

CHAPTER 2

SCOPE AND OBJECTIVE OF THE THESIS WORK

2.1. Introduction :

The aim of this chapter is to suggest simple, straightforward and significant theories on dielectric behaviour of polar liquid in suitable non-polar solvents to shed light on various molecular and intra-molecular aspects through relaxation phenomena. Several theories so far developed are based on Debye-Smyth model of polar-nonpolar liquid mixtures to get relaxation parameters like dipole moment μ , energy parameters of dielectropolar liquid molecules.

The entire formulations of the theories have been made in SI units because of its rationalised, coherent and unified nature. The more recent trend to study the dielectric relaxation mechanism of a dielectropolar liquid molecule through high frequency dielectric orientation susceptibility χ_{ij}^* rather than hf complex permittivity ϵ_{ij}^* or hf complex conductivity σ_{ij}^* . This chapter contains an elaborate discussion on various theories with a greater emphasis on orientational susceptibility measurement technique in comparison to the other existing theories so far derived by this research group.

Besides experimentally determining such parameters, an important aim of a worker in the field of dielectric is to analyse the experimental information from the available models. He then tried to develop a unified theory to predict the new behaviour of dielectric materials.

2.2. Relaxation Phenomena :

As stated earlier in Chapter 1, the phenomenon of dielectric relaxation in liquids and solids (DRL and DRS) is one of the greatest unresolved problems of physics today [2.1-2.4]. The dielectropolar molecular liquid dissolved in a non-polar solvent absorbs electric energy of very longer wavelengths. The absorption often becomes maximum at some particular wavelength. In this case, the tendency of an applied electric field is to orient the molecular dipole along the field direction. The alignment is, however, opposed by molecular inertia and thermal motion of the molecules. The viscous force of the medium, on the other hand, also imposes a lag between the alternation of the applied alternating high frequency (hf) electric field and the rotation of the molecules. The consequent absorption of electric energy leads to an anomalous dispersion. The fall of relative permittivity with decreasing wavelength and the consequent absorption of electric energy by the dielectropolar molecule is of particular interest so far the power loss of dielectric concerned.

The past few years have greatly advanced the available experimental information and the entire thesis work is devoted to a review of such information starting from the relative permittivity to dielectric susceptibility to interpret the relaxation phenomena (DRL) of polar-nonpolar liquid mixture. The point, which needs to be kept in mind, is that all the relaxation phenomena are usually connected with the presence of some form of disorder in the system of polar liquid in a non-polar

solvent. There can be no relaxation in a perfectly ordered system, because nothing can relax from the perfection [2.5].

Debye, however, formulated a rigorous deterministic theoretical basis for such phenomena in terms of the properties of molecular dipoles and the 'relaxation time' required for the molecular rotation. The lag in response to the alternation of the applied electric field is commonly known as dielectric relaxation and the time in which the orientation polarisation reduces to $1/e$ times the initial polarisation is called the relaxation time and usually denoted by τ_j . The τ_j gives a measure of the rate of restoration of random order after removal of the applied electric field. The relaxation phenomena are nowadays concerned with the various devices obtaining the relaxation time τ_j 's and hence the hf dipole moments μ_j 's along with the static or low frequency μ_s . The correlation between the conformational structures of the dipolar liquids with the observed results enhances the scientific contents of this thesis in order to add a better understanding of the existing knowledge of dielectric relaxation phenomena. However, Fröhlich, Onsager, Fuoss, Kirkwood, Eyring, Kauzmann, Bauer [2.6-2.12] and others had attempted to overcome the defects of the original theory of Debye to study the relaxation mechanism.

In addition to the novel approach to Thermally Stimulated Depolarisation Current Density (TSDCD) and Isothermal Frequency Domain AC Spectroscopy (IFDS) – a subject as old as the science of dielectrics, still the simpler Debye model mixed with Smyth and Fröhlich appears to be more reliable till now to yield more information of relaxation of dipolar molecules of Debye like behaviour found in all the materials as presented in the thesis.

2.3. Debye Equation in Solution (SI Unit) :

In SI unit, the dielectric displacement vector \vec{D} for a homogeneous, isotropic dielectric medium of absolute permittivity ϵ in Farad.metre⁻¹ can be written as:

$$\vec{D} = \epsilon_r \epsilon_o \vec{E} \quad \dots (2.1)$$

where ϵ_r is the dimensionless relative permittivity defined by ϵ / ϵ_o and ϵ_o is the absolute permittivity of free space = 8.854×10^{-12} F.m⁻¹.

If \vec{P} is the total polarisation of the medium due to external electric field \vec{E} , the displacement vector \vec{D} is:

$$\vec{D} = \epsilon_o \vec{E} + \vec{P} \quad \dots (2.2)$$

From Eqs.(2.1) and (2.2) one gets:

$$\vec{P} = (\epsilon_r - 1) \epsilon_o \vec{E} \quad \dots (2.3)$$

Again,

$$\vec{P} = n\alpha_T \vec{E}_{loc} \quad \dots (2.4)$$

where \vec{E}_{loc} is local electric field within a dielectropolar liquid.

Thus the Clausius-Mossotti relation in SI unit for a non-polar liquid molecule is:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{N\alpha_d}{3\epsilon_o} \quad \dots (2.5)$$

where N is the Avogadro's number, M is the molecular weight and ρ is the density of a dielectric material.

Similarly for a polar molecule Debye equation is:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{N}{3\epsilon_o} \left(\alpha_d + \frac{\mu_p^2}{3k_B T} \right) \quad \dots (2.6)$$

where α_d is the polarisability due to distortion polarisation and μ_p is the permanent dipole moment of a dipolar molecule.

The same Debye equation in case of a polar-nonpolar liquid mixture is:

$$\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} \frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{N}{3\epsilon_o} (\alpha_i f_i + \alpha_j f_j) \quad \dots (2.7)$$

The symbols have usual meanings as in Chapter 1.

The Eq.(2.7) can be written in the simplified form with the help of Eqs.(1.67), (1.68) and (1.69) respectively

$$\left(\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} - \frac{n_{Dij}^2 - 1}{n_{Dij}^2 + 2} \right) = \left(\frac{\epsilon_i - 1}{\epsilon_i + 2} - \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) + \frac{N}{3\epsilon_o} \frac{\mu_s^2}{3k_B T} c_j \quad \dots (2.8)$$

in SI unit in order to obtain the dipole moment μ_s of a dipolar liquid molecule.

2.4. Static Dipole Moment μ_s from Static Experimental Parameter X_{ij} :

Under static or low frequency electric field, Debye equation for polar-nonpolar liquid mixture can have the form:

$$\left(\frac{\epsilon_{oij} - 1}{\epsilon_{oij} + 2} - \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} \right) = \left(\frac{\epsilon_{oi} - 1}{\epsilon_{oi} + 2} - \frac{\epsilon_{\infty oi} - 1}{\epsilon_{\infty oi} + 2} \right) + \frac{N}{3\epsilon_o} \frac{\mu_s^2}{3k_B T} \frac{\rho_{ij}}{M_j} w_j \quad \dots (2.9)$$

Here, ϵ_{oij} , $\epsilon_{\infty ij}$ and ϵ_{oi} , $\epsilon_{\infty oi}$ are the static and infinite frequency relative permittivities of the solution and solvent respectively, w_j is the weight fraction of a polar solute and μ_s is the static dipole moment in Coulomb metre (C.m).

Let a polar solute of weight W_j and volume V_j is made to dissolve in a non-polar solvent of weight W_i and volume V_i to make a solution of density ρ_{ij} .

ρ_{ij} is given by :

$$\begin{aligned}\rho_{ij} &= \frac{W_i + W_j}{V_i + V_j} = \frac{W_i + W_j}{W_i/\rho_i + W_j/\rho_j} \\ &= \frac{\rho_i \rho_j}{w_i \rho_j + w_j \rho_i} = \frac{\rho_i}{1 - (1 - \rho_i/\rho_j)w_j} = \rho_i (1 - \gamma w_j)^{-1}\end{aligned}\quad \dots (2.10)$$

where $w_i (=W_i / W_i + W_j)$ and $w_j (=W_j / W_i + W_j)$ are defined by the weight fractions of the solvent and solute of densities ρ_i and ρ_j respectively such that $w_i + w_j = 1$. $\gamma = (1 - \rho_i/\rho_j)$ is constant for a particular polar-nonpolar liquid mixture at a fixed temperature [2.13-2.14].

Thus Eq.(2.9) becomes :

$$\begin{aligned}\frac{\epsilon_{oij} - \epsilon_{\infty ij}}{(\epsilon_{oij} + 2)(\epsilon_{\infty ij} + 2)} &= \frac{\epsilon_{oi} - \epsilon_{\infty oi}}{(\epsilon_{oi} + 2)(\epsilon_{\infty oi} + 2)} + \frac{N\rho_i \mu_s^2}{27\epsilon_o M_j k_B T} (1 - \gamma w_j)^{-1} w_j \\ X_{ij} &= X_i + \frac{N\rho_i \mu_s^2}{27\epsilon_o M_j k_B T} w_j + \frac{N\rho_i \mu_s^2}{27\epsilon_o M_j k_B T} \gamma w_j^2 + \dots\end{aligned}\quad \dots (2.11)$$

$$X_{ij} = X_i + R w_j + R \gamma w_j^2 + \dots \quad \dots (2.12)$$

The L.H.S. is defined as the static experimental parameter X_{ij} of the solution in terms of measured static and infinite frequency relative permittivities ϵ_{oij} and $\epsilon_{\infty ij}$ of the solution and

$R = \frac{N\rho_i \mu_s^2}{27\epsilon_o k_B T M_j}$. X_{ij} for most of the polar-nonpolar liquid mixtures, often behave non-linearly

with w_j . This at once indicates that X_{ij} is a polynomial function of w_j like:

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 \quad \dots (2.13)$$

neglecting the higher powers of w_j in Eq.(2.12) as they contain the factors arising due to orientation effect, relative density effect, dipole-dipole interactions, associations etc. It is seen that a_1 in Eq.(2.13) are free from all factors to yield a dipole moment for a quasi-isolated polar molecule. The experimental plots of X_{ij} with w_j for most of the solutions also support this statement. Equating the coefficients of the first power of w_j from Eqs.(2.13) and (2.12) one gets μ_s of a polar liquid molecule in Coulomb.metre from:

$$\mu_s = \left(\frac{27\epsilon_o M_j k_B T}{N\rho_i} a_1 \right)^{1/2} \quad \dots (2.14)$$

Here ϵ_0 = relative permittivity in free space. k_B = Boltzmann constant, M_j = molecular weight of the solute. N = Avogadro's number and ρ_i = density of the solvent used. This theory so far derived, is tested in some interesting dipolar liquids in non-polar solvents. The findings of the study is, however, presented in Chapters 3 and 9 respectively of this thesis.

2.5. High Frequency Complex Conductivity σ_{ij}^* :

The high frequency complex conductivity σ^* of a dielectropolar material under an alternating electric field $E = E_0 e^{j\omega t}$ appears in Ohm's law:

$$I = \sigma^* E_0 e^{j\omega t} \quad \dots (2.15)$$

where I = the current density.

In SI unit the dielectric displacement D is related to charge q by:

$$D = q \quad \dots (2.16)$$

The *hf* complex relative permittivity ϵ_r^* of a system is:

$$\epsilon_r^* = \frac{\epsilon^*}{\epsilon_0} \quad \dots (2.17)$$

where ϵ^* and ϵ_0 are the absolute permittivities of the medium and free space in SI units respectively.

Again,

$$D = \epsilon^* E = \epsilon_0 \epsilon_r^* E \quad \dots (2.18)$$

Hence the current density I is given by:

$$\begin{aligned} I &= \frac{dq}{dt} = \frac{dD}{dt} = \frac{d}{dt} (\epsilon_0 \epsilon_r^* E_0 e^{j\omega t}) \\ &= \epsilon_0 \epsilon_r^* j\omega E_0 e^{j\omega t} \end{aligned} \quad \dots (2.19)$$

Comparing Eqs.(2.15) and (2.19) one gets :

$$\sigma^* = j\omega \epsilon_0 \epsilon_r^* \quad \dots (2.20)$$

For a polar-nonpolar liquid mixtures (*ij*) Eq.(2.20) can be written as:

$$\sigma_{ij}^* = j\omega \epsilon_0 \epsilon_{ij}^*$$

or,

$$\sigma'_{ij} + j\sigma''_{ij} = j\omega \epsilon_0 (\epsilon'_{ij} - j\epsilon''_{ij})$$

Equating the real and imaginary parts,

$$\begin{aligned}\sigma'_{ij} &= \omega \varepsilon_o \varepsilon''_{ij} \\ \sigma''_{ij} &= \omega \varepsilon_o \varepsilon'_{ij}\end{aligned}\quad \dots (2.21)$$

where σ'_{ij} and σ''_{ij} are the real and imaginary parts of hf complex conductivity σ_{ij}^* expressed in $\Omega^{-1} \text{m}^{-1}$.

2.6. Relaxation Time, Dipole Moment and Conductivity of Solution under High Frequency Electric Field :

In hf region, the total conductivity of a polar-nonpolar liquid mixture is [2.15]:

$$\sigma_{ij} = \sqrt{\sigma'^2_{ij} + \sigma''^2_{ij}} = \omega \varepsilon_o \sqrt{\varepsilon'^2_{ij} + \varepsilon''^2_{ij}} \quad \dots (2.22)$$

In high frequency electric field ε'_{ij} of a solution is usually very small and is nearly equal to optical dielectric constant of the solution. But still $\varepsilon'_{ij} \gg \varepsilon''_{ij}$ where ε''_{ij} is responsible for the absorption of electric energy by the dielectric medium to offer resistance to polarisation.

ε'_{ij} is again related to the ε''_{ij} by [2.16]

$$\varepsilon'_{ij} = \varepsilon_{\infty ij} + \frac{1}{\omega \tau_j} \varepsilon''_{ij} \quad \dots (2.23)$$

where $\varepsilon_{\infty ij}$ is the infinite frequency relative permittivity of the solution and τ_j is the relaxation time of the polar unit in a non-polar solvent.

Multiplying both sides by $\omega \varepsilon_o$ we have,

$$\begin{aligned}\omega \varepsilon_o \varepsilon'_{ij} &= \omega \varepsilon_o \varepsilon_{\infty ij} + \frac{1}{\omega \tau_j} \omega \varepsilon_o \varepsilon''_{ij} \\ \sigma''_{ij} &= \sigma_{\infty ij} + \frac{1}{\omega \tau_j} \sigma'_{ij}\end{aligned}\quad \dots (2.24)$$

$$\frac{d\sigma''_{ij}}{d\sigma'_{ij}} = \frac{1}{\omega \tau_j} \quad \dots (2.25)$$

The slope of the linear curve of $\sigma''_{ij} - \sigma'_{ij}$ [2.17] could provide a direct method to obtain τ_j 's.

In the higher concentration, σ''_{ij} does not vary linearly with σ'_{ij} and the polar-polar interaction seems to occur. In order to avoid this effect it is better to use the ratio of the slopes of the individual variations of σ''_{ij} and σ'_{ij} with weight fractions w_j at $w_j \rightarrow 0$ instead of using direct slope

$\left(\frac{d\sigma''_{ij}}{d\sigma'_{ij}} \right)_{w_j \rightarrow 0}$ of Eq.(2.25)

Hence, τ_j could, however, be measured from [2.18]

$$\left(\frac{d\sigma_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \frac{1}{\omega\tau_j} \left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} \quad \dots (2.26)$$

Here, one polar molecule is supposed to be surrounded by a large number of non-polar solvent molecules. The polar unit thus remains in a quasi-isolated state. The polar-polar interactions are fully avoided when we use the Eq.(2.26) at $w_j \rightarrow 0$.

In *hf* region of Giga hertz range it is observed experimentally that $\sigma_{ij}'' \approx \sigma_{ij}'$. Hence Eq.(2.24) can be written as [2.19]:

$$\sigma_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma_{ij}'$$

$$\left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \omega\tau_j \beta \quad \dots (2.27)$$

where β is the slope of the variation of σ_{ij} with w_j in the limit $w_j = 0$.

The real part of *hf* conductivity σ_{ij}' at *TK* of a given solution of w_j is [2.20]:

$$\sigma_{ij}' = \frac{N\rho_{ij}\mu_j^2}{27M_j k_B T} \left(\frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \right) (\varepsilon_{ij} + 2)^2 w_j \quad \dots (2.28)$$

On differentiation with respect to w_j at $w_j \rightarrow 0$.

$$\left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{27M_j k_B T} \left(\frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \right) (\varepsilon_i + 2)^2 \quad \dots (2.29)$$

Here, the density ρ_{ij} and the relative permittivity ε_{ij} of the solution become ρ_i and ε_i of the solvent only in the limit $w_j = 0$.

Comparing Eqs.(2.27) and (2.29) one gets the *hf* dipole moment μ_j of a dielectropolar molecule in a given solvent:

$$\mu_j = \left(\frac{27M_j k_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 \omega b} \right)^{1/2} \quad \dots (2.30)$$

where $b = [1/(1 + \omega^2 \tau_j^2)]$ is the dimensionless parameter involved with the measured τ_j by both the methods mentioned above.

The formulations, so far derived in SI units, are applied in various dipolar liquids in non-polar solvents at different experimental temperatures to test the validity of the formulations arrived

at on the part of the present group. The findings are thoroughly discussed in Chapters 4, 5, 6, and 7 of this thesis.

2.7. Thermodynamic Energy Parameters from Eyring's Rate Theory :

The rotation of a dipolar unit under hf electric field requires activation energy sufficient to overcome the energy barrier, between two equilibrium positions. In order to infer the molecular dynamics of a polar molecule in a non-polar solvent, one can write τ from Eyring's [2.21-2.22] rate theory:

$$\tau = \frac{h}{k_B T} \exp(\Delta F_\tau / RT) \quad \dots (2.31)$$

The free energy of activation ΔF_τ is the difference between the free energies of the activated and non-activated states of the dipolar molecule. It is given by:

$$\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad \dots (2.32)$$

ΔH_τ and ΔS_τ are enthalpy and entropy of activation of the dielectric relaxation process respectively.

Eq.(2.31) thus becomes:

$$\tau = \frac{h}{k_B T} \exp(-\Delta S_\tau / R) \exp(\Delta H_\tau / RT) \quad \dots (2.33)$$

$$\ln(\tau T) = \ln A + \frac{\Delta H_\tau}{RT} \quad \dots (2.34)$$

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

Eq.(2.34) is satisfied by linear curve of $\ln \tau T$ against $1/T$ if ΔH_τ and ΔS_τ are independent of temperature. The thermodynamic energy parameters like ΔH_τ , ΔF_τ and ΔS_τ of relaxation process can easily be measured from the slope and the intercept of the least squares fitted curve of Eq.(2.34).

ΔH_τ gives the molecular energy involved with the relaxation process. ΔS_τ however, indicates the stability of the activated state. The negative value of ΔS_τ often reveals that the activated states are more ordered than the normal states. On the other hand, high value of ΔS_τ indicates that the activated states are not stable due to internal resistance suffered by larger dipolar rotation.

The relaxation time τ is related to the coefficient of viscosity η of the solvent at different experimental temperatures by

$$\tau = \frac{A\eta^\gamma}{T} \quad \dots (2.35)$$

$$\ln(\tau T) = \ln A + \gamma \ln \eta \quad \dots (2.36)$$

The Eq.(2.36) is a linear plot between $\ln(\tau T)$ against $\ln \eta$ and γ can be determined from the slope of the linear curve. γ value thus obtained, signifies that the solute molecule behaves as a solid phase rotator. The ΔH_η for viscous process could, however, be obtained from γ and the relation $\Delta H_\eta = \Delta H_\tau / \gamma$. The Kalman factor $\tau T / \eta^\gamma$ at different experimental temperatures can be obtained with γ in order to compare with the Debye factor $\tau T / \eta$. The comparison often provides the applicability of Debye model of relaxation behaviour for a large number of polysubstituted benzenes in benzene presented in Chapter 4 of this thesis [2.23].

2.8. Multiple Relaxation Phenomena :

A non-rigid molecule possesses more than one τ to exhibit the distribution of τ between two limiting values of τ_1 and τ_2 . The concept of existence of multiple τ for a polar molecule was first put forward by Budo [2.24] in a compact form:

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_j \frac{c_j}{1 + i\omega\tau_j} \quad \dots (2.37)$$

The complex dielectric constant ϵ^* is expressed as the sum of a number of non-interacting Debye type dispersions as illustrated graphically in Fig.2.1. The term c_j is the weight factor of the j th type relaxation mechanism such that $\sum c_j = 1$.

Crossley *et al* [2.25] and Glasser *et al* [2.26] then proposed three relaxation phenomena in pure primary aliphatic alcohols and octanols. The lower value of τ_3 may be due to rotation of $-OH$ group, the intermediate τ_2 due to orientation of the smaller molecular species while the longer τ_1 is associated with hydrogen bonded structure respectively. However, the relative contribution in hf relaxation increases for alcohols when they are diluted with non-polar solvents. The conclusion was drawn from the systematic measurement of ϵ_{ij}' , ϵ_{ij}'' , ϵ_{0ij} and $\epsilon_{\infty ij}$ at different frequencies of electric field with increasing concentration of alcohols and octanols in *n*-heptane solution.

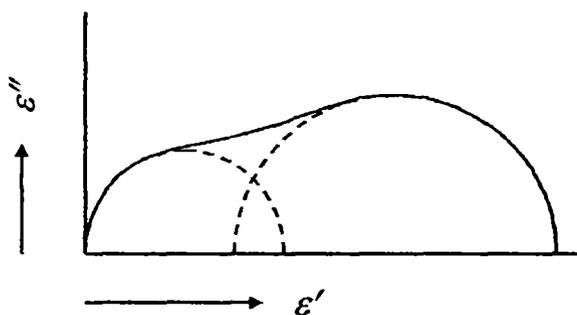


Figure 2.1: Plot of ϵ_{ij}'' against ϵ_{ij}' for two Debye semi-circle with double relaxation

2.9. Double Relaxation Phenomena :

Bergmann *et al* [2.27] subsequently applied the concept of two Debye type dispersions on diphenyl ether, diethyl ether, anisole and o-dimethoxy benzene respectively from ϵ' , ϵ'' , ϵ_o and ϵ_∞ measured under different angular frequencies ω 's of the hf electric field in GHz range at 20°C to 80°C.

The Bergmann equations are:

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_o - \epsilon_\infty} = c_1 \frac{1}{1 + \omega^2 \tau_1^2} + c_2 \frac{1}{1 + \omega^2 \tau_2^2} \quad \dots (2.38)$$

$$\frac{\epsilon''}{\epsilon_o - \epsilon_\infty} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots (2.39)$$

c_1 and c_2 are the weighted contributions due to τ_1 and τ_2 such that $c_1 + c_2 = 1$.

The above Eqs.(2.38) and (2.39) can be put in the form:

$$Y = c_1 Y_1 + c_2 Y_2 \quad \dots (2.40)$$

$$Z = c_1 Z_1 + c_2 Z_2 \quad \dots (2.41)$$

where

$$Y = \frac{\epsilon''}{\epsilon_o - \epsilon_\infty}; Z = \frac{\epsilon' - \epsilon_\infty}{\epsilon_o - \epsilon_\infty}$$

$$Y_1 = \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2}; Y_2 = \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2}$$

$$Z_1 = \frac{1}{1 + \omega^2 \tau_1^2}; Z_2 = \frac{1}{1 + \omega^2 \tau_2^2}$$

Bergmann *et al* [2.27] plotted the normalized experimental points on a complex plane as shown in Fig.2.2. A number of chords were then drawn through the experimental points to obtain a set of parameters in consistent with all the experimental points. A suitable point (Y,Z) was then selected between the points (Y₁,Z₁) and (Y₂,Z₂) of the normalized Debye semi-circle dividing the chord in the ratio $b/a = c_1/c_2$ to yield τ_1 and τ_2 [2.28]. The experimental values of ϵ' , ϵ'' , ϵ_o and ϵ_∞ were measured at different angular frequencies of the electric field of GHz range at a given temperature in °C.

Bhattacharyya *et al* [2.29] proposed the following equations for pure polar liquids of phenetole, aniline and o-chloro aniline molecules capable of rotations under GHz electric field as:

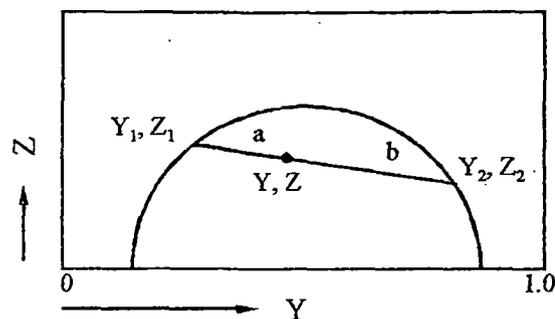


Figure 2.2: Graphical plot of Z against Y for two independent Debye type dispersions.

$$\frac{\varepsilon_o^* - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} \frac{\varepsilon_o + 2}{\varepsilon_\infty + 2} = p - iq \quad \dots (2.42)$$

where ,

$$p = c_1 \frac{1}{1 + \omega^2 \tau_1^2} + c_2 \frac{1}{1 + \omega^2 \tau_2^2} \quad \dots (2.43)$$

$$q = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2}$$

The terms τ_1 , τ_2 and c_1 , c_2 carry usual meanings. The above equations were simplified further in to:

$$\frac{\varepsilon_o - \varepsilon'}{\varepsilon'' \omega} = (\tau_1 + \tau_2) - \frac{(\varepsilon' - \varepsilon_\infty)}{\varepsilon''} \omega \tau_1 \tau_2 \quad \dots (2.44)$$

provided $c_1 + c_2 = 1$ and $\varepsilon_o \approx \varepsilon' \approx \varepsilon_\infty$ and ε'' is small for a pure polar liquid. τ_1 , τ_2 and c_1 , c_2 could, however, be estimated from Eq.(2.44) if ε' , ε'' , ε_o and ε_∞ measured at least at two different angular frequencies ω_1 and ω_2 respectively.

2.10. Double Relaxation Phenomena of a Polar-Nonpolar Liquid Mixture under Single Frequency Measurement of Relative Permittivities :

Saha *et al* [2.30] and Sit *et al* [2.31], under such context derived a very simple, straightforward and significant formulation to get τ_2 and τ_1 from the real part ε_{ij}' and imaginary part ε_{ij}'' of complex relative permittivity ε_{ij}^* , static and hf relative permittivities ε_{oij} and $\varepsilon_{\infty ij}$ of a polar solute (j) dissolved in a non-polar solvent (i) measured under a single GHz electric field at a given temperature. If a polar solute possesses two distinct Debye type dispersions each with a characteristic relaxation time, Bergmann equations in case of polar-nonpolar liquid mixture become:

$$\frac{\varepsilon_{ij}' - \varepsilon_{\infty ij}}{\varepsilon_{oij} - \varepsilon_{\infty ij}} = c_1 \frac{1}{1 + \omega^2 \tau_1^2} + c_2 \frac{1}{1 + \omega^2 \tau_2^2} \quad \dots (2.45)$$

$$\frac{\varepsilon_{ij}''}{\varepsilon_{oij} - \varepsilon_{\infty ij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots (2.46)$$

provide $c_1 + c_2 = 1$. Here, τ_1 , τ_2 and c_1 , c_2 carry usual meanings [2.30-2.31].

Let us substitute $(\varepsilon_{ij}' - \varepsilon_{\infty ij})/(\varepsilon_{oij} - \varepsilon_{\infty ij}) = x$, and $\varepsilon_{ij}''/(\varepsilon_{oij} - \varepsilon_{\infty ij}) = y$ with $\omega \tau = \alpha$ in the Eqs.(2.45) and (2.46) one gets:

$$x = c_1 a_1 + c_2 a_2 \quad \dots (2.47)$$

$$y = c_1 b_1 + c_2 b_2 \quad \dots (2.48)$$

where $a=1/(1+\alpha^2)$ and $b=a/(1+\alpha^2)$. The suffice 1 and 2 with a and b are, however, related to τ_1 and τ_2 respectively. From Eqs.(2.47) and (2.48) since $\alpha_2 \neq \alpha_1$ it is derived that

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots (2.49)$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots (2.50)$$

Since $c_1 + c_2 = 1$, one gets from Eqs.(2.49) and (2.50) the straight line equation :

$$\frac{\varepsilon_{oij} - \varepsilon'_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\varepsilon''_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2 \quad \dots (2.51)$$

between $(\varepsilon_{oij} - \varepsilon'_{ij})/(\varepsilon'_{ij} - \varepsilon_{\infty ij})$ and $\varepsilon''_{ij}/(\varepsilon'_{ij} - \varepsilon_{\infty ij})$ having slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2 \tau_1 \tau_2$ respectively. Here, the angular frequency ω is $\omega = 2\pi f$ and f is the frequency of the alternating electric field. The Eq.(2.51) is found to be satisfied by least squares fittings or Newton-Raphson method with ε'_{ij} , ε''_{ij} , ε_{oij} and $\varepsilon_{\infty ij}$ of a polar-nonpolar liquid mixture for different w_j 's under a single frequency electric field measurement at a given temperature in $^{\circ}\text{C}$ to yield the slope and intercept. They are finally used to get τ_2 and τ_1 to represent molecular and intra-molecular τ 's of a polar liquid in non-polar solvent. The theory thus developed is beautifully used and discussed in Chapters 3 and 6 of this thesis.

2.11. High Frequency Dielectric Susceptibility :

The hf dielectric orientation susceptibility χ^* is related to P and E by:

$$P = \chi^* E \quad \dots (2.52)$$

From the approximation of $P \propto E$ and $D \propto E$, we define the relative dielectric permittivity ε^* by

$$D = \varepsilon^* E \quad \dots (2.53)$$

So,

$$\varepsilon^* = 1 + 4\pi\chi^* \quad \dots (2.54)$$

Which is expressed in SI units

$$\begin{aligned} \varepsilon^* &= 1 + \chi^* \\ \chi^* &= \varepsilon^* - 1 \end{aligned} \quad \dots (2.55)$$

The dielectric susceptibility is given by the subtraction of either 1 or ε_{∞} from the high and low frequency relative permittivities ε_r' and ε_o [2.5]. If 1 is subtracted, the susceptibility due to all operating polarisation processes results. If ε_{∞} is subtracted from both ε_r' and ε_o it is only due to

orientation polarisation process [2.32]. It should be distinguished between the fast or rapidly responding component of the polarisation ϵ_∞ representing the processes, which respond to external fields practically instantaneously on the time domain, and the frequency dependent component referred to the dielectric susceptibility. $\chi^*(\omega)$'s refers to delayed processes. The fast component of polarisation ϵ_∞ is purely real since no energy loss can be involved in this rapid response. But $\chi^*(\omega)$ has a finite imaginary component. It is, therefore, a pure complex number.

The study of the dielectric relaxation becomes easier if the various processes are sufficiently well separated with respect to frequency ω of the applied electric field such that they do not overlap significantly. The dielectric behaviour of a homogeneous medium under hf electric field is then best represented in terms of the frequency dependent real and imaginary components of the complex dielectric orientation susceptibility $\chi^*(\omega)$:

$$\chi^*(\omega) = \chi'(\omega) - j\chi''(\omega) = \epsilon^*(\omega) - \epsilon_\infty \quad \dots (2.56)$$

where $j = \sqrt{-1}$ is a complex number.

For a polar molecule (j) dissolved in a non-polar solvent (i), the hf susceptibility and hf permittivity are related by:

$$\begin{aligned} \chi'_{ij} &= \epsilon'_{ij} - \epsilon_{\infty ij} \\ \chi''_{ij} &= \epsilon''_{ij} \\ \chi_{oij} &= \epsilon_{oij} - \epsilon_{\infty ij} \end{aligned} \quad \dots (2.57)$$

where χ'_{ij} and χ''_{ij} are the real and the imaginary parts of complex hf dielectric susceptibility χ_{ij}^* and χ_{oij} is the low frequency susceptibility, which is real. Here, $\epsilon_{\infty ij}$ is the limit at frequencies of sufficiently high for the particular polarisation mechanism in question to show negligible loss and dispersion. The hf complex $\chi_{ij}^*(\omega)$ represents the dielectric response of the solution and it may be due to several independent mechanisms, which may overlap in any given frequency or time domain.

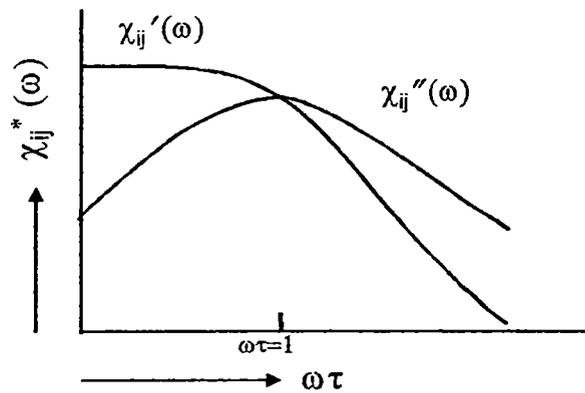


Figure 2.3: Variation of χ'_{ij} and χ''_{ij} with $\omega\tau$

The classical Debye relation of χ_{ij} 's of a system of polar-nonpolar liquid mixture is:

$$\chi_{ij}^*(\omega) = \frac{\chi_{oij}}{1 + j\omega\tau} \quad \dots (2.58)$$

where τ is the temperature dependent relaxation time characterising the Debye process and $\omega\tau$ is the dimensionless parameter. Separating the real and the imaginary parts of Eq.(2.58) one gets:

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{1}{1 + \omega^2\tau^2} \quad \dots (2.59)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{\omega\tau}{1 + \omega^2\tau^2} \quad \dots (2.60)$$

and their variations with respect to $\omega\tau$ are shown graphically in Fig.2.3.

2.12. Double Relaxation Phenomena of Polar-Nonpolar Liquid Mixture from *hf* Susceptibility Measurement Technique :

τ_1 and τ_2 due to rotation of the flexible parts as well as the whole molecule can be estimated from χ_{ij} 's measured under the single frequency electric field [2.33-2.34]. The equations of Bergmann *et al* [2.27] are concerned with molecular orientation polarisation processes. Thus in order to avoid the clumsiness of algebra and to exclude the fast polarisation process Bergmann equations in terms of established symbols of χ'_{ij} , χ''_{ij} and χ_{oij} can be written as:

$$\frac{\chi'_{ij}}{\chi_{oij}} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad \dots (2.61)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad \dots (2.62)$$

Assuming that the molecule possesses two separate broad dispersions for which the relative weight factors c_1 and c_2 are such that $c_1 + c_2 = 1$.

Let $\alpha_1 = \omega\tau_1$, $\alpha_2 = \omega\tau_2$, $\chi'_{ij}/\chi_{oij} = x$ and $\chi''_{ij}/\chi_{oij} = y$ Eqs.(2.61) and (2.62) take the form:

$$x = \frac{c_1}{1 + \alpha_1^2} + \frac{c_2}{1 + \alpha_2^2} \quad \dots (2.63)$$

and,

$$y = \frac{c_1\alpha_1}{1 + \alpha_1^2} + \frac{c_2\alpha_2}{1 + \alpha_2^2} \quad \dots (2.64)$$

From Eqs.(2.63) and (2.64) one gets:

$$(x\alpha_2 - y) = \frac{c_1}{1 + \alpha_1^2}(\alpha_2 - \alpha_1)$$

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots (2.65)$$

Similarly;

$$(y - x\alpha_1) = \frac{c_2}{1 + \alpha_2^2}(\alpha_2 - \alpha_1)$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots (2.66)$$

Putting the values of x, y and α 's in Eqs.(2.65) and (2.66) one gets:

$$c_1 = \frac{\left(\frac{\chi'_{ij}}{\chi_{oij}} \omega \tau_2 - \frac{\chi''_{ij}}{\chi_{oij}} \right) (1 + \omega^2 \tau_1^2)}{\omega(\tau_2 - \tau_1)} \quad \dots (2.67)$$

and

$$c_2 = \frac{\left(\frac{\chi''_{ij}}{\chi_{oij}} - \frac{\chi'_{ij}}{\chi_{oij}} \omega \tau_1 \right) (1 + \omega^2 \tau_2^2)}{\omega(\tau_2 - \tau_1)} \quad \dots (2.68)$$

The experimental values of relative contributions c_1 and c_2 towards dielectric dispersions for a polar-nonpolar liquid mixture is also obtained by graphically established values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} in the limit $w_j=0$ from the above two Eqs.(2.67) and (2.68). The plots of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} against w_j 's of a given solute are obtained by least squares fitting technique with the experimental data placed upon them [2.34-2.35]. The curves are usually convex and concave nature as illustrated in Chapters 7 and 8.

The polar-nonpolar liquid mixtures under consideration are often of the complex type. A continuous distribution of τ with two discrete values of τ_1 and τ_2 could, therefore, be expected. Thus Fröhlich's equations [2.6] based on the single frequency distribution of τ between two extreme values of τ_1 and τ_2 in terms of $hf \chi_{ij}^*$'s can be obtained from Debye equation for a polar-nonpolar liquid mixture:

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \int_0^{\infty} \frac{f(\tau) d\tau}{1 + j\omega\tau} \quad \dots (2.69)$$

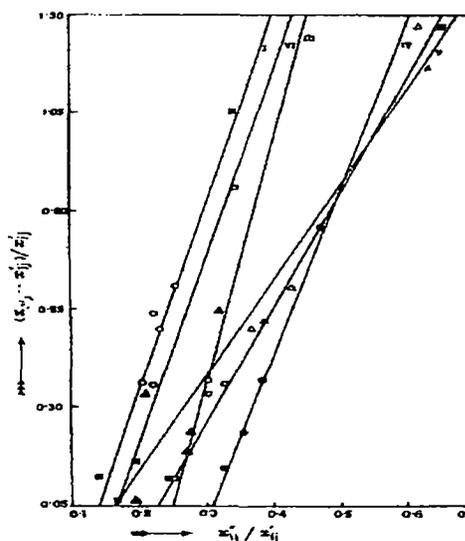


Figure 2.4: Linear plot of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} for monosubstituted anilines

where $f(\tau)$ is the Fröhlich distribution function for τ such that:

$$\begin{aligned} f(\tau) &= \frac{1}{A\tau}; & \tau_1 < \tau < \tau_2 \\ &= 0; & \tau_1 > \tau, \tau_2 < \tau \end{aligned} \quad \dots (2.70)$$

and A is the Fröhlich parameter given by $A = \ln(\tau_2 / \tau_1)$.

Separating the real and the imaginary parts of both sides of Eq.(2.69) the following equations are obtained:

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{1}{A} \int_{\tau_1}^{\tau_2} \frac{d\tau}{\tau(1 + \omega^2 \tau^2)} \quad \dots (2.71)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \int_{\tau_1}^{\tau_2} \frac{\omega d\tau}{(1 + \omega^2 \tau^2)} \quad \dots (2.72)$$

Let $\ln \omega \tau = z$,

$$\text{at } \tau = \tau_1; \quad z = \ln \omega \tau_1 \text{ and,}$$

$$\text{at } \tau = \tau_2; \quad z = \ln \omega \tau_2$$

The Eq.(2.71) is then transformed to:

$$\begin{aligned} \frac{\chi'_{ij}}{\chi_{oij}} &= \frac{1}{A} \int_{\ln \omega \tau_1}^{\ln \omega \tau_2} \frac{dz}{1 + e^{2z}} \\ &= \frac{1}{A} \left[\int_{\ln \omega \tau_1}^{\ln \omega \tau_2} \frac{1 + e^{2z} - e^{2z}}{1 + e^{2z}} dz \right] \\ &= \frac{1}{A} \left(\ln \frac{\omega \tau_2}{\omega \tau_1} \right) - \frac{1}{A} \int_{\ln \omega \tau_1}^{\ln \omega \tau_2} \frac{e^{2z}}{1 + e^{2z}} dz \end{aligned}$$

Again, $e^{2z} + 1 = u$ so,

$$\begin{aligned} \frac{\chi'_{ij}}{\chi_{oij}} &= 1 - \frac{1}{2A} \int_{1 + \omega^2 \tau_1^2}^{1 + \omega^2 \tau_2^2} \frac{du}{u} \\ &= 1 - \frac{1}{2A} \ln \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \quad \dots (2.73) \end{aligned}$$

Similarly let $\omega \tau = z$ then from Eq.(2.72):

$$\begin{aligned} \frac{\chi''_{ij}}{\chi_{oij}} &= \frac{1}{A} \int_{\omega \tau_1}^{\omega \tau_2} \frac{dz}{1 + z^2} \\ &= \frac{1}{A} \left[\tan^{-1}(\omega \tau_2) - \tan^{-1}(\omega \tau_1) \right] \quad \dots (2.74) \end{aligned}$$

The above Eqs.(2.73) and (2.74) are the modified forms of Fröhlich's equations for a distribution of τ between two limiting values τ_1 and τ_2 in terms of $hf \chi_{ij}$.

The theoretical values of c_1 and c_2 towards dielectric dispersion can be calculated from Eqs.(2.67); (2.68) and (2.73); (2.74) respectively with the estimated τ_1 and τ_2 in order to compare with the experimentally measured c_1 and c_2 values.

Now adding Eqs.(2.65) and (2.66) and since $c_1+c_2=1$, we have,

$$\frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} + \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} = 1 \quad \dots (2.75)$$

which, after simplification becomes:

$$\left(\frac{1}{x} - 1\right) = \frac{y}{x}(\alpha_2 + \alpha_1) - \alpha_1\alpha_2$$

Putting the values of x, y and α 's the above equation is transformed into:

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad \dots (2.76)$$

The Eq.(2.76) is a linear equation with the variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ plotted against χ''_{ij}/χ'_{ij} for different w_j 's of solute under a given angular frequency $\omega (=2\pi f)$ of the electric field as illustrated in Fig.2.4 [2.35]. The intercept $-\omega^2 \tau_1 \tau_2$ and slope $\omega(\tau_1 + \tau_2)$ of Eq.(2.76) can be used to get τ_1 and τ_2 respectively.

2.13. Dipole Moment from hf Dielectric Susceptibility :

Clausius-Mossotti equation in case of a polar-nonpolar liquid mixture under static or low frequency electric field is:

$$\frac{\epsilon_{oij} - 1}{\epsilon_{oij} + 2} \frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{N}{3\epsilon_o} (\alpha_i f_i + \alpha_j f_j) + \frac{N}{3\epsilon_o} \frac{f_j \mu_j^2}{3k_B T} \quad \dots (2.77)$$

and at infinitely hf region (say sodium D light) the Lorentz equation is:

$$\frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} \frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{N}{3\epsilon_o} (\alpha_i f_i + \alpha_j f_j) \quad \dots (2.78)$$

Subtracting Eq.(2.78) from Eq.(2.77) and after simplification one gets:

$$\frac{\epsilon_{oij} - \epsilon_{\infty ij}}{(\epsilon_{oij} + 2)(\epsilon_{\infty ij} + 2)} = \frac{N}{9\epsilon_o} \frac{\rho_{ij} \mu_j^2}{3M_j k_B T} w_j \quad \dots (2.79)$$

where w_j is the weight fraction of the polar unit $= M_j f_j / (M_i f_i + M_j f_j)$.

Since in *hf* region it may be assumed that $\epsilon_{oij} \approx \epsilon_{\infty ij} \approx \epsilon_{ij}$ where ϵ_{ij} is the relative permittivity of the solution and $\mu = \mu_j$ dipole moment measured under *hf* electric field, the Eq.(2.79) in terms of dielectric orientation susceptibility becomes:

$$\chi_{oij} = \frac{N\mu_j^2 \rho_{ij} F_{ij}}{3\epsilon_o M_j k_B T} w_j \quad \dots (2.80)$$

Here $F_{ij} =$ the local field of the solution $= (\epsilon_{ij} + 2)^2 / 9$.

The above Eq.(2.80) when compared with Eq.(2.60) takes the form

$$\chi_{ij}'' = \frac{N\mu_j^2 \rho_{ij} F_{ij}}{3\epsilon_o M_j k_B T} \frac{\omega \tau_j}{1 + \omega^2 \tau_j^2} w_j \quad \dots (2.81)$$

Differentiating Eq.(2.81) with respect to w_j in the limit $w_j \rightarrow 0$,

$$\left(\frac{d\chi_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\mu_j^2 \rho_i F_i}{3\epsilon_o M_j k_B T} \frac{\omega \tau_j}{1 + \omega^2 \tau_j^2} \quad \dots (2.82)$$

Here, $\rho_{ij} \rightarrow \rho_i$ and $F_{ij} \rightarrow (\epsilon_i + 2)^2 / 9$ in the limit $w_j = 0$ where ρ_i and ϵ_i are density and relative permittivity of the solvent respectively.

From Eqs.(2.59) and (2.60) one gets:

$$\frac{\chi_{ij}'}{\chi_{ij}''} = \frac{1}{\omega \tau_j} \quad \dots (2.83)$$

or,

$$\left(\frac{d\chi_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \omega \tau_j \left(\frac{d\chi_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \omega \tau \beta \quad \dots (2.84)$$

Eqs.(2.83) and (2.84) can conveniently be used to measure τ_j 's of any polar unit in a non-polar solvent.

Now, β is the slope of the variation of χ_{ij}' with w_j at $w_j \rightarrow 0$. One gets *hf* μ_j of the polar solute in a non-polar solvent from the following Eq.(2.85) by comparing Eqs.(2.82) and (2.84)

$$\mu_j = \left(\frac{27\epsilon_o M_j k_B T \beta}{N \rho_i (\epsilon_i + 2)^2 b} \right)^{1/2} \quad \dots (2.85)$$

where $b = 1/(1 + \omega^2 \tau_j^2)$ is a dimensionless parameter. The methodology so far achieved in getting τ_j 's and μ_j 's has been used in Chapters 7, 8 and 10 of the thesis.

2.14. Substituent Polar Groups in a Dipolar Molecule under Low and *hf* Electric Field :

The measured *hf* dipole moment μ_j or static μ_s of a polar liquid molecule may be compared with the theoretical dipole moment μ_{theo} as obtained from the vector addition method of bond length and bond angles of the substituent polar groups attached to the parent molecule to get its conformational structure as displayed in different Chapters of the thesis. The bond length is the distance between the centres of two atomic nuclei when a co-valent bond links two atoms. Structural conformations of the whole molecule are studied in terms of atomic orbital, which often overlaps to form hybridised orbitals and this phenomenon is known as hybridisation. The bond due to overlap of two *s*-orbitals is called σ -bond whereas the sidewise overlap of two half filled *p*-orbitals having a nodal plane forms a π -bond. The bond angle, on the other hand, is the angle between the dipolar axis of the parent molecule and the bond axis of a flexible polar groups or atoms linked with the parent molecule. It depends on the nature of hybridisation due to size and the electro-negativity of the atoms or groups.

The slight disagreement of μ_j and μ_s with μ_{theo} is, however, observed for the presence of various effects suffered by the substituent polar groups under low and *hf* electric fields. The inductive, mesomeric and electromeric effects play the vital role to yield the conformational structure of a dipolar molecule.

The difference in electro-negativity in the atoms of a molecule produces a displacement of electrons towards the more electronegative atoms to induce a certain degree of polarity on the atom. The more or less electronegative atoms acquire a small negative δ^- or positive δ^+ charges. The inductive effect (I-effect) refers to the induced polarity in a molecule as a result of higher electro-negativity of one atom compared to another. Electron attracting groups are $-\text{NO}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OH}$, $-\text{C}_6\text{H}_5$ etc which pull electrons away from C-atom ($-I$ effect) while electron releasing groups are $(\text{CH}_3)_3\text{C}-$, $(\text{CH}_3)_2\text{CH}-$, CH_3CH_2- , CH_3- etc push electrons towards the C-atom ($+I$ effect).

The mesomeric effect (M-effect) refers to the polarity produced in a molecule as a result of interaction between two π -bonds or a π -bond and lone pair of electrons. It is a permanent effect that is transmitted along the chain of C-atoms linked alternately by single and double bonds in a conjugated compound. Atoms or groups such as $-\text{NO}_2$, $-\text{C}\equiv\text{N}$, $>\text{C}=\text{O}$ etc pull electrons away from C-atom to produce $-M$ effect whereas $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{NH}_2$, $-\text{NR}_2$, $-\text{OH}$, $-\text{OCH}_3$ etc pushing electrons towards C-atom are said to have $+M$ effect.

Electromeric effect, on the other hand, is a temporary effect. It involves with the complete transfer of a shared pair of π -electrons to one or other atoms joined by double or triple bonds.

Resonance, however, occurs in a polar molecule in which electrons may oscillate from one position to another. The molecule, as a result of this oscillation, may be said to have resonant

structure, each of which does not differ significantly so far the total energy is concerned. This effect involves with the delocalisation of electron cloud of a molecule by two or more structures differing only in the arrangement of electrons without shifting any atom.

All these effects were taken into account to sketch conformation structures of different dipolar liquids like dimethylsulphoxide, N,N-diethylformamide, N,N-dimethylformamide, N,N-dimethylacetamide, polysubstituted-benzenes, methyl-benzenes, ketones, chloral, ethyltrichloroacetate, trifluoroethanol, trifluoroacetic acid, octanoyl-chloride, disubstituted-benzenes and some normal and isomeric octyl alcohols etc in agreement with the measured μ_j 's and μ_s 's in the thesis. For all the compounds referred to above, due to their aromaticity the resonance effect combined with inductive effect known as mesomeric effect are important. The so-called mesomeric moments have significant values. These are caused by the permanent polarisation of different substituent groups acting as pusher or puller of electrons towards or away from the electrons of C-atoms attached to the parent compound. The non-polar solvent C_6H_6 unlike CCl_4 , *n*-heptane and *n*-hexane is also a cyclic and planar compound having three double bonds and six *p*-electrons on C-atoms. Here π - π interaction or mesomeric effect play the role in calculating μ_{theo} . The reduction or elongation in bond moments evidently occur in almost all the polar liquids by a factor μ_s/μ_{theo} or μ_j/μ_{theo} in order to conform to the exact μ_s or μ_j .

2.15. Chi-squares Fitting Technique :

It is often found that the experimental data set may be involved with errors arising out of Gaussian, binomial, Poisson etc known type of distributions. The hypothesis may be tested by comparing the experimental data of the measured dielectric relative permittivities and susceptibilities as a function of w_j 's at a given experimental temperature in $^{\circ}C$ in disagreement of the assumed theoretical distribution. The parameters of this distribution will not be known from prior considerations. It will have to be estimated from the experimental data. It may be shown that if *n* parameters are to be determined by the method of maximum likelihood of the limiting distribution of the goodness of fit of chi-squares technique given by:

$$K_n = \sum_{i=1}^n \frac{(O_i - E_i)^2}{E_i} \quad \dots (2.86)$$

where ,

O_i = the experimentally measured value of the *i*th type

E_i = the theoretical value of the *i*th type. $i = 1, 2, 3, \dots, n$

This sort of technique has been employed in Chapter 8 to show the material property of the double relaxation phenomena of systems under consideration.

2.16. Material Property of Relaxation Phenomena :

From the prolonged studies on the relaxation mechanism of dipolar liquids by Raiganj [2.34-2.35] and other groups [2.36-2.37] all over the world, it is appearing that the relaxation phenomena may be the material property of the system under consideration. If any system of polar-nonpolar liquid mixture shows double relaxation times at one frequency ω it will show the same τ_1 and τ_2 at all the ω 's measurements, because τ 's are expected to be independent of ω of the applied alternating electric field. The Eq.(2.73) can be written as:

$$\begin{aligned} \frac{\chi'_{ij}}{\chi''_{ij}} &= \frac{1}{2A} \left(2A - \ln \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \\ &= \frac{1}{2A} \left(\ln \frac{\omega^2 \tau_2^2}{\omega^2 \tau_1^2} - \ln \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \\ &= \frac{1}{2A} \left(\ln \frac{\tau_2^2 (1 + \omega^2 \tau_1^2)}{\tau_1^2 (1 + \omega^2 \tau_2^2)} \right) \end{aligned} \quad \dots (2.87)$$

From Eqs.(2.74) and (2.87) one can write:

$$\frac{\chi''_{ij}}{\chi'_{ij}} = \frac{2 \left| \tan^{-1}(\omega \tau_2) - \tan^{-1}(\omega \tau_1) \right|}{\ln \frac{\tau_2^2 (1 + \omega^2 \tau_1^2)}{\tau_1^2 (1 + \omega^2 \tau_2^2)}} \quad \dots (2.88)$$

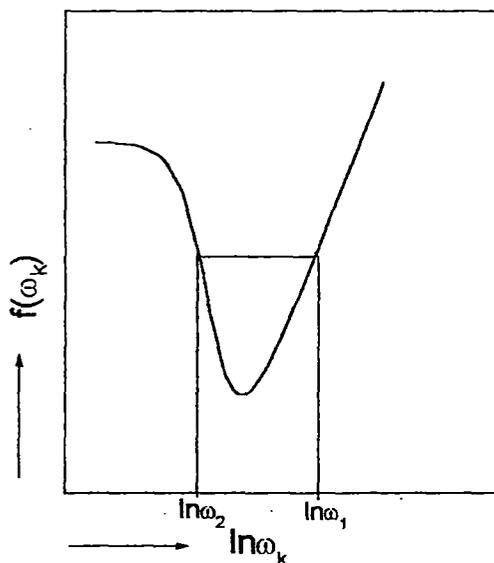


Figure 2.5: Variation of $f(\omega_k)$ with $\ln \omega_k$ for a fixed value of ω

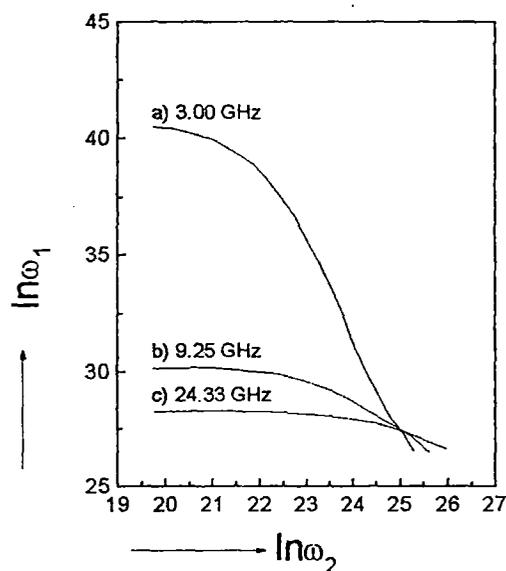


Figure 2.6: Variation of $\ln \omega_1$ against $\ln \omega_2$ of 3-methyl 3-heptanol under 3.00, 9.25 and 24.33 GHz electric field.

Assuming $\tau_1=1/\omega_1$ and $\tau_2=1/\omega_2$ such that $\omega\tau=1$ but $\omega_2<\omega_1$ Eq.(2.88), after simplification becomes [2.37]:

$$\frac{\chi_{ij}''}{\chi_{ij}'} \ln(\omega_1^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_1} = \frac{\chi_{ij}''}{\chi_{ij}'} \ln(\omega_2^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_2} \quad \dots (2.89)$$

The Eq.(2.89) holds good for a number of $\omega_1, \omega_2, \dots, \omega_k$ i.e.,

$$f(\omega_1) = f(\omega_2) = f(\omega_3) = \dots = f(\omega_k)$$

where,

$$f(\omega_k) = \left[\frac{\chi_{ij}''}{\chi_{ij}'} \ln(\omega_k^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_k} \right] \quad \dots (2.90)$$

The term χ_{ij}''/χ_{ij}' of Eq.(2.90) is a function of w_j of a polar solute at a temperature T K and ω of the electric field. $f(\omega_k)$ is, however, made constant for a fixed τ_1 and τ_2 of a system at a given ω by introducing the least squares fitted extrapolated value of $(\chi_{ij}''/\chi_{ij}')_{w_j \rightarrow 0}$. Eq.(2.90) then becomes:

$$f(\omega_k) = \left[\left(\frac{\chi_{ij}''}{\chi_{ij}'} \right)_{w_j \rightarrow 0} \ln(\omega_k^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_k} \right] \quad \dots (2.91)$$

A curve of $f(\omega_k)$ against $\ln \omega_k$ can be obtained by varying ω_k in order to get the arbitrary values of $\ln \omega_2$ and $\ln \omega_1$ ($\omega_2 < \omega_1$) for the same $f(\omega_k)$ as sketched in Fig.2.5. Graphs of $\ln \omega_1$ vs $\ln \omega_2$ for different ω as shown in Fig.2.6 are used to obtain the points of intersection which yields the values of τ_2 and τ_1 of the polar molecular liquids. An attempt has been made in Chapter 10 of the thesis for a large number of alcohols which are supposed to behave as polymer type molecules due to their H-bonding to show the material property of the systems.

All these theoretical formulations in Chapter 2, so far derived, have been used to test their validity for a large number of dipolar liquids of different shapes, sizes and structures in all the subsequent chapters of this thesis to enhance the scientific contents of the relaxation phenomena under low and hf electric field.

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