

CHAPTER 2

SCOPE AND OBJECTIVE OF THE PRESENT WORK

2. SCOPE AND OBJECTIVE OF THE PRESENT WORK

2.1 INTRODUCTION

Almost all the liquids either organic or inorganic are usually called the solvents. Inorganic liquids are practically said to be ionic solvents. The main object of this thesis work is to find out the correlations among solutes and solvents. Some of the organic liquids are of highly nonspherical shapes and sizes and possess a considerable dipole moment μ . Under a high frequency (hf) electric field of Giga hertz (GHz) range, they give rise to what is known as dielectric relaxations. Dielectric relaxation phenomena of single polar solutes or binary polar solutes in non polar solvents under hf electric field are of considerable importance as the phenomena are considered to be an essential tool to investigate the physico-chemical properties as well as structural and associational aspects of the nonspherical polar molecules. The theories so far developed are based on the evaluation of relaxation times τ_j , double relaxation times τ_1 & τ_2 , hf dipole moments μ_1 , μ_2 and μ_j , static dipole moment μ_s , theoretical dipole moment μ_{theo} by bond angles and bond moments of substituted polar groups from the infra-red spectroscopic data. The thermodynamic energy parameters such as the enthalpy of activation ΔH_τ , the entropy of activation ΔS_τ , the free energy of activation ΔF_τ of dielectric relaxation and enthalpy of activation ΔH_η due to viscous flow of the solvents by the formulations advanced within the framework of Eyring's rate theory. Thus the main purpose of the work is to modify the existing theories to enhance new concept of the physico-chemical properties of the liquid molecules concerned in terms of dielectric relaxation phenomena.

2.2 THEORETICAL FORMULATIONS TO ESTIMATE hf τ_j and hf μ_j

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex dielectric permittivity ϵ^*_{ij} of a polar – non polar liquid mixture of weight fraction w_j are related by [1]:

$$\begin{aligned} \epsilon'_{ij} &= \epsilon_{\infty ij} + (1 / \omega \tau_j) \epsilon''_{ij} \\ \text{or } \epsilon'_{ij} - \epsilon_{\infty ij} &= (1 / \omega \tau_j) \epsilon''_{ij} \end{aligned} \quad (2.1)$$

With the internationally accepted real χ'_{ij} ($= \epsilon'_{ij} - \epsilon_{\infty ij}$) and imaginary χ''_{ij} ($= \epsilon''_{ij}$) parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} we get

$$\chi'_{ij} = (1 / \omega \tau_{ij}) \chi''_{ij} \quad \dots\dots (2.2)$$

which is clearly a straight line between the variables χ''_{ij} and χ'_{ij} as seen in Fig. 2.1, the slope of which can be used to get τ_{ij} 's of some solutes in terms of the angular frequency ω of the applied electric field.

But for most of the associative polar liquids like aromatic polar nitro compound [2], aprotic polar liquids [3] normal and octyl alcohols [4], the curves

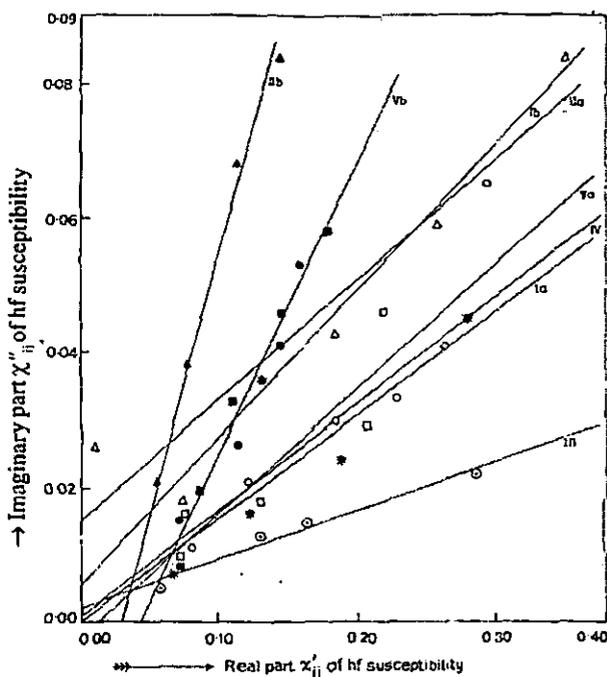


Fig. 2. 1 : Linear plot of imaginary part of hf susceptibility χ''_{ij} against real part χ'_{ij} of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (-O-), (Ib) o-anisidine at 22.06 GHz (-●-), (IIa) m-anisidine at 3.86 GHz (-Δ-), (IIb) m-anisidine at 22.06 GHz (-▲-), (III) o-toluidine at 2.02 GHz (-⊖-), (IV) m-toluidine at 3.86 GHz (-*-), (Va) p-toluidine at 3.86 GHz (-□-) and (Vb) p-toluidine at 22.06 GHz (-■-) respectively.

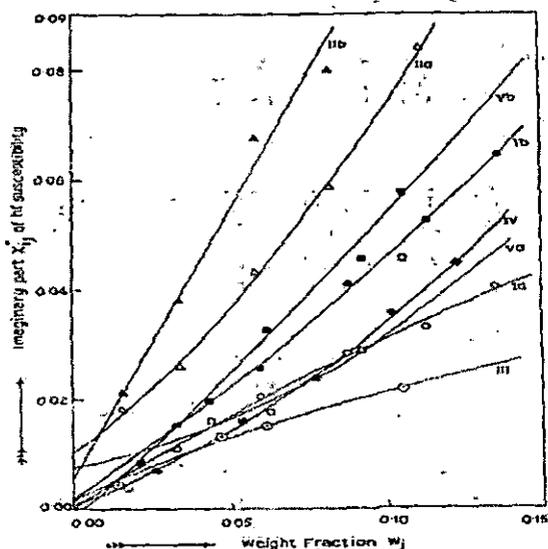


Fig. 2. 2 : Variation of imaginary part of hf susceptibility χ''_{ij} against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (-O-), (Ib) o-anisidine at 22.06 GHz (-●-), (IIa) m-anisidine at 3.86 GHz (-Δ-), (IIb) m-anisidine at 22.06 GHz (-▲-), (III) o-toluidine at 2.02 GHz (-⊖-), (IV) m-toluidine at 3.86 GHz (-*-), (Va) p-toluidine at 3.86 GHz (-□-) and (Vb) p-toluidine at 22.06 GHz (-■-) respectively.

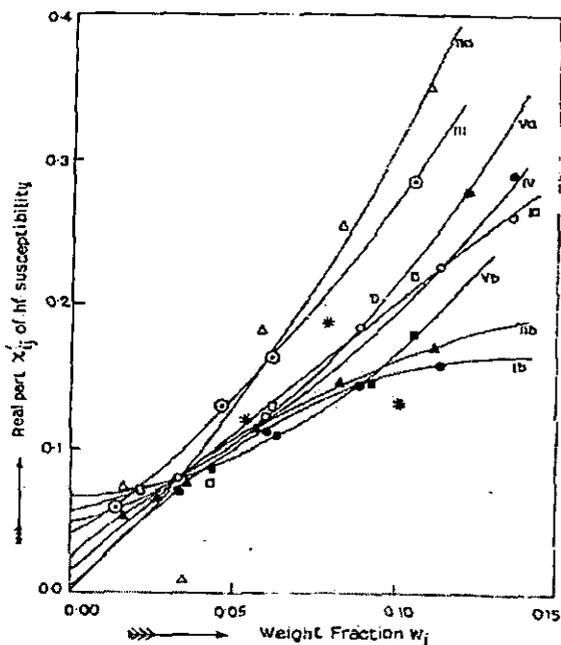


Fig 2. 3 Variation of real part of hf susceptibility χ'_{ij} against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (-O-), (Ib) o-anisidine at 22.06 GHz (-●-), (IIa) m-anisidine at 3.86 GHz (-Δ-), (IIb) m-anisidine at 22.06 GHz (-▲-), (III) o-toluidine at 2.02 GHz (-⊖-), (IV) m-toluidine at 3.86 GHz (-*-), (Va) p-toluidine at 3.86 GHz (-□-) and (Vb) p-toluidine at 22.06 GHz (-■-) respectively.

showing the variations of χ''_{ij} against χ'_{ij} are not strictly linear. The ratio of linear coefficients of variations of χ''_{ij} and χ'_{ij} with w_j 's in Figs 2.2 and 2.3 is a better representation of slopes of eq. (2.2) in which polar-polar interactions are supposed to be almost eliminated [2-4].

$$\text{Thus } \frac{(d\chi''_{ij} / dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij} / dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (2.3)$$

The eq. (2.3) has widely been used to get τ_j of a polar solute for a large number of systems as seen in almost all the chapters of this thesis.

The imaginary part χ''_{ij} of hf complex susceptibility χ^*_{ij} is related to weight fraction w_j of a polar solute by [2,5]

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1+\omega^2\tau_j^2} \right) (\varepsilon_{ij} + 2)^2 w_j \quad (2.4)$$

which on differentiation with respect to w_j and at $w_j \rightarrow 0$ yields that

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1+\omega^2\tau_j^2} \right) (\varepsilon_i + 2)^2 \quad (2.5)$$

From eqs. (2.3) and (2.5) one obtains hf dipole moment in terms of measured τ_j 's by the

$$\mu_j = \left[\frac{27\varepsilon_0 M_j k_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 \omega b} \right]^{1/2} \quad (2.6)$$

where

M_j = Molecular weight of solute in Kilogramme

ε_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹

k_B = Boltzmann constant = 1.38×10^{-23} Joule mole⁻¹ K⁻¹

T = Temperature in absolute scale

β = Linear coefficients of $\chi'_{ij} - w_j$ curves of Fig 2.3 i.e, $(d\chi'_{ij} / dw_j)$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent in kgm⁻³

ε_i = Dielectric relative permittivity of solvent

$b = 1/(1+\omega^2\tau_j^2)$ a dimensionless parameter involved with the estimated τ_j of eq. (2.3)

The eq. (2.6) has been tested successfully for a large number of polar liquids to obtain hf μ_j of a polar solute as seen in almost all the chapters of this thesis.

Again the hf complex conductivity σ_{ij}^* of a polar non-polar liquid mixture is given by [6].

$$\sigma_{ij}^* = \sigma'_{ij} + j\sigma''_{ij} = \omega\epsilon_0 (\epsilon''_{ij} + \epsilon'^2_{ij})^{1/2} \quad (2.7)$$

The real σ'_{ij} and imaginary σ''_{ij} parts of σ_{ij}^* are related by [7]

$$\sigma''_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma'_{ij} \quad (2.8)$$

where $\sigma_{\infty ij}$ is the constant conductivity at infinite dilution i.e., at $w_j \rightarrow 0$. The eq. (2.8) on differentiation with respect to σ'_{ij} yields

$$\frac{d\sigma''_{ij}}{d\sigma'_{ij}} = \frac{1}{\omega\tau_j} \quad (2.9)$$

which provides also a convenient method to obtain τ_j of a polar solute.

It is again, better to use the ratio of the slopes of individual variations of σ''_{ij} and σ'_{ij} as functions of w_j 's and at $w_j \rightarrow 0$ to get τ_j from the relation

$$\frac{(d\sigma''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\sigma'_{ij}/dw_j)_{w_j \rightarrow 0}} = \frac{1}{\omega\tau_j} \quad (2.10)$$

The eq. (2.10) eliminates polar-polar interactions in a given solution and furnishes a method to estimate τ_j of a polar solute.

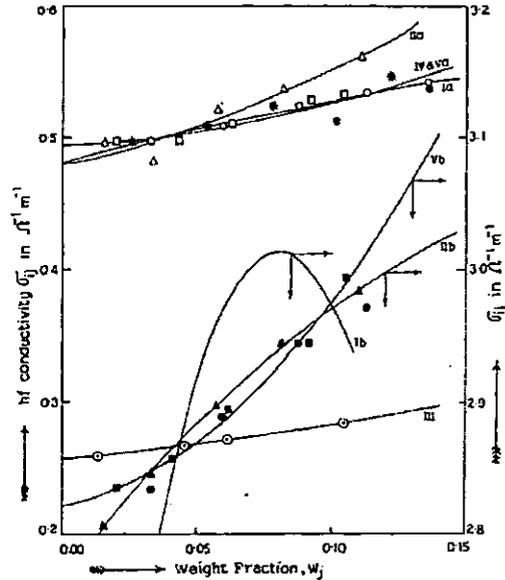


Fig 2.1 : Plot of σ_{ij} against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—), (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—), (III) o-toluidine at 2.02 GHz (—○—), (IV) m-toluidine at 3.86 GHz (—□—), (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

In the giga hertz range of applied electric field it is observed [8] that $\sigma''_{ij} \approx \sigma_{ij}$ = the total hf conductivity of the solution. So eq. (2.8) becomes

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

$$\text{Hence } (d\sigma'_{ij} / d\omega)_{\omega \rightarrow 0} = \omega \tau_j \beta \quad (2.11)$$

where $\beta = d\sigma'_{ij} / d\omega$ i.e, the linear coefficient of the curves of Fig 2.4

The real part σ'_{ij} of total hf conductivity of polar – nonpolar liquid mixture is given [5,8] by:

$$\sigma'_{ij} = \frac{N\rho_{ij}\mu_j^2}{27k_B TM_j} \left(\frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \right) (\epsilon_j + 2)^2 \omega$$

which on differentiation with respect to ω and at $\omega \rightarrow 0$. yields

$$(d\sigma'_{ij} / d\omega)_{\omega \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27k_B TM_j} \left(\frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \right) (\epsilon_j + 2)^2 \quad (2.12)$$

Now comparing (2.11) & (2.12) we get

$$\mu_j = \left(\frac{27 M_j k_B T \beta}{N\rho_{ij} (\epsilon_j + 2)^2 \omega b} \right)^{\frac{1}{2}} \quad (2.13)$$

where $\omega (=2\pi f)$ is the angular frequency of the applied electric field and all the other symbols carry the usual meanings as discussed earlier. The eqs. (2.10) and (2.13) provide a convenient method to estimate τ_j and μ_j of a polar solute as seen in the chapter 4 of this thesis .

2.3 DOUBLE RELAXATION TIMES τ_1, τ_2 AND DIPOLE MOMENT μ_1, μ_2 DUE TO ROTATIONS OF THE FLEXIBLE POLAR GROUPS & ROTATIONS OF THE WHOLE MOLECULE

Saha et al [9] and Sit et al [10] , however, advanced an analytical method to estimate double relaxation times τ_1 & τ_2 from single frequency measurement in terms of measured

relative permittivities. Another object of the thesis is to detect τ_1 & τ_2 and hence μ_1 & μ_2 using χ_{ij} 's. The aspect of molecular orientational polarization, is, however, achieved by χ_{ij} 's because $\epsilon_{\infty ij}$ includes all the polarizations including the fast polarization. $\epsilon_{\infty ij}$ appears frequently as a subtracted term in Bergmann et al [11] equations. Thus to avoid the clumsiness of algebra and to use the modern concept of dielectric terminology and parameter one can write

$$\chi'_{ij} = \epsilon_{ij} - \epsilon_{\infty ij}, \quad \chi''_{ij} = \epsilon''_{ij}, \quad \chi_{0ij} = \epsilon_{0ij} - \epsilon_{\infty ij}$$

The Bergmann et al equations becomes

$$\frac{\chi''_{ij}}{\chi_{0ij}} = c_1 \frac{1}{1 + \omega^2 \tau_1^2} + c_2 \frac{1}{1 + \omega^2 \tau_2^2} \quad (2.14)$$

$$\frac{\chi'_{ij}}{\chi_{0ij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (2.15)$$

where χ_{0ij} is the low frequency susceptibility which is real. c_1 and c_2 are the relative weight factors such that $c_1 + c_2 = 1$. Putting $\omega \tau_1 = \alpha_1$ and $\omega \tau_2 = \alpha_2$ eqs. (2.14) and (2.15) are now solved to get

$$c_1 = \frac{(\chi'_{ij} \alpha_2 - \chi''_{ij} \alpha_1)(1 + \alpha_1^2)}{\chi_{0ij} (\alpha_2 - \alpha_1)} \quad (2.16)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij} \alpha_1)(1 + \alpha_2^2)}{\chi_{0ij} (\alpha_2 - \alpha_1)} \quad (2.17)$$

provided $\alpha_2 - \alpha_1 > 0$

As $c_1 + c_2 = 1$, the eq. (2.16) and (2.17) yields

$$\frac{(\chi_{0ij} - \chi'_{ij})}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad (2.18)$$

which is clearly a straight line as illustrated in Fig 2.5 for some interesting liquids in suitable solvent previously studied between the variables $\left(\frac{\chi_{0ij} - \chi'_{ij}}{\chi'_{ij}} \right)$ and χ''_{ij} / χ'_{ij} with

slope $\omega (\tau_1 + \tau_2)$ and intercept $-\omega^2 \tau_1 \tau_2$ of eq. (2.18). They can be used to measure double relaxation times τ_1 & τ_2 due to rotations of the flexible polar groups attached to the parent ones and end over end rotations of the whole molecules in terms of known $\omega = 2\pi f$, where f is the frequency of the applied electric field in GHz range.

The estimated τ_1 and τ_2 can be used to obtain μ_1 and μ_2 from eqs. (2.6) and (2.13) of the flexible parts and the whole molecules.

This method of estimation of τ_1 and τ_2 & μ_1 and μ_2 has been applied on some alcohols at a single and different frequencies of the applied electric field, as seen in

chapters 5 and 6 of the thesis. The validity of eq. (2.18) is based on the fact that $c_1 + c_2 = 1$. The estimation of c_1 and c_2 can, however, be measured from Fröhlich's [12] theoretical equations and the graphical techniques [2,13] as discussed in those chapters. The later ones are shown graphically in Figs 2.6 and 2.7 for a large number of systems of polar – non polar mixtures.

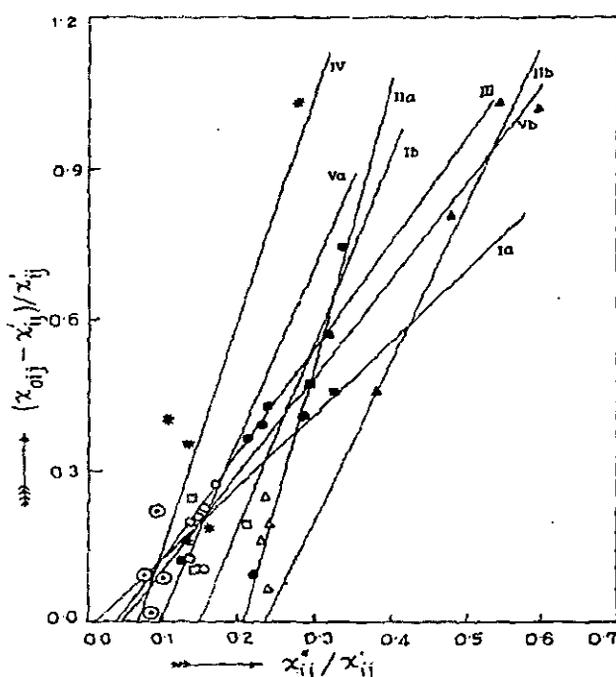


Fig 2.5: Linear variation of $(\chi_{0ij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij} / χ'_{ij} of monosubstituted anilines in benzene at 35°C under GHz electric field. (Ia) o-anisidine at 3.86 GHz (○), (Ib) o-anisidine at 22.06 GHz (●). (IIa) m-anisidine at 3.86 GHz (△), (IIb) m-anisidine at 22.06 GHz (▲). (III) o-toluidine at 2.02 GHz (⊙), (IV) m-toluidine at 3.86 GHz (*), (Va) p-toluidine at 3.86 GHz (□) and (Vb) p-toluidine at 22.06 GHz (■) respectively.

2.4 FORMULATIONS TO ESTIMATE SYMMETRIC AND CHARACTERISTIC RELAXATION TIMES τ_s

& τ_{cs}

The solute like normal and octyl alcohols and amides (DMSO, DMF, DEF) under investigation appears to behave like non-rigid ones having symmetric and asymmetric distribution parameters γ and δ involved with the following equation

[14]:

$$\frac{\chi_{ij}^*}{\chi_{0ij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (2.19)$$

and

$$\frac{\chi_{ij}^*}{\chi_{0ij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (2.20)$$

on separating the real and imaginary parts of eq. (2.19) & (2.20) and rearranging them in terms of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} at $\omega_j \rightarrow 0$ as seen in Fig 2.6 and 2.7 one obtains

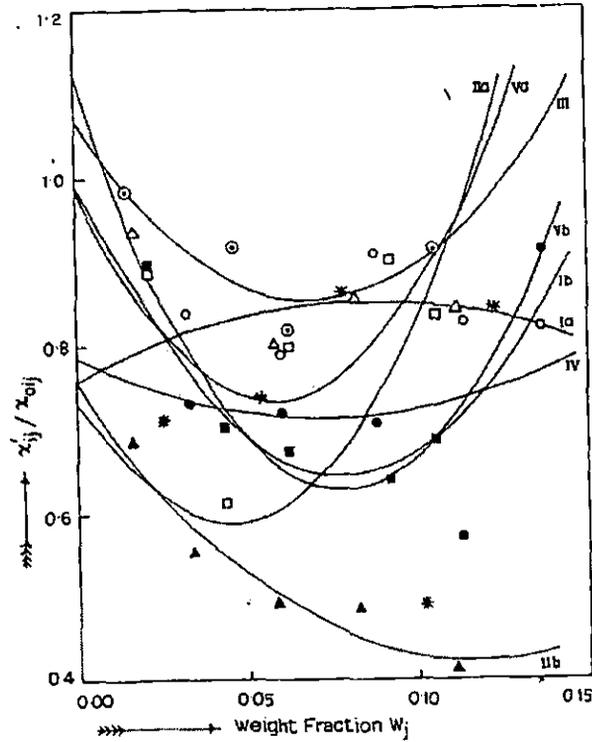


Fig. 2.6: Plot of χ'_{ij}/χ_{0ij} against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—), (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—), (III) O-toluidine at 2.02 GHz (—○—), (IV) m-toluidine at 3.86 GHz (—*—), (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{0ij}} \right) \frac{\chi'_{ij}}{\chi''_{ij}} - \frac{\chi''_{ij}}{\chi_{0ij}} \right] \quad (2.21)$$

and

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\left(\frac{\chi'_{ij}}{\chi_{0ij}} \right) \cos \left(\frac{\gamma\pi}{2} \right) - \sin \left(\frac{\gamma\pi}{2} \right)} \right]^{1/(1-\gamma)} \quad (2.22)$$

similarly δ and τ_{cs} can be had from eq. (2.20) as

$$\tan(\phi\delta) = \frac{(\chi''_{ij} / \chi_{0ij})_{w_j \rightarrow 0}}{(\chi'_{ij} / \chi_{0ij})_{w_j \rightarrow 0}} \quad (2.23)$$

$$\text{and } \tan \phi = \omega \tau_{cs} \quad (2.24)$$

As ϕ can not be estimated directly, an ordinary theoretical curve between $(1/\phi) \log(\cos \phi)$ against ϕ in degree is drawn in Fig 2.8 from which

$$\left(\frac{1}{\phi} \right) \log(\cos \phi) = \frac{\log \{ (\chi'_{ij} / \chi_{0ij}) (\cos \phi \delta) \}}{\phi \delta}$$

can be known. The estimated $1/\phi \log(\cos \phi)$ is used to estimate ϕ from Fig 2.8. With known ϕ eqs. (2.23) and (2.24) δ and τ_{cs} estimated. This formulations has been applied with considerable success in chapters 4, 5, and 6 of the thesis.

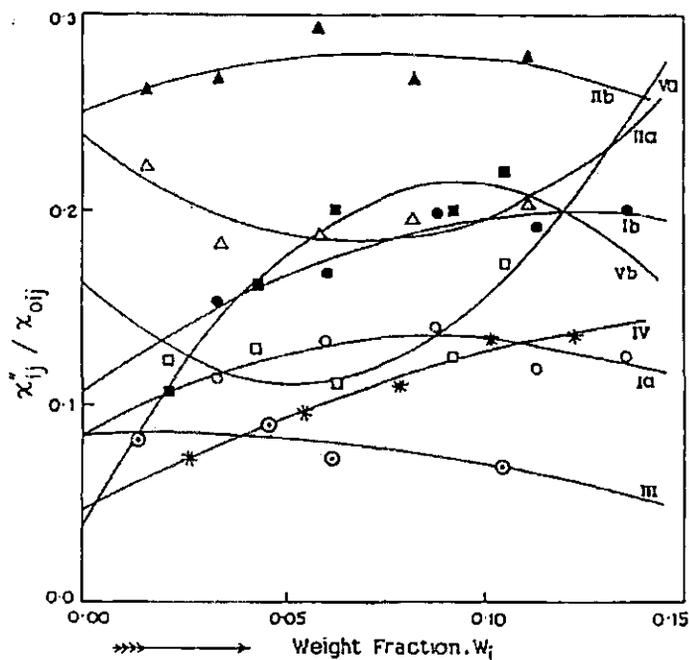


Fig 2.7: Plot of $\chi''_{ij} / \chi'_{0ij}$ against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—), (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—), (III) o-toluidine at 2.02 GHz (—○—), (IV) m-toluidine at 3.86 GHz (—*—), (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

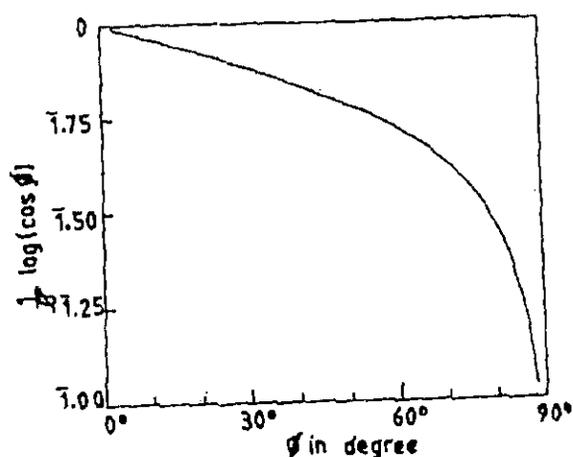


Fig 2.8 Plot of $(1/\phi) \log(\cos \phi)$ against ϕ in degree.

2.5 STATIC EXPERIMENTAL PARAMETER X_{ij} AND STATIC DIPOLE MOMENT μ_s

The static dipole moment μ_s of a polar solute (j) in a nonpolar solvent (i) is related with static relative permittivity ϵ_{0ij} and hf relative permittivity $\epsilon_{\infty ij}$ by [15]

$$\frac{\epsilon_{0ij} - 1}{\epsilon_{0ij} + 2} - \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} = \frac{\epsilon_{0i} - 1}{\epsilon_{0i} + 2} - \frac{\epsilon_{\infty i} - 1}{\epsilon_{\infty i} + 2} + \frac{N\mu_s^2}{9\epsilon_0 k_B T} c_j \quad (2.25)$$

The molar concentration c_j of solute is expressed in terms of w_j by

$$c_j = \frac{\rho_j w_j}{M_j}$$

The weight W_j and volume V_j of a polar solute when dissolved in a solvent of weight W_i and volume V_i to have the solution density ρ_{ij} of the mixture

$$\rho_{ij} = \frac{W_i + W_j}{V_i + V_j} = \frac{W_i + W_j}{\frac{W_i}{\rho_i} + \frac{W_j}{\rho_j}}$$

Or,

$$\rho_{ij} = \frac{\rho_i \rho_j}{\left(\frac{W_i}{W_i + W_j}\right) \rho_j + \left(\frac{W_j}{W_i + W_j}\right) \rho_i}$$

As

$$\frac{W_i}{W_i + W_j} = w_i \text{ and } \frac{W_j}{W_i + W_j} = w_j$$

The weight fractions of solvent and solute respectively . Again, the above equation can be written for ρ_{ij} as the density of the solution,

$$\rho_{ij} = \frac{\rho_i \rho_j}{w_i \rho_j + w_j \rho_i}$$

or,

$$\rho_{ij} = \frac{\rho_i}{w_i + \frac{\rho_i}{\rho_j} w_j}$$

$$\rho_{ij} = \frac{\rho_i}{1 - \left(1 - \frac{\rho_i}{\rho_j}\right) w_j} = \frac{\rho_i}{1 - \gamma w_j}$$

Or, $\rho_{ij} = \rho_i (1 - \gamma w_j)^{-1}$ [as $w_1 + w_2 = 1$ and $(1 - \rho_1 / \rho_2) = \gamma$]

$$\text{Or, } \rho_{ji} = \rho_i (1 + \gamma w_j + \dots) \tag{2.26}$$

where ρ_i and ρ_j are the densities of solvent and solute respectively. With eq. (2.26), and the eq.(2.25) becomes

$$\frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{(\epsilon_{0ij} + 2)(\epsilon_{\infty ij} + 2)} = \frac{\epsilon_{0i} - \epsilon_{\infty i}}{(\epsilon_{0i} + 2)(\epsilon_{\infty i} + 2)} + \frac{N\mu_s^2 w_j \rho_i (1 + \gamma w_j + \dots)}{27\epsilon_0 M_j k_B T}$$

$$\text{or, } X_{ij} = X_i + \frac{N\rho_i \mu_s^2}{27\epsilon_0 M_j k_B T} w_j + \frac{N\rho_i \mu_s^2}{27\epsilon_0 M_j k_B T} \gamma w_j^2 + \dots \tag{2.27}$$

Since $0 < w_j < 1$, the above eq. (2.27) can be expressed as a polynomial equation of w_j like

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \dots \tag{2.28}$$

comparing the coefficient of first powers w_j 's of eqs. (2.27) and (2.28) one obtains

$$\mu_s = \left(\frac{27\epsilon_0 M_j k_B T}{N\rho_i} a_1 \right)^{1/2} \tag{2.29}$$

where a_1 is the linear coefficient of X_{ij} versus w_j

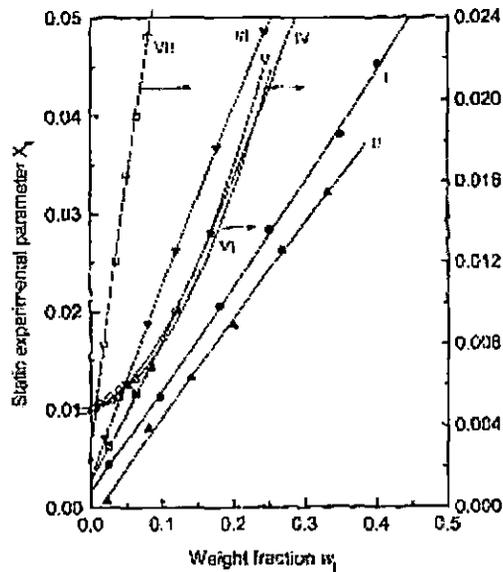


Fig 2.2 . Variation of the measured static experimental parameter X_{ij} with weight fraction w_j of the solutes for I - chloral in benzene (—●—); II - chloral in n-heptane (—▲—); III - ethyl trichloroacetate in benzene (—▼—); IV - ethyl trichloroacetate in n-hexane (—⊗—); V - trifluoroethanol in benzene (—○—); VI - trifluoroacetic acid in benzene (—△—) and VII - octanoyl chloride in benzene (—□—).

curves of Fig. 2.9 for a number of interesting compounds as seen elsewhere [8]. μ_s 's from higher powers of τ_j of eq. (2.27) are not reliable as the term γ is influenced by various effects like solute-solute interactions, relative density, macroscopic viscosity, internal field etc. This formulation of eq. (2.27) has been applied on some interesting polar liquids of para compounds in nonpolar solvents to have their static μ_s as seen in the 7 th chapter of this thesis

2.6 THEORETICAL FORMULATIONS TO ESTIMATE THERMODYNAMIC ENERGY PARAMETERS:

Dielectric relaxation is a process of rotation of a molecular dipole . The dipole requires an activation energy ΔF_τ , called free energy of activation to overcome the potential energy barrier between two equilibrium positions of normal and excited states.. Eyring's rate process [16] eq. (2.30) can be used with the temperature dependence of measured τ_j 's from eqs. (2.3) and (2.10).

According to Eyring's rate theory one gets that

$$\tau_j = \frac{A}{T} \exp(\Delta F_\tau / RT) \quad (2.30)$$

where $A = h / k$,is the ratio of Planck's and Boltzmann constants respectively and R is the gram molecular constant.

Again $\Delta F_\tau = \Delta H_\tau - T \Delta S_\tau$, the above eq. (2.30) becomes

$$\begin{aligned} \tau_j T &= A \exp (\Delta H_\tau - T \Delta S_\tau) / RT \\ \text{or, } \tau_j T &= A \exp (-\Delta S_\tau / R) \cdot \exp (\Delta H_\tau / RT) \end{aligned}$$

$$\text{hence } \ln \tau_j T = \ln A' + \frac{\Delta H_\tau}{R} \cdot \frac{1}{T} \quad (2.31)$$

$$\text{where } A' = A \exp (-\Delta S_\tau / R)$$

The (2.31) represents a linear curve between $\ln (\tau_j T)$ against $1/T$, the intercept and slope of the curve have been employed to get ΔH_τ , ΔS_τ and ΔF_τ known as enthalpy, entropy and free energy of activation due to dielectric relaxation as illustrated in Fig. 2.10. for some p-compounds. These thermodynamic energy parameters so far measured help one to make strong comment on the physico-chemical properties of the systems as seen in chapters 3,7,8 & 9 of this thesis.

The Kalman factor $\tau_j T / \eta_i^\delta$ is equal to the volume of the rotating unit and is given by [17]:

$$A = \tau_j T / \eta_i^\delta$$

Hence $\ln \tau_j T = \ln a + \delta \ln \eta_i$ (2.32)

The slope $\delta (= \Delta H\tau / \Delta H\eta_i)$ of the linear eq. (2.32) is used to estimate the enthalpy of activation $\Delta H\eta_i$, due to viscous flow of the solvent as shown in the different chapters of this thesis to come to the conclusion of the solvent environment about the solute ones.

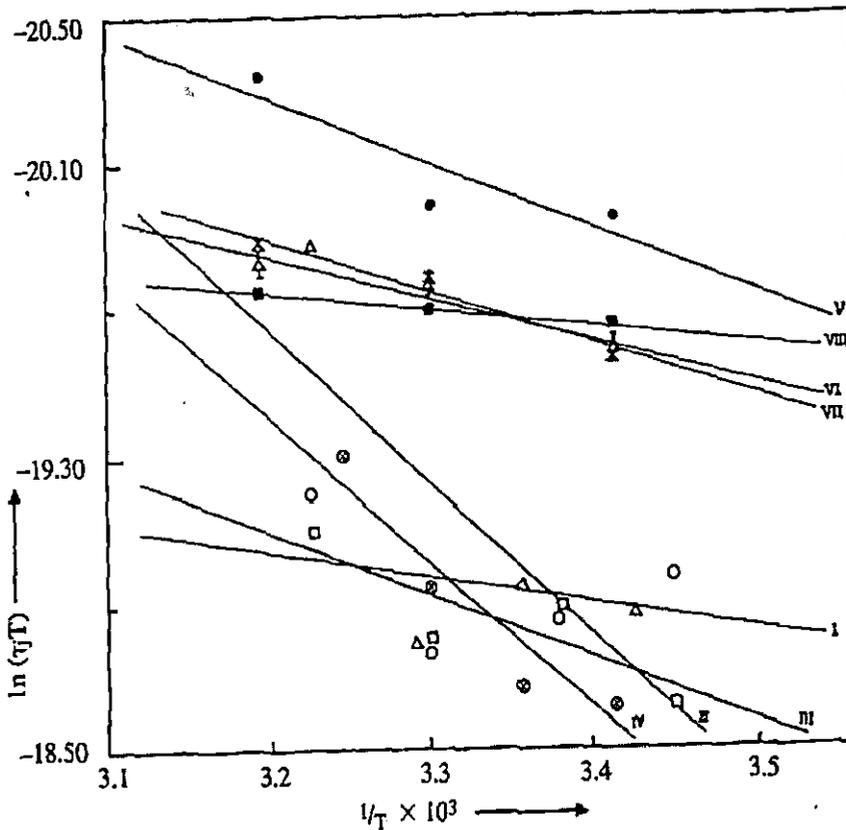


Fig 2.10 . Straight line plots of $\ln (\tau_j T)$ against $1/T$. (I) parahydroxypropiophenone ($-\circ-$), (II) parachloropropiophenone ($-\triangle-$), (III) paraacetamidobenzaldehyde ($-\square-$), (IV) parabenzoyloxybenzaldehyde ($-\otimes-$), (V) paraanisidine ($-\bullet-$) (VI) parafenitidine ($-\bar{\Delta}-$), (VII) orthochloroparanitroaniline ($-\times-$) and (VIII) parabromonitrobenzene ($-\blacksquare-$)

Chapter 2 , thus presents a brief account of the new theoretical formulations widely used in the several CHAPTERS 3,4,5,6,7 of this thesis to come to various conclusions in terms of measured parameters. They have significant contributions to study the physico-

chemical properties of a large number of polar liquids in non-polar solvents under hf and static electric fields.

REFERENCES

- [1] A K Jonscher, *Physics of Dielectric solids*, Invited papers edited by CHL Goodman Canterbury (1980)
- [2] U K Mitra, N Ghosh, P Ghosh and S Acharyya *J Indian Chem Soc* **83** (2006) 674
- [3] A Karmakar, U K Mitra, K Dutta and S Acharyya *Indian J Pure & Appl Phys* **44** (2006) 856
- [4] U K Mitra, N Ghosh, P Ghosh and S Acharyya *J Molecular Liquids* **126** (2006) 53
- [5] C P Smyth "*Dielectric Behaviour and structure*", (MC Graw Hill : New York) 1955
- [6] F J Morphy and S O Morgan *Bell Syst Tech J* **18** (1939) 502
- [7] M B R Murthy, R L Patil and D K Deshpande *Indian J Phys* **63B** (1989) 491
- [8] N Ghosh PhD Dissertation (North Bengal University, India), 2002
- [9] U Saha, S K Sit, R C Basak and S Acharyya *J Phys D: Appl Phys* (UK) **27** (1994) 596
- [10] S K Sit, R C Basak, U Saha and S Acharyya *J Phys D: Appl Phys* (UK) **27** (1994) 2194
- [11] K Bergmann, D Moberti and C P Smyth *J Phys Chem* **64** (1960) 665
- [12] H Fröhlich, "*Theory of Dielectrics*"(Oxford University Press: Oxford) 1949
- [13] U K Mitra, N Ghosh , P Ghosh and S Acharyya *J Indian Chem Soc* communicated (2006)
- [14] S C Srivastava and S Chandra '*Indian J Pure & Appl Phys* **13** (1975) 101
- [15] P Debye "*Polar molecules*" The Chemical Catalogue Company Inc (1929)
- [16] H Eyring, S Glasstone and K J Laidler "*The theory of Rate Process* " (MC Graw Hill: New York) 1941
- [17] B Sinha, S B Roy and G S Kastha '*Indian J Phys* **40** (1966) 101