

Chapter 2

SCOPE AND OBJECTIVE OF THE THESIS

2.1. Introduction:

The aim of this chapter is to suggest simple, straightforward and significant theories of dispersion and absorption phenomena of dipolar liquid in nonpolar solvent. The theories so far developed are on the basis of Debye-Smyth model [2.1] of polar-nonpolar liquid mixtures and the relaxation parameters like dipole moments, energy parameters etc. were determined.

2.2. Debye equation in solution in S.I unit:

S.I unit version of dielectric displacement vector \vec{D} for a homogeneous, isotropic dielectric medium of absolute permittivity ϵ in Farad metre⁻¹ is

$$\vec{D} = \epsilon_r \epsilon_0 \vec{E} \quad \dots (2.1)$$

where ϵ_r is the dimensionless relative permittivity defined by ϵ / ϵ_0 and $\epsilon_0 =$ absolute permittivity of free space $= 8.854 \times 10^{-12} \text{ F.m}^{-1}$.

The total polarisation \vec{P} of the medium due to external electric field \vec{E} are related as :

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} \quad \dots (2.2)$$

From eqs. (2.1) and (2.2) one gets,

$$\vec{P} = (\epsilon_r - 1) \epsilon_0 \vec{E} \quad \dots (2.3)$$

Again,

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

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

Clausius-Mossotti relation [2.2-2.3] in SI unit for a non-polar liquid molecule is

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{N\alpha_d}{3\epsilon_0} \quad \dots (2.5)$$

where N = Avogadro's number = $6.023 \times 10^{23} \text{ mol}^{-1}$, M = molecular weight and ρ = the density of the dielectric medium.

Similarly the Debye equation for a polar molecule is given by:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{N}{3\epsilon_0} \left(\alpha_d + \frac{\mu_p^2}{3k_B T} \right) \quad \dots (2.6)$$

where α_d = the polarisability due to distortion polarisation and μ_p = the permanent dipole moment of the polar molecule.

Now if a polar liquid (j) is dissolved in a non-polar solvent (i) then the Debye equation for the solution will be:

$$\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} \frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{N}{3\epsilon_0} (\alpha_i f_i + \alpha_j f_j) \quad \dots (2.7)$$

The above Eq. (2.7) can be written as

$$\left(\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} - \frac{n_{Dij}^2 - 1}{n_{Dij}^2 + 2} \right) = \left(\frac{\epsilon_i - 1}{\epsilon_i + 2} - \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) + \frac{N}{3\epsilon_0} \frac{\mu_s^2}{3k_B T} c_j \quad \dots (2.8)$$

The Eq.(2.8) in S.I. unit is used to estimate the static dipole moment μ_s of a polar liquid molecule.

2.3. High frequency complex conductivity, relaxation time and dipole moment:

Let us consider a dielectropolar material is subjected by an alternating electric field $E=E_0e^{j\omega t}$ and then if I be the current density, the relation between I and E is given by

$$I = \sigma_{ij}^* E_0 e^{j\omega t} \quad \dots (2.9)$$

where σ_{ij}^* the high frequency complex conductivity.

Now in SI unit the dielectric displacement D is equal to q i.e,

$$D = q \quad \dots (2.10)$$

Also the hf complex relative permittivity is given by

$$\epsilon_r^* = \frac{\epsilon^*}{\epsilon_0} \quad \dots (2.11)$$

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

Again

$$D = \epsilon^* E = \epsilon_0 \epsilon_r^* E \quad \dots (2.12)$$

Now the current density I is given by

$$\begin{aligned} I &= \frac{dq}{dt} = \frac{dD}{dt} = \frac{d}{dt} (\epsilon_0 \epsilon_r^* E_0 e^{j\omega t}) \\ &= \epsilon_0 \epsilon_r^* j\omega E_0 e^{j\omega t} \quad \dots (2.13) \end{aligned}$$

Comparison of Eqs. (2.9) and (2.13) results:

$$\sigma^* = j\omega\varepsilon_0\varepsilon_i^* \quad \dots (2.14)$$

For a polar nonpolar solution (ij), the Eq.(2.14) can be written as:

$$\sigma_{ij}^* = j\omega\varepsilon_0\varepsilon_{ij}^*$$

or,

$$\sigma'_{ij} + j\sigma''_{ij} = j\omega\varepsilon_0(\varepsilon'_{ij} - j\varepsilon''_{ij})$$

Equating the real and imaginary parts we get,

$$\sigma'_{ij} = \omega\varepsilon_0\varepsilon''_{ij} \quad \dots (2.15a)$$

$$\sigma''_{ij} = \omega\varepsilon_0\varepsilon'_{ij} \quad \dots (2.15b)$$

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

In hf region, the total conductivity of a polar non-polar liquid mixture [2.4] is given by,

$$\sigma_{ij} = \sqrt{\sigma'^2_{ij} + \sigma''^2_{ij}} = \omega\varepsilon_0\sqrt{\varepsilon''^2_{ij} + \varepsilon'^2_{ij}} \quad \dots (2.16)$$

In high frequency electric field ε_{ij}' of a solution is usually very small and 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 electrical energy by the dielectric medium to offer resistance to polarisation.

Now ε_{ij}' and ε_{ij}'' are related [2.1] by

$$\varepsilon'_{ij} = \varepsilon_{\infty ij} + \frac{1}{\omega\tau_j}\varepsilon''_{ij} \quad \dots (2.17)$$

where $\varepsilon_{\infty ij}$ = the infinite frequency relative permittivity of the solution and τ_j = the relaxation time of the polar solute in nonpolar solvent.

From Eq.(2.17) it can be shown that,

$$\sigma_{ij}'' = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma_{ij}' \quad \dots (2.18)$$

where $\sigma_{\infty ij}$ = the constant conductivity at infinite dilution i.e $w_j \rightarrow 0$. The Eq.(2.18) on differentiation with respect to σ_{ij}' yields:

$$\frac{d\sigma_{ij}''}{d\sigma_{ij}'} = \frac{1}{\omega\tau_j} \quad \dots (2.19)$$

which provides a convenient method to obtain τ_j of a polar molecule [2.5]. It is, however, better to use the ratio of variation of σ_{ij}'' and σ_{ij}' with w_j in order to avoid polar-polar interactions at $w_j \rightarrow 0$ in a given solvent to get τ_j from [2.6]:

$$\left(\frac{d\sigma_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \frac{1}{\omega\tau_j} \left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} \quad \dots (2.20)$$

In GHz range hf region, it is generally observed that $\sigma_{ij}'' \approx \sigma_{ij}$. Therefore, the Eq.(2.18) can be written as [2.7]:

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

$$\left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \omega\tau_j \beta \quad \dots (2.21)$$

where β = the slope of σ_{ij} with w_j . The real σ_{ij}' of a polar nonpolar liquid mixture at T K is given by [2.8]:

$$\sigma'_{ij} = \frac{N\rho_{ij}\mu_j^2}{27M_jk_B T} \left(\frac{\omega^2\tau_j}{1+\omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 w_j$$

$$\left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27M_jk_B T} \left(\frac{\omega^2\tau_j}{1+\omega^2\tau_j^2} \right) (\epsilon_i + 2)^2 \quad \dots (2.22)$$

Now comparing Eqs (2.21) and (2.22) one gets hf μ_j from

$$\mu_j = \left(\frac{27M_jk_B T\beta}{N\rho_i(\epsilon_i + 2)^2 \omega b} \right)^{1/2} \quad \dots (2.23)$$

where $b = [1/(1+\omega^2\tau_j^2)]$ involved with τ_j 's from Eqs (2.19) and (2.20) and is a dimensionless parameter and β is the slope of σ_{ij} against w_j curves at $w_j \rightarrow 0$. The derived formulations in SI units are applied in different solvents at a given experimental temperatures.

2.4. High frequency dielectric susceptibility χ_{ij} :

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

$$P = \chi^* E \quad \dots (2.24)$$

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

$$D = \epsilon^* E \quad \dots (2.25)$$

Now,

$$D = E + 4\pi P \quad \dots (2.26)$$

$$= E + 4\pi\chi^* E$$

$$\varepsilon^* E = (1 + 4\pi\chi^*)E$$

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

Now if it is expressed in SI units we have,

$$\varepsilon^* = 1 + \chi^*$$

$$\chi^* = \varepsilon^* - 1 \quad \dots (2.27)$$

The dielectric susceptibilities are obtained either by subtracting 1 or ε_∞ from the high and low frequency relative permittivities ε' and ε_0 [2.9]. If 1 is subtracted from the relative permittivities ε' and ε_0 one gets χ' and χ_0 containing all types of polarisation processes including fast polarisations. When high frequency relative permittivity or optical permittivity ε_∞ be subtracted from ε' and ε_0 , the susceptibilities χ' and χ_0 results due to orientation polarisation only [2.10]. It should be distinguished between the fast or rapidly responding component of the polarisation ε_∞ representing the processes, which respond to the external field almost instantaneously on the time domain and the frequency dependent component is referred to the dielectric susceptibility. $\chi^*(\omega)$'s refers to the delayed processes. The fast component of polarisation ε_∞ is purely real and since no energy loss can be involved in this rapid response. But hf dielectric susceptibility has a finite imaginary component and thus $\chi^*(\omega)$ is a pure complex quantity.

The dielectric relaxation study becomes simpler if the various processes are sufficiently separated with respect to frequency of the applied electric field so that there will be no overlapping amongst them. Thus the dielectric behaviour of a homogeneous medium under hf electric field is well represented in terms of the frequency dependent real and imaginary components of the complex dielectric orientation susceptibility $\chi^*(\omega)$:

$$\chi^*(\omega) = \chi'(\omega) - j\chi''(\omega) = \varepsilon^*(\omega) - \varepsilon_\infty \quad \dots (2.28)$$

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

Now if a polar molecule (j) is dissolved in a non-polar solvent (i), then from Eqs. (2.27) and (2.28) one can have:

$$\chi'_{ij} = \epsilon'_{ij} - \epsilon_{\infty ij} \quad \dots (2.29)$$

$$\chi''_{ij} = \epsilon''_{ij} \quad \dots (2.30)$$

$$\chi_{oij} = \epsilon_{oij} - \epsilon_{\infty ij} \quad \dots (2.31)$$

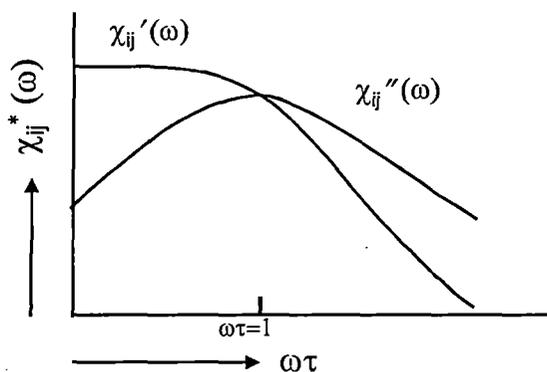


Figure 2.1: Variation of χ'_{ij} and χ''_{ij} with $\omega\tau$

The parameters χ'_{ij} , χ''_{ij} and χ_{oij} of the above equations are the real, imaginary and low frequency susceptibilities respectively. $\epsilon_{\infty ij}$ is the limit at frequencies of sufficiently high for the particular polarisation mechanism in question which shows 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.

Now for the system of polar-nonpolar liquid mixture the classical Debye relation of χ_{ij} 's [2.11] is:

$$\chi_{ij}^*(\omega) = \frac{\chi_{ojj}}{1 + j\omega\tau} \quad \dots (2.32)$$

where τ is the temperature dependent relaxation time characterising the Debye process and $\omega\tau$ is the dimensionless parameter. If we separate the real χ_{ij}' and imaginary χ_{ij}'' parts of complex orientation susceptibility we get:

$$\frac{\chi_{ij}'}{\chi_{ojj}} = \frac{1}{1 + \omega^2\tau^2} \quad \dots (2.33)$$

$$\frac{\chi_{ij}''}{\chi_{ojj}} = \frac{\omega\tau}{1 + \omega^2\tau^2} \quad \dots (2.34)$$

The variations of $\chi_{ij}'(\omega)$ and $\chi_{ij}''(\omega)$ against $\omega\tau$ are depicted in Fig. 2.1 where both the curves show maxima at $\omega\tau=1$.

2.5. Double relaxation phenomena from susceptibility measurement of polar-nonpolar liquid mixture:

τ_1 and τ_2 due to rotation of the flexible parts attached to the parent ones as well as the whole molecule can be estimated from χ_{ij} 's measured under single frequency electric field [2.12-2.13]. Bergmann et al [2.14] proposed a graphical technique to get τ_1 , τ_2 , c_1 and c_2 for pure polar liquid at different frequencies of the microwave electric field. In order to avoid fast polarisation processes, the molecular orientational polarisations in terms of established symbols of χ_{ij} 's can be written as [2.15].

$$\frac{\chi_{ij}'}{\chi_{ojj}} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad \dots (2.35)$$

$$\frac{\chi_{ij}''}{\chi_{ojj}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad \dots (2.36)$$

assuming two separate broad Debye type dispersions of which $c_1+c_2=1$.

Let us assume that $\alpha_1 = \omega\tau_1$, $\alpha_2 = \omega\tau_2$, $\chi_{ij}'/\chi_{oij} = x$ and $\chi_{ij}''/\chi_{oij} = y$. Now with this substitutions from Eqs. (2.35) and (2.36)

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots (2.37)$$

and,

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots (2.38)$$

Putting the values of x , y , α_1 and α_2 , the Eqs. (2.37) and (2.38) become:

$$c_1 = \frac{\left(\frac{\chi_{ij}'}{\chi_{oij}} \omega\tau_2 - \frac{\chi_{ij}''}{\chi_{oij}} \right) (1 + \omega^2\tau_1^2)}{\omega(\tau_2 - \tau_1)} \quad \dots (2.39)$$

and

$$c_2 = \frac{\left(\frac{\chi_{ij}''}{\chi_{oij}} - \frac{\chi_{ij}'}{\chi_{oij}} \omega\tau_1 \right) (1 + \omega^2\tau_2^2)}{\omega(\tau_2 - \tau_1)} \quad \dots (2.40)$$

The experimental values of relative contributions c_1 and c_2 towards dielectric dispersions for a polar-nonpolar liquid mixtures are also obtained graphically by plotting χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} against w_j 's at $w_j \rightarrow 0$.

The polar-nonpolar liquid mixtures under consideration are of complex type. A continuous distribution of τ with two discrete values of τ_1 and τ_2 could, therefore be expected. Thus Frohlich's Eq. [2.16] based on the single frequency distribution of τ between two extreme values of τ_1 and τ_2 in terms of hf χ_{ij}^* 's can be obtained from Debye equation for polar-nonpolar liquid mixtures:

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \int_0^{\infty} \frac{f(\tau)d\tau}{(1 + j\omega\tau)} \quad \dots (2.41)$$

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

$$\begin{aligned} f(\tau) &= \frac{1}{A\tau}; & \tau_1 < \tau < \tau_2 \\ &= 0; & \tau_1 > \tau, \tau_2 < \tau \end{aligned} \quad \dots (2.42)$$

and A is the Fröhlich parameter given by $A = \ln(\tau_2 / \tau_1)$. Now separating the Eq.(2.41) into real and imaginary parts with the substitutions of $f(\tau)$ of Eq. (2.42) we get,

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{1}{A} \int_{\tau_1}^{\tau_2} \frac{d\tau}{\tau(1 + \omega^2 \tau^2)} \quad \dots (2.43)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \int_{\tau_1}^{\tau_2} \frac{\omega d\tau}{(1 + \omega^2 \tau^2)} \quad \dots (2.44)$$

Let us consider $\ln \omega \tau = z$, then the Eq.(2.43) becomes:

$$\begin{aligned} \frac{\chi'_{ij}}{\chi_{oij}} &= \frac{1}{A} \int_{\ln \omega \tau_1}^{\ln \omega \tau_2} \frac{dz}{1 + e^{2z}} \\ &= 1 - \frac{1}{2A} \ln \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \end{aligned} \quad \dots (2.45)$$

Similarly, the Eq.(2.44) reduces to

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \left[\tan^{-1}(\omega \tau_2) - \tan^{-1}(\omega \tau_1) \right] \quad \dots (2.46)$$

The Eqs (2.45) and (2.46) 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 χ_{ij} .

The relative contributions of c_1 and c_2 towards the dielectric dispersion can be evaluated from Eqs (2.39), (2.40) and (2.45), (2.46) respectively with the estimated τ_1 and τ_2 . Now addition of Eqs (2.37) and (2.38) with the approximation c_1 and c_2 yields:

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

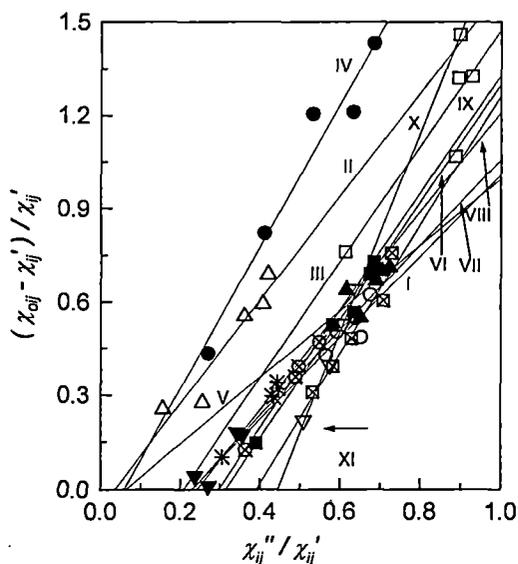


Figure 2.2 : Linear variation of $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$ with χ_{ij}''/χ_{ij}' for different w_j 's at 35°C under 9.945 GHz electric field.

- I. o-chloronitrobenzene in C_6H_6 (-○-); II. 4-chloro 3-nitrobenzotrifluoride in CCl_4 (-△-); III. 4-chloro 3-nitrotoluene in C_6H_6 (-□-); IV. 4-chloro 3-nitrotoluene in CCl_4 (-●-); V. o-nitrobenzotrifluoride in C_6H_6 (-▲-); VI. m-nitrobenzotrifluoride in C_6H_6 (-■-); VII. 2-chloro 6-methyl aniline in C_6H_6 (-▼-); VIII. 3-chloro 2-methyl aniline in C_6H_6 (-*-); IX. 3-chloro 4-methyl aniline in C_6H_6 (-⊗-); X. 4-chloro 2-methyl aniline in C_6H_6 (-∇-) and XI. 5-chloro 2-methyl aniline in C_6H_6 (-⊗-)

On simplification the above equation reduces to

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

Now putting the values of x , y , α_1 and α_2 , the above equation becomes:

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad \dots (2.47)$$

The Eq.(2.47) is a linear equation with variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} . When $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ are plotted against χ''_{ij}/χ'_{ij} for different weight fractions w_j 's of solute under a given angular frequency ω of the electric field as illustrated in Fig 2.2 [2.13], τ_1 and τ_2 can be estimated from the intercept $\omega(\tau_1 + \tau_2)$ and slope $-\omega^2 \tau_1 \tau_2$ of Eq.(2.47).

2.6. Dipole moment measurement from dielectric susceptibility:

The Clausius Mossotti equation for polar-nonpolar liquid mixture under static or low frequency electric field is given by:

$$\frac{\epsilon_{oij} - 1}{\epsilon_{oij} + 2} \frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{N}{3\epsilon_o} (\alpha_i f_i + \alpha_j f_j) + \frac{N}{3\epsilon_o} \frac{f_j \mu^2}{3k_B T} \quad \dots (2.48)$$

and the Lorentz [2.17] equation in case of it at infinitely hf region is

$$\frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} \frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{N}{3\epsilon_o} (\alpha_i f_i + \alpha_j f_j) \quad \dots (2.49)$$

From Eqs. (2.48) and (2.49) one can write,

$$\frac{\epsilon_{oij} - \epsilon_{\infty ij}}{(\epsilon_{oij} + 2)(\epsilon_{\infty ij} + 2)} = \frac{N}{9\epsilon_o} \frac{\rho_{ij} \mu^2}{3M_j k_B T} w_j \quad \dots (2.50)$$

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

Now if ϵ_{ij} is the relative permittivity of the solution then in hf region it may be assumed that $\epsilon_{oij} \approx \epsilon_{\infty ij} \approx \epsilon_{ij}$ and $\mu = \mu_j =$ the dipole moment measured under hf electric field. Then the Eq.(2.50) in terms of dielectric orientational susceptibility becomes:

$$\chi_{oij} = \frac{N\mu_j^2 \rho_{ij} F_{ij}}{3\epsilon_o M_j k_B T} w_j \quad \dots (2.51)$$

where $F_{ij} = (\epsilon_{ij} + 2)^2 / 9 =$ the local field of the solution. Now the comparison of Eq.(2.51) with Eq.(2.34) yields,

$$\chi_{ij}'' = \frac{N\mu_j^2 \rho_{ij} F_{ij}}{3\epsilon_o M_j k_B T} \frac{\omega \tau_j}{1 + \omega^2 \tau_j^2} w_j \quad \dots (2.52)$$

Differentiating Eq.(2.52) w.r.to w_j in the limit $w_j=0$

$$\left(\frac{d\chi_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\mu_j^2 \rho_i F_i}{3\epsilon_o M_j k_B T} \frac{\omega \tau_j}{1 + \omega^2 \tau_j^2} \quad \dots (2.53)$$

In Eq.(2.53) $\rho_{ij} \rightarrow \rho_i$ and $F_{ij} \rightarrow F_i = (\epsilon_i + 2)^2 / 9$ in the limit $w_j=0$ where ρ_i and ϵ_i are the density and relative permittivity of the solvent respectively.

From Eqs (2.33) and (2.34) we have

$$\frac{\chi_{ij}'}{\chi_{ij}''} = \frac{1}{\omega \tau_j} \quad \dots (2.54)$$

or,

$$\left(\frac{d\chi_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \omega \tau_j \left(\frac{d\chi_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \omega \tau_j \beta \quad \dots (2.55)$$

where β is the slope of the variation of χ_{ij}' with w_j at $w_j \rightarrow 0$. The Eq.(2.54) and (2.55) can conveniently be used to measure τ_j 's of any polar unit in a non-polar solvent. Now in order

to obtain μ_j , i.e the dipole moment of the polar solute in non-polar solvent one can compare Eqs(2.53) and (2.55) to get

$$\mu_j = \left(\frac{27\varepsilon_0 M_j k_B T \beta}{N \rho_i (\varepsilon_i + 2)^2 b} \right)^{1/2} \quad \dots (2.56)$$

In Eq.(2.56), $b=1/(1+\omega^2\tau_j^2)$ is a dimensionless parameter. The methodology so far developed is used in different chapters of the thesis in getting τ_j 's and μ_j 's.

2.7. Material property of relaxation phenomena :

From the prolonged studies on the relaxation mechanism of dipolar liquids by Raiganj [2.13-2.15] and other groups [2.18-2.19] 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.(2.45) can be written as:

$$\begin{aligned} \frac{\chi'_{ij}}{\chi_{\omega ij}} &= \frac{1}{2A} \left(2A - \ln \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \\ &= \frac{1}{2A} \left(\ln \frac{\omega^2 \tau_2^2}{\omega^2 \tau_1^2} - \ln \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \\ &= \frac{1}{2A} \left(\ln \frac{\tau_2^2 (1 + \omega^2 \tau_1^2)}{\tau_1^2 (1 + \omega^2 \tau_2^2)} \right) \quad \dots (2.57) \end{aligned}$$

From Eqs (2.46) and (2.57) one can write:

$$\frac{\chi''_{ij}}{\chi'_{ij}} = \frac{2[\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)]}{\ln \frac{\tau_2^2 (1 + \omega^2 \tau_1^2)}{\tau_1^2 (1 + \omega^2 \tau_2^2)}} \quad \dots (2.58)$$

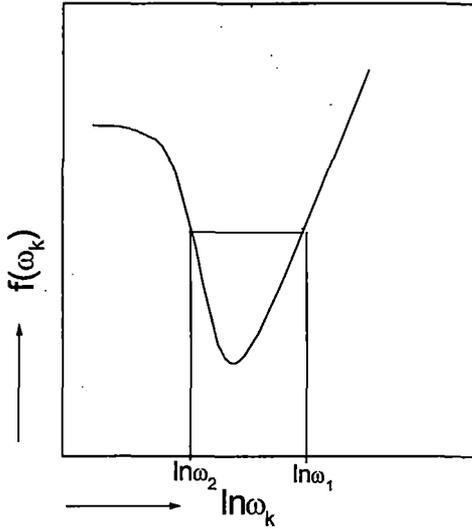


Figure 2.3: Variation of $f(\omega_k)$ with $\ln\omega_k$ for a fixed value of ω

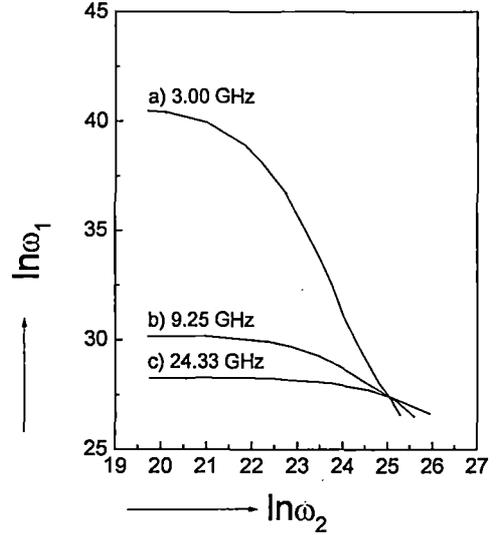


Figure 2.4: Variation of $\ln\omega_1$ against $\ln\omega_2$ of 3-methyl 3-heptanol under 3.00, 9.25 and 24.33 GHz electric field.

Assuming $\tau_1=1/\omega_1$ and $\tau_2=1/\omega_2$ such that $\omega\tau = 1$ but $\omega_2 < \omega_1$ Eq.(2.58), after simplification becomes [2.19]:

$$\frac{\chi''_{ij}}{\chi'_{ij}} \ln(\omega_1^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_1} = \frac{\chi''_{ij}}{\chi'_{ij}} \ln(\omega_2^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_2} \quad \dots (2.59)$$

The Eq.(2.59) 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,

$$f(\omega_k) = \left[\frac{\chi''_{ij}}{\chi'_{ij}} \ln(\omega_k^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_k} \right] \quad \dots (2.60)$$

The term χ''_{ij}/χ'_{ij} of Eq.(2.60) 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.(2.60) then becomes:

$$f(\omega_k) = \left[\left(\frac{\chi''_{ij}}{\chi'_{ij}} \right)_{\omega_j \rightarrow 0} \ln(\omega_k^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_k} \right] \quad \dots (2.61)$$

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.2.3. Graphs of $\ln\omega_1$ vs $\ln\omega_2$ for different ω as shown in Fig.2.4 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 6 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.

2.8. Substituent polar groups in a dipolar molecule:

The measured hf or static dipole moments μ_j or μ_s of a polar liquid molecule may be compared with the theoretical dipole moments μ_{theo} 's obtained from the vector addition method of bond lengths and bond angles of all the substituent polar groups attached to the parent molecules to get their conformational structures as displayed in different chapters of the thesis. The bond length is the distance between the centres of the two atomic nuclei when two atoms are connected by a covalent bond. The structural conformations of the whole molecule are studied in terms of atomic orbitals, which often overlaps to form hybridised orbitals and this phenomenon is called the 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. The bond angle depends on the nature of hybridisation, the electro-negativity of the atoms or groups and due to size of it. 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 and hence a certain degree of polarity on the atom is induced. The atoms of the molecule with more electro-negativity acquires negative δ^- and less electro-negativity acquires positive δ^+ charges. The inductive effect (I-effect) is referred to the induced polarity in a molecule as a result of higher electro-negativity of one atom compared to other atom. The functional groups such as $-\text{NO}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OH}$, etc are electron attracting and thus pull electrons away from C-atom of the polar molecule. They thus produce $-I$ effect. The electron releasing groups such as $(\text{CH}_3)_3\text{C}-$, $(\text{CH}_3)_2\text{CH}-$, CH_3CH_2- , CH_3- etc, on the other hand, push electrons towards the C-atom and gives rise to $+I$ effect.

The mesomeric effect (M-effect) refers to the polarity produced in a molecule as a result of interaction between two π -bonds or one π -bond and lone pair of electrons. This effect is a permanent one and is transmitted along the chain of C-atoms linked alternately by single and double bonds in a conjugated component. 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 $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{OCH}_3$ etc pushing electrons towards C-atom and are said to have $+M$ effect.

Electromeric effect unlike mesomeric effect 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 like $>\text{C}=\text{O}$ bond.

Resonance may occur 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. So far the energy is concerned, each of them does differ significantly. The resonance effect involves with the delocalisation of electron cloud of a molecule by two or more conformations differing only in the arrangement of electrons without shifting any atom.

The inductive, mesomeric, electromeric and resonance effects are taken into consideration to sketch the conformational structures of a large number of dipolar liquid molecules as shown in different chapters of this thesis works. For all the materials concerned due to their aromaticity the resonance effect combined with inductive effect

known as mesomeric effect plays a prominent role to get the required conformations. These are caused by the permanent polarisation of different substituent polar groups acting as pusher or puller of electrons towards or away from atoms attached to the parent molecule. The non-polar solvent C₆H₆ unlike CCl₄, n-hexane, n-heptane etc is a cyclic planer compound and has three double bonds and six p-electrons on six C atoms. Hence π - π interaction or mesomeric effect play the role in calculating μ_{theo} 's. The contraction or elongation of bond moments obviously occur in almost all polar liquids by the factor $\mu_s / \mu_{\text{theo}}$ or $\mu_j / \mu_{\text{theo}}$ in order to confirm to the exact μ_s or μ_j values.

2.9. Debye – Pellat's equations:

The available real ϵ_{ij}' and imaginary ϵ_{ij}'' parts of the complex permittivity ϵ_{ij}^* at a given experimental temperature under electric field of frequency ω can be used to get the low frequency or rather the static permittivity ϵ_{oij} and ultra high frequency permittivity $\epsilon_{\infty ij}$ ($=n_{Dij}^2$) of a polar-nonpolar liquid mixture from

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_o - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \quad \dots (2.62)$$

and

$$\epsilon'' = (\epsilon_o - \epsilon_{\infty}) \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad \dots (2.63)$$

which are known as the Debye – Pellat's equations [2.11]. These Eqs (2.62) and (2.63) are used for several para compounds in different solvents of chapter 8 in this thesis to get static μ_s .

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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