molecular viscosity which is smaller than the macroscopic viscosity. Although, general theory becomes unable to explain the behaviour of alcohols, but the results of acetone, nitrobenzene and monochlorobenzene in pure state are in agreement with Debye theory.

τ 's of some polar molecules in benzene and paraffin were calculated by Jackson and Powles ²⁵⁾ and observed that the values are found to increase by 4 to 7 times for an increase in viscosity of eight fold.

An excellent method for the determination of dipole moment and relaxation time of a polar molecule in a nonpolar solvent was offered by Gopalakrishna ²⁶⁾ in 1957 without the prior knowledge of density of solution.

Higasi et al ¹⁸⁾ analysed the experimental data of n-alkyl bromide in liquid state in terms of distribution of relaxation time between two limits as suggested by Fröhlich ⁵⁾. The lower values of τ were associated with the relaxation time of internal rotation of CH₂ Br group while the larger one due to the end-over end rotation of whole molecule.

Bergmann et al ²⁰⁾ using a graphical method analysed the systems like diphenyl ether, dibenzyl ether, anisol and o-dimethoxy benzene in terms of two relaxation times. The results are consistent with the interpretation of a larger relaxation time due to

molecular rotation and a smaller relaxation time due to intramolecular motion of a polar molecule.

By using Cole-Cole plot Kalman and Smyth ²⁷⁾ calculated the most probable relaxation times and the distribution parameters for the solutes like d,l-camphor, isoquinoline and 4-bromobiphenyl dissolved in a viscous oil or acridine. The effect of viscosity on relaxation time increases from the slight viscosity dependence of spherical camphor molecule to a considerable dependence for the elongated molecules.

Matsumoto and Higasi ¹⁹⁾ observed that the plot of complex dielectric constants of supercooled, branched alkyl halides obeys skewed arc expression of Davidson and Cole. Besides this, dielectric properties of a great majority of straight chain alkyl halides at room temperature are in fair accord with the circular arc plot of Cole and Cole.

In order to solve Fröhlich's expression for complex dielectric constant at microwave frequencies Mansingh and Kumar ²⁸⁾ proposed a graphical technique to evaluate the minimum and maximum dielectric relaxation times τ_1 and τ_2 of a polar solute. Calculations were also made at three frequencies for ethyl bromide and butyl bromide at 25°C and dibenzyl ether at 20°, 40° and 60°C. It was found that the results were affected considerably by the inaccuracy of measurements and by the nonapplicability of Fröhlich distribution.

Higasi ²⁹⁾ observed that the dielectric relaxation data from dilute solutions consists of two slopes a' and a'' as defined by $\epsilon' = \epsilon'_1 + a'c_2$ and $\epsilon'' = a''c_2$. In this article it was seen that the Debye equations for dilute solutions can be described by the use of a' and a'' . The equations were obtained by replacing ϵ' and ϵ'' in Debye's equations by a' and a'' for polar liquids.

Sinha, Roy and Kastha ³⁰⁾ showed the temperature dependence of relaxation times and dipole moments of a number of polar molecules in nonpolar solvents. They also observed the viscosity dependence of τ with T is represented as $\tau T/\eta^\gamma = \text{constant}$, where γ is the ratio of the enthalpies of activation for dielectric relaxation and viscous flow.

The dielectric relaxation data of pure phenetole, aniline and orthochloro aniline in terms of two relaxation times for molecular and intramolecular rotations was analysed by

Bhattacharyya et al ³¹⁾ using the modified relation of Bergmann et al ²⁰⁾ for at least two different electric field frequencies of GHz range.

ϵ' and ϵ'' of six isomeric octyl alcohols at 25°C in n-heptane solution for various wavelengths of electric fields were measured by Crossley et al ³²⁾. For these isomers in which —CH₃ group is attached to the same carbon atom as the —OH group or to the adjacent carbon, the dielectric absorption may be characterised by two τ 's at all concentrations employed. The isomers containing relatively less shielded—OH group exhibit an additional low frequency τ at higher alcohol concentration.

Higasi et al ³³⁾ used the four Debye equations for dilute solutions of a non-rigid polar-nonpolar mixture to calculate the crude values of τ_2 and τ_1 for molecular and intramolecular rotations of the solute molecules under a single frequency electric field.

Glasser et al ³⁴⁾ measured dielectric relaxation parameters of four normal alcohols at 25°C in n-heptane solution under various electric fields. According to them, at lower concentration, the dielectric absorption may be characterised by two relaxation times. In higher concentration, another long relaxation time appears which is strongly concentration dependent.

Dielectric relaxation parameters like ϵ' and ϵ'' of some long chain para compounds in dilute solution of dioxane under 3 cm wavelength electric field were measured by Dhar et al ³⁵⁾. The data thus obtained were utilised to study the dipole orientation and viscous flow process by using Eyring's rate theory. It was observed that the dipole orientation was contributed by both molecular and intramolecular rotation. The comparatively higher τ 's are, however, attributed to the intermolecular hydrogen bonding between solute and solvent molecules.

Purohit et al ³⁶⁾ measured molar polarisation of trifluoro ethanol and trifluoro acetic acid in benzene at 25°C. Measurements were performed on ϵ' and ϵ'' at 9.83 GHz. The dielectric behaviour of the molecules has been studied by plotting $\tan \delta$ - concentration curves and their behaviour in respect of hydrogen bonding has been explained.

Measurements of ϵ' and ϵ'' of chloral and ethyl trichloro acetate dissolved in nonpolar solvents like benzene, n-heptane and n-hexane were made by Srivastava and Srivastava³⁷⁾ at three different microwave electric fields. The data were analysed by Cole-Cole plot and Gopalakrishna's single frequency method. The values of τ and μ suggest some type of association or interaction between polar-nonpolar mixture.

Jai Prakash³⁸⁾ examined different existing methods for the determination of dipole moment of a polar solute in nonpolar solvent. It has been observed that the Palit's method in its suggested form with the weight fraction as the concentration unit is most suitable.

The dielectric relaxation data of fluorobenzene, o-chlorobenzene and o-chlorotoluene and their binary mixtures were measured by Gupta et al³⁹⁾ under 3 cm wavelength electric field in the temperature range 20°C to 60°C to estimate τ and thermodynamic energy parameters of them using Gopalakrishna's method. The results were explained on the basis of different molecular parameters.

Khameshara and Sisodia⁴⁰⁾ measured the ϵ' , ϵ'' , ϵ_0 and n_D of some disubstituted anilines in benzene solution under X-band electric field. τ 's were determined following the methods of Higasi et al, Gopalakrishna and Higasi. The values of τ and distribution parameter α show the existence of more than two relaxation mechanism.

In 1982 Dhull and Sharma⁴¹⁾ measured the ϵ' and ϵ'' of N, N-dimethyl formamide (DMF) at 9.987 GHz for a range of temperature to estimate τ and μ of DMF in different nonpolar solvents. The energy parameters were also estimated to infer the monomer associations in nonpolar solvents.

Acharyya and Chatterjee⁴²⁾ used the slope of the curve of the variation of the microwave conductivity with concentration at infinite dilution to get dipole moments of some substituted benzotrifluorides in benzene at 35°C under microwave electric field. The estimated data are in excellent agreement with the reported ones suggesting the uniqueness of the method adopted.

Using the dielectric absorption data of isobutyl methacrylate, allyl methacrylate and their mixtures in benzene solution Gandhi and Sharma⁴³⁾ estimated most probable

relaxation time τ_0 , molecular and intramolecular relaxation times τ_2 and τ_1 as well as distribution parameters of polar solutes. The results indicate that the properties of single polar solute are also retained in mixtures, too.

Onsager's equation was used to calculate dipole moments of five liquids in nonpolar solvents by Makosz⁴⁴⁾ assuming ellipsoidal shape of the molecules.

A least square fit method was suggested to determine the dipole moment and relaxation time of polar-nonpolar liquid mixture by Suryavanshi and Mehrotra⁴⁵⁾.

Using uhf conductivity method; Chatterjee et al⁴⁶⁾ estimated the dipole moments of some binary protic polar mixtures under Giga hertz range electric field for a wide range of temperature. The result indicates the existence of monomer and dimer formations in such liquid mixtures under uhf electric field.

Saha and Acharyya⁴⁷⁾ estimated the dipole moments of monomer and dimer of binary protic polar liquids under 3 cm wavelength electric field from the concentration variation of ultra-high frequency conductivity. The results showed the solute-solute molecular associations in benzene solution, too.

In terms of measured relaxation parameters of polar nonpolar mixture Sit et al⁴⁸⁾ estimated the double relaxation times of mono-substituted anilines dissolved in nonpolar solvents from the measured relaxation parameters under a single Giga Hertz electric field. The data also predict relative weight factors of two relaxations.

Sit and Acharyya⁴⁹⁾, however, showed that monosubstituted anilines exhibit the double relaxation behaviours under an electric field of nearly 10 GHz which is the most prominent dispersive region for such liquids in benzene solutions.

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