

## **CHAPTER -2**

### **SCOPE AND OBJECTIVE OF THE PRESENT WORK**

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### 2.1. Introduction

Dielectric relaxation phenomena of dielectropolar liquid molecules in nonpolar solvents at a single or different temperatures under hf electric field is of much importance as it provides with a valuable information regarding shape, size and structure of dipolar molecules. Moreover solute-solvent and solute-solute molecular associations can be inferred from such study. The structural and associational aspects of dipolar liquid molecules can be made from the measured dielectric relaxation parameters viz the hf dipole moment  $\mu_j$ , static or low frequency dipole moment  $\mu_s$ , double relaxation times  $\tau_1$  and  $\tau_2$ , theoretical dipole moment  $\mu_{\text{theo}}$  obtained from bond angles and bond moments of substituent polar groups attached to parent polar molecule. Different thermodynamic energy parameters  $\Delta H_\tau$  and  $\Delta H_\eta$  due to dielectric relaxation and viscous flow respectively can, however, be measured from the estimated  $\tau_j$  at different temperatures by a method in Chapter 2. The entropy of activation  $\Delta S_\tau$ , free energy of activation  $\Delta F_\tau$  are then obtained. The main objective of this thesis is to modify the existing theories to get new formulations within the frame work of Debye-Smyth and Hill model. The concrete concept about structural conformation and various associational aspects of dipolar liquid molecules could thus be attempted for.

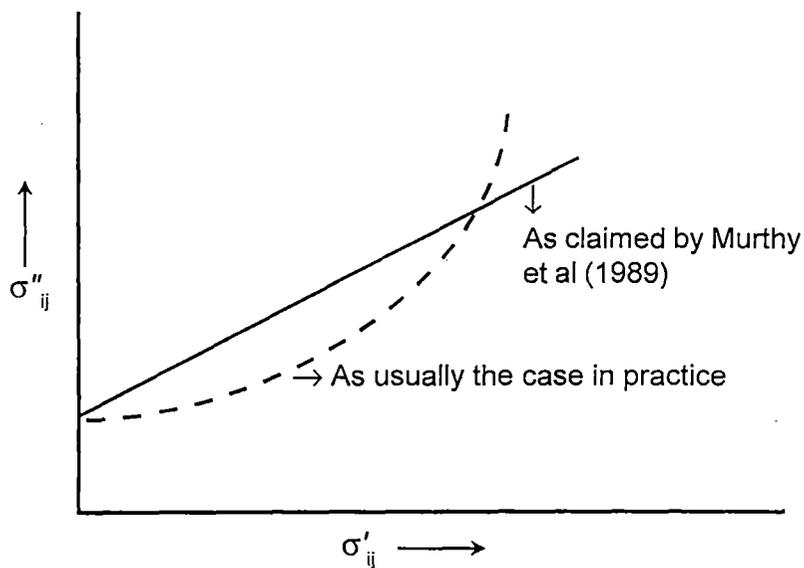
### 2.2. Theoretical Formulations to Estimate hf $\tau_j$ and $\mu_j$

The real  $\sigma_{ij}'$  and imaginary  $\sigma_{ij}''$  parts of hf complex conductivity  $\sigma_{ij}^*$  of solution (ij) are related by [1]

$$\sigma_{ij}'' = \sigma_{\infty ij} + \left( \frac{1}{\omega \tau_j} \right) \sigma_{ij}' \quad (2.1)$$

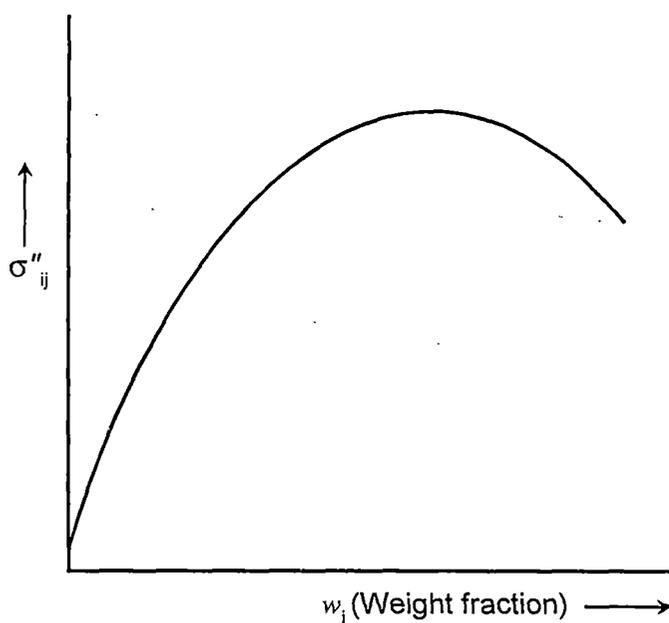
This is a straight line between the variables  $\sigma_{ij}''$  and  $\sigma_{ij}'$  of different weight fractions  $w_j$ 's whose slope  $(1/\omega \tau_j)$  is used to estimate  $\tau_j$  of a dipolar molecule.

But the variation of  $\sigma_{ij}''$  against  $\sigma_{ij}'$  for highly nonspherical associative polar liquids for different  $w_j$ 's at a given temperature does not obey the linear curve (Figure 2.1) as claimed by Murthy et al [1].

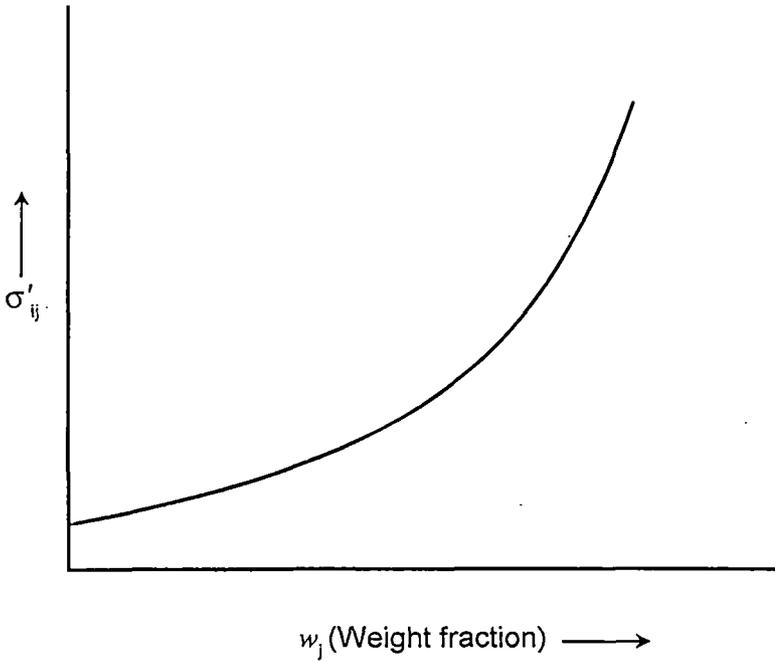


**Figure 2.1**

For such liquids, the individual variations of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  with  $w_j$ 's of dipolar solute as shown in Figures 2.2 and 2.3 can be used to estimate  $\tau_j$  [2].



**Figure 2.2**



**Figure 2.3**

$$\frac{(d\sigma_{ij}''/dw_j)w_{j \rightarrow 0}}{(d\sigma_{ij}'/dw_j)w_{j \rightarrow 0}} = \frac{1}{\omega\tau_j} \quad (2.2)$$

The estimated  $\tau_j$  from Eq (2.2) are in good agreement with Gopalakrishna's formulation [3]. The simple and straight forward theoretical formulation has been used to estimate  $\tau_j$ 's in Chapters 5 and 6 respectively.

Since the total hf conductivity  $\sigma_{ij} = \omega\epsilon_0 (\epsilon_{ij}'^2 + \omega_{ij}''^2)^{1/2} \simeq \sigma_{ij}''$ , we have from Eq (2.2)  $(d\sigma_{ij}'/dw_j)w_{j \rightarrow 0} = \omega\tau_j\beta$  (2.3)

The real part  $\sigma_{ij}'$  of hf complex conductivity  $\sigma_{ij}^*$  is [4,5]

$$\sigma_{ij}' = \frac{N\mu_j^2\rho_{ij}}{27M_jkT} \left( \frac{\omega^2\tau_j}{1+\omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 w_j \quad (2.4)$$

which on differentiation w.r. to  $w_j$  and at  $w_j \rightarrow 0$  yields that

$$(d\sigma_{ij}'/dw_j)w_{j \rightarrow 0} = \frac{N\mu_j^2\rho_{ij}}{27M_jkT} \left( \frac{\omega^2\tau_j}{1+\omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 \quad (2.5)$$

From Eqs. (2.3) and (2.5) one gets.

$$\mu_j = \left[ \frac{27 M_j k T \beta}{N \rho_j (\epsilon_j + 2)^2 \omega b} \right]^{1/2} \quad (2.6)$$

where  $M_j$  is molecular weight of a polar molecule,  $k$  = Boltzmann constant =  $1.38 \times 10^{-23} \text{ J mole}^{-1} \cdot \text{K}^{-1}$ ,  $N$  = Avogadro's number =  $6.023 \times 10^{23}$ ,  $\rho_j$  and  $\epsilon_j$  are the density and dielectric relative permittivity of solvent used and  $\beta$  is the linear coefficient of  $\sigma_{ij} - w_j$  curve in the limit  $w_j = 0$ . The dimensionless parameter 'b' involved with  $\tau_j$  is  $b = 1/(1 + \omega^2 \tau_j^2)$ . We have employed Eq (2.6) to get hf  $\mu_j$  as given in chapters 5, 6 and 8 of this thesis in terms of measured  $\tau_j$ 's.

The hf  $\sigma_{ij}$  is, however, involved with the transport of bound molecular charges. A new formulation is, therefore, advanced by introducing  $\chi_{ij}$ 's where  $\chi_{ij}$  is the hf dielectric susceptibility of orientational polarisation.

The real  $\epsilon_{ij}'$  and imaginary  $\epsilon_{ij}''$  parts of hf complex  $\epsilon_{ij}^*$  are related by :

$$\epsilon_{ij}' = \epsilon_{\infty ij} + \left( \frac{1}{\omega \tau} \right) \epsilon_{ij}'' \quad (2.7)$$

In terms of real  $\chi_{ij}' = \epsilon_{ij}' - \epsilon_{\infty ij}$  and imaginary  $\chi_{ij}'' = \epsilon_{ij}''$  parts of complex  $\chi_{ij}^*$  we have :

$$\chi_{ij}'' = (\omega \tau) \chi_{ij}' \quad (2.8)$$

variation of  $\chi_{ij}''$  with  $\chi_{ij}'$  is expected to be linear, the slope  $(\omega \tau)$  of which could yield  $\tau_j$  of a polar liquid.

Again, for complicated polar molecules the variations of  $\chi_{ij}''$  with  $\chi_{ij}'$  are not strictly linear unlike Figure 2.1 under such context Eq (2.8) becomes :

$$(d\chi_{ij}'' / dw_j)_{w_j \rightarrow 0} / (d\chi_{ij}' / dw_j)_{w_j \rightarrow 0} = \omega \tau \quad (2.9)$$

to give  $\tau_j$ 's. The polar-polar interactions are supposed to be fully eliminated to obtain  $\tau_j$ 's by Eq. (2.9).

The imaginary part  $\chi_{ij}''$  of dimensionless complex susceptibility  $\chi_{ij}^*$  of solution (ij) in S.I. unit is written as [4,6] :

$$\chi_{ij}'' = \frac{N\mu_j^2\rho_{ij}}{27\varepsilon_0M_jkT} \frac{\omega\tau_j}{1+\omega^2\tau_j^2} \cdot (\varepsilon_{ij} + 2)^2 w_j \quad (2.10)$$

$$\text{or, } \left(\frac{d\chi_{ij}''}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_0M_jkT} \frac{\omega\tau_j}{1+\omega^2\tau_j^2} (\varepsilon_i + 2)^2 \quad (2.11)$$

The approximation  $\chi_{ij} \simeq \chi_{ij}''$  like  $\sigma_{ij} \simeq \sigma_{ij}''$  was not made in order to obtain  $\mu_j$  from  $\tau_j$  in the dielectric susceptibility measurement.

From Eqs. (2.9) and (2.11) one obtains to get hf  $\mu_j$ 's from :

$$\mu_j = \left[ \frac{27\varepsilon_0M_jkT\beta}{N\rho_i(\varepsilon_i + 2)^2 b} \right]^{1/2} \quad (2.12)$$

in terms of the linear coefficient  $\beta$  of  $\chi_{ij}' - w_j$  curve in the limit  $w_j = 0$ .

$\varepsilon_0$  is the permittivity of free space =  $8.854 \times 10^{-12}$  F.m<sup>-1</sup> and the other symbols have their usual meanings as stated earlier.

The hf  $\mu_j$  in chapter 7 of this thesis are computed from Eq. (2.12). But the Eq.(2.6) showed higher  $\mu_j$ 's in comparison to Eq (2.12). The difference  $\Delta\mu_j$  may provide an additional information [7] of bound molecular charges as seen in Chapter 8.

### 2.3. Static Experimental Parameter $X_{ij}$ and Static $\mu_s$

The Eq (1.77) is :

$$\therefore \frac{\varepsilon_{oij} - 1}{\varepsilon_{oij} + 2} - \frac{\varepsilon_{\infty ij} - 1}{\varepsilon_{\infty ij} + 2} = \frac{\varepsilon_{oi} - 1}{\varepsilon_{oi} + 2} - \frac{\varepsilon_{\infty i} - 1}{\varepsilon_{\infty i} + 2} + \frac{N\mu_s^2}{9\varepsilon_0kT} c_j \quad (2.13)$$

where  $\varepsilon_{oij}$  and  $\varepsilon_{\infty ij}$  are the low and infinite frequency relative permittivities of solution (ij). The molar concentration  $c_j$  is  $c_j = \rho_{ij} w_j / M_j$ , where  $w_j$  is the weight

fraction of polar liquid.

$$\frac{\epsilon_{oij} - \epsilon_{\infty ij}}{(\epsilon_{oij} + 2)(\epsilon_{\infty ij} + 2)} = \frac{\epsilon_{oi} - \epsilon_{\infty i}}{(\epsilon_{oi} + 2)(\epsilon_{\infty i} + 2)} + \frac{N\mu_s^2}{27\epsilon_0 kT} \frac{\rho_{ij} w_j}{M_j} \quad (2.14)$$

The weight  $W_i$  of volume  $V_i$  of a nonpolar solvent is mixed with the weight  $W_j$  of a polar solute of volume  $V_j$  to make a solution. The solution density  $\rho_{ij}$  is :

$$\begin{aligned} \rho_{ij} &= \frac{W_i + W_j}{V_i + V_j} = \frac{W_i + W_j}{W_i/\rho_i + W_j/\rho_j} \\ &= \frac{\rho_i \rho_j}{\left(\frac{W_i}{W_i + W_j}\right) \rho_j + \left(\frac{W_j}{W_i + W_j}\right) \rho_i} \\ &= \frac{\rho_i \rho_j}{w_i \rho_j + w_j \rho_i} = \frac{\rho_i}{1 - \gamma w_j} \end{aligned} \quad (2.15)$$

where  $w_i = \frac{W_i}{W_i + W_j}$  and  $w_j = \frac{W_j}{W_i + W_j}$  are the weight fractions of solvent and solute respectively such that  $w_i + w_j = 1$  and  $\gamma = (1 - \rho_i/\rho_j)$ , where  $\rho_i$  and  $\rho_j$  are the densities of pure solvent and solute respectively. Thus Eq. (2.14) becomes :

$$\frac{\epsilon_{oij} - \epsilon_{\infty ij}}{(\epsilon_{oij} + 2)(\epsilon_{\infty ij} + 2)} = \frac{\epsilon_{oi} - \epsilon_{\infty i}}{(\epsilon_{oi} + 2)(\epsilon_{\infty i} + 2)} + \frac{N\mu_s^2 \rho_i (1 - \gamma w_j)^{-1} w_j}{27\epsilon_0 kT M_j} \quad (2.16)$$

$$\text{or } X_{ij} = X_i + \frac{N\mu_s^2 \rho_i}{27\epsilon_0 M_j kT} w_j + \frac{N\mu_s^2 \rho_i}{27\epsilon_0 M_j kT} \gamma w_j^2 + \dots \quad (2.17)$$

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \dots \quad (2.18)$$

The static experimental parameter  $X_{ij}$  of a solution is thus a function of  $w_j$ 's. The Eq (2.17) is highly converging in nature since  $w_j$  lies within  $0 < w_j < 1$ . The

computed error in the regression analysis of Eq. (2.18) shed much light on its functional dependence on estimated  $\mu_s$ .

Equating the coefficients of equal powers of  $w_j$  from both right hand sides of Eqs. (2.17) and (2.18) one gets

$$\mu_s = \left( \frac{27 \epsilon_0 M_j kT}{N \rho_j} a_1 \right)^{1/2} \quad (2.19)$$

and

$$\mu_s = \left( \frac{27 \epsilon_0 M_j kT}{N \rho_j \gamma} a_2 \right)^{1/2} \quad (2.20)$$

to estimate static dipole moment  $\mu_s$  at any stage of dilution.

The present extrapolation technique on  $X_{ij}-w_j$  curve unlike Lefevre [8] and Guggenheim [9] is a single one which seems to be better over the usual procedures where at least two extrapolations are needed to obtain  $\mu_s$  of a polar liquid. But  $\mu_s$  from Eq (2.20) is not reliable because the term  $\gamma$  is influenced by the effects of solvent, relative density, solute-solute or, dipole-dipole interaction, internal field, and macroscopic viscosity etc. [5].

This theory has widely been tested [5] on a large number of straight long chain alcohols in chapter 6 of this thesis.

## 2.4. Double Relaxation Times $\tau_1, \tau_2$ and Dipole Moments $\mu_1, \mu_2$

The orientational polarisation is however, achieved by introducing the orientational susceptibility  $\chi_{ij}$  because  $\epsilon_{\infty ij}$  which includes the fast polarisation, always appears as a subtracted term in Bergmann et. al. equations. The clumsiness of algebra and the effects of fast polarisation can thus be avoided by the established symbols of dielectric terminologies and parameters  $\chi_{ij}' = \epsilon_{ij}' - \epsilon_{\infty ij}$ ,  $\chi_{ij}'' = \epsilon_{ij}''$  and  $\chi_{oij} = \epsilon_{oij} - \epsilon_{\infty ij}$  in Bergmann et. al equations [10].

$$\chi_{ij}''/\chi_{oij} = c_1 \frac{1}{1+\omega^2\tau_1^2} + c_2 \frac{1}{1+\omega^2\tau_2^2} \quad (2.21)$$

$$\chi_{ij}''/\chi_{oij} = c_1 \frac{\omega\tau_1}{1+\omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1+\omega^2\tau_2^2} \quad (2.22)$$

$\chi_{ij}'$  and  $\chi_{ij}''$  are the real and imaginary parts of the complex dielectric orientational susceptibility  $\chi_{ij}^*$  and  $\chi_{oij}$  is the low frequency susceptibility which is real.

Let  $\alpha_1 = \omega\tau_1$  and  $\alpha_2 = \omega\tau_2$  Eqs. (2.21) and (2.22) are solved to get.

$$c_1 = \frac{(\chi_{ij}'\alpha_2 - \chi_{ij}'')(1+\alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (2.23)$$

$$c_2 = \frac{(\chi_{ij}'' - \chi_{ij}'\alpha_1)(1+\alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (2.24)$$

which are the relative weight factors for the two separate broad dispersions and  $\alpha_2 > \alpha_1$ .

Now, adding Eqs. (2.23) and (2.24) since  $c_1 + c_2 = 1$  we get.

$$\frac{(\chi_{oij} - \chi_{ij}')}{\chi_{ij}'} = \omega(\tau_2 + \tau_1) \frac{\chi_{ij}''}{\chi_{ij}'} - \omega^2\tau_1\tau_2 \quad (2.25)$$

It is a straight line between the variables  $(\chi_{oij} - \chi_{ij}') / \chi_{ij}'$  and  $\chi_{ij}''/\chi_{ij}'$  having slope  $\omega(\tau_2 + \tau_1)$  and intercept  $-\omega^2\tau_1\tau_2$ . It is solved for different  $\omega$ 's of a polar molecule for a fixed value of angular frequency  $\omega (= 2\pi f)$  of the electric field to get  $\tau_1$  and  $\tau_2$  for the rotations of flexible polar groups attached to the parent molecule and the molecule itself respectively.

The estimated  $\tau_1$  and  $\tau_2$  can be used to obtain  $\mu_1$  and  $\mu_2$  from Eqs (2.6) and (2.12) of the flexible part and the whole molecule.

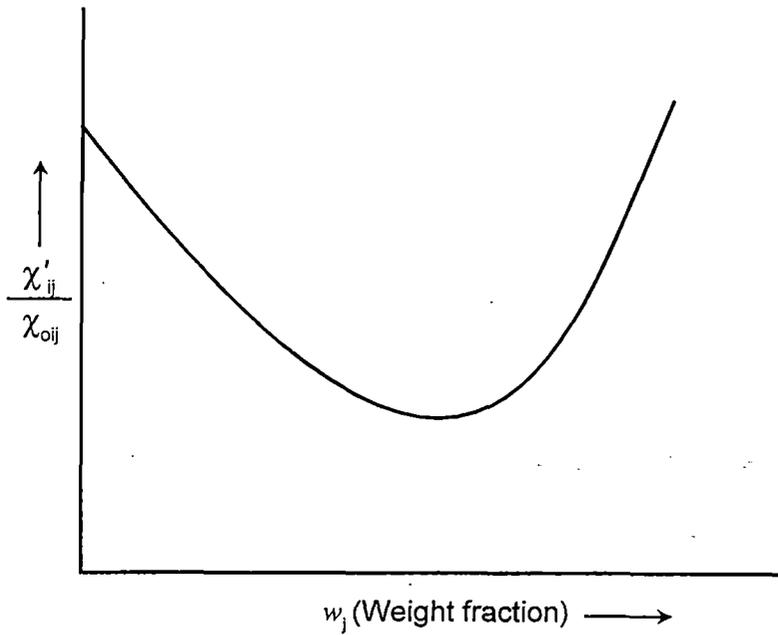
The theoretical values of  $c_1$  and  $c_2$  towards dielectric dispersions are derived from Fröhlich's [11] Eqs. (2.26) and (2.27), with known  $\tau_1$  and  $\tau_2$  of Eq. (2.25):.

$$\chi_{ij}' / \chi_{oij} = 1 - \frac{1}{2A} \ln \left( \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \quad (2.26)$$

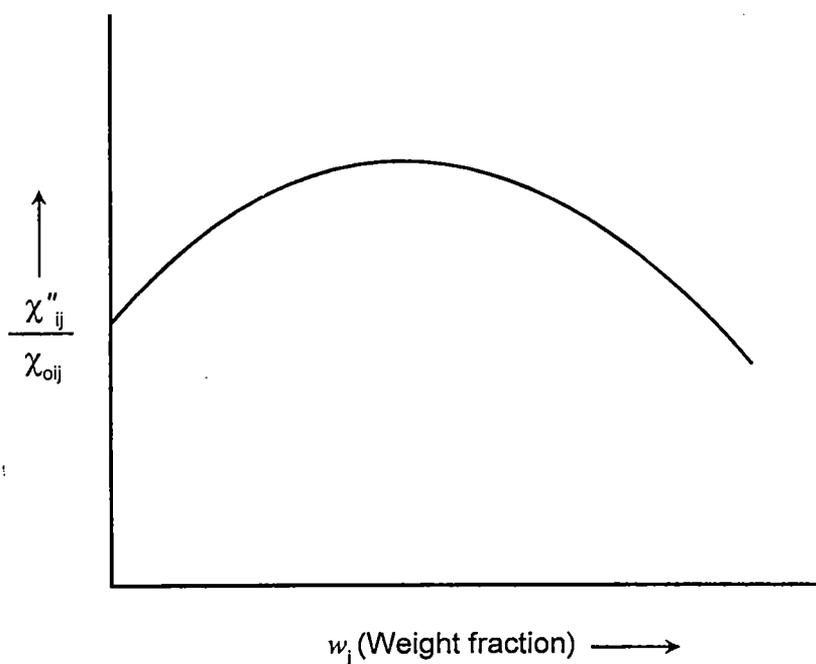
$$\chi_{ij}'' / \chi_{oij} = \frac{1}{A} [\tan^{-1}(\omega \tau_2) - \tan^{-1}(\omega \tau_1)] \quad (2.27)$$

$A =$  the Fröhlich parameter  $= \ln(\tau_2/\tau_1)$ .

The experimental  $c_1$  and  $c_2$  are also obtained from Eqs. (2.23) and (2.24) with the known intercepts  $(\chi_{ij}' / \chi_{oij})_{w_j \rightarrow 0}$  and  $(\chi_{ij}'' / \chi_{oij})_{w_j \rightarrow 0}$  from concentration ( $w_j$ ) variation of  $\chi_{ij}' / \chi_{oij}$  and  $\chi_{ij}'' / \chi_{oij}$  of Figures. 2.4 and 2.5. The theoretical and experimental  $c_1$  and  $c_2$  satisfy  $|c_1 + c_2| \simeq 1$ , suggesting the validity [6,7] of the suggested method.



**Figure 2.4**



**Figure 2.5**

The derived theoretical formulations were tested on isomers of anisidine and toluidine and monosubstituted anilines presented in chapter 7 and 8 of this thesis.

## 2.5. Relaxation Parameters under Rf Electric Field

The rf conductivity of polar - nonpolar liquid mixture is measured by the resonance method. The block diagram of experimental set-up is shown in Figure 2.6a & b. A Hartley oscillator feeds power to the resonant circuit consisting of a coil and a variable air condenser in series with a rf milliammeter. The cylindrical pyrex glass tube of diameter 2cm provided with a pair of stainless steel electrodes of diameter 1.5cm, separated by 1cm is used as a cell. The oscillator is set to the desired frequency. The resonant circuit is tuned with the cell connected in parallel to tuning condenser ( $c_v$ ) and in series with the rf meter.

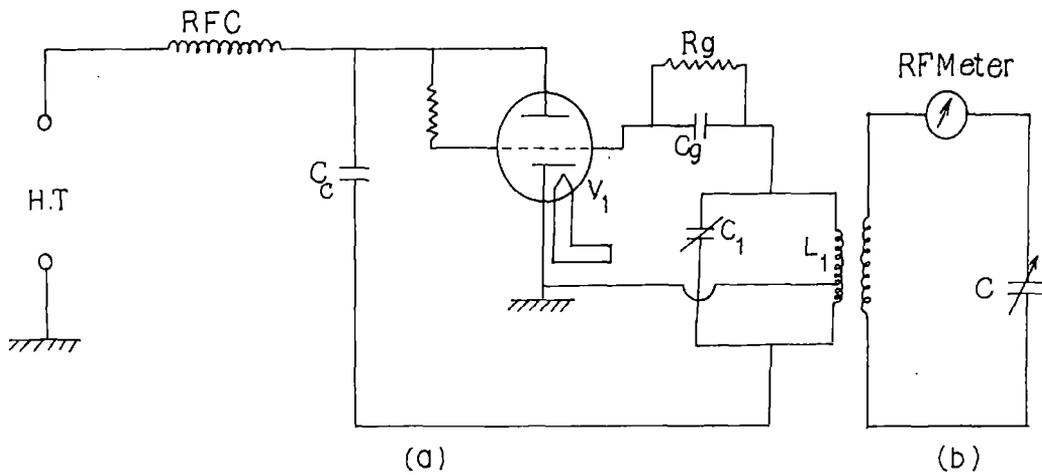


Figure 2.6

- a. Radio Frequency Oscillator  
 b. Secondary Tuning Circuit.

### LIST OF COMPONENTS

$V_1 = 6L6$   
 $R_g = 30K\Omega$   
 $C_g = 350\text{pF}$   
 $C = 0 - 500\text{pF}$

RFC = Radio Frequency Choke  
 RF Meter = Radio Frequency  
 Milliammeter  
 $C_c = 0.01\mu\text{F}$

## 2.6. RF Resistance and Conductivity of a Polar Liquid

The resonant currents  $I_1$  and  $I_2$  in the rf milliammeter is measured when the cell is empty and filled up with the dielectric liquid. After the introduction of dielectric cell the secondary circuit is modified as shown in Figure 2.6c and the equivalent circuit is in Figure 2.6d. In case of parallel combination as in Figure (2.6c). let  $Z_p$  = equivalent impedance, where

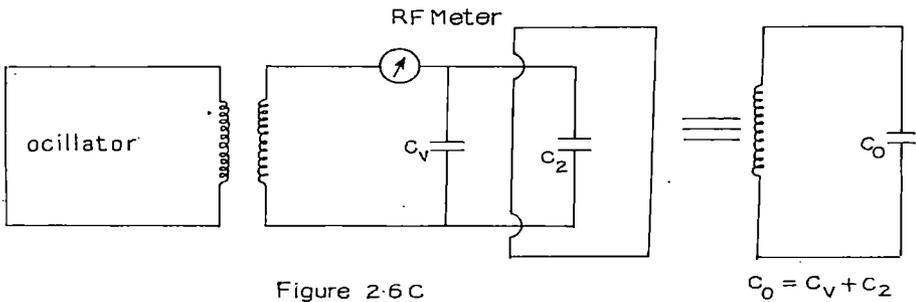


Figure 2-6c  
(circuit Arrangement )

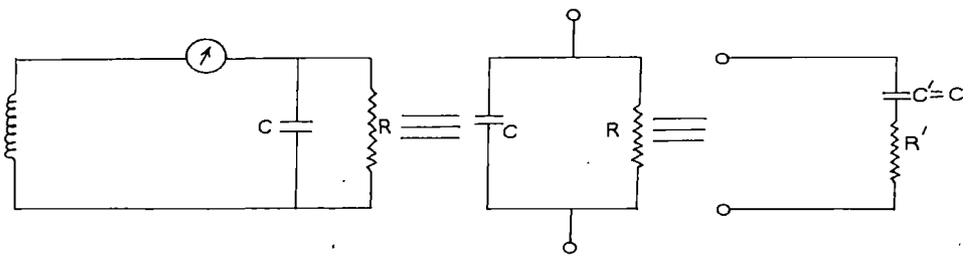


Figure 2-6d  
[Equivalent Circuit ]

$$Z_p = \frac{R}{1 + j\omega CR} = \frac{R(1 - j\omega CR)}{1 + \omega^2 C^2 R^2} \quad (2.28)$$

In case of series combination as in Figure 2.6d.

$$Z_p = R' + \frac{1}{1 + j\omega CR'} \quad (2.29)$$

Equating the real and imaginary parts of Eqs. (2.28) and (2.29) one obtains :

$$R' = \frac{R}{1 + \omega^2 C^2 R^2} \quad (2.30)$$

further  $I_1 = E/R_0$ , where  $R_0$  is the rf resistance of the secondary circuit and is given by :

$$R_0 = \frac{C_2 - C_1}{2\omega C_1 C_2} \sqrt{\frac{I_1^2}{I_0^2 - I_1^2}} \quad (2.31)$$

where  $I_0$  and  $I_1$  are the resonant currents in the rf meter without and with the cell,  $C_1$  and  $C_2$  are the capacities for reducing the resonant current  $I_0$  by  $1/\sqrt{2}$  where  $C_0$  is the capacity of the tuning condenser for the resonant current  $I_0$ .

$$\text{Again } I_2 = \frac{E}{R_0 + R'} \quad (2.32)$$

$$= \frac{E}{R_0 + \frac{R}{1 + \omega^2 C^2 R^2}} \quad (2.33)$$

Let  $I_1/I_2 = \alpha$  we get

$$(\alpha - 1) = \frac{R}{R_0 + \omega^2 C^2 R^2 R_0}$$

$$R = \frac{1 \pm [1 - 4R_0^2 (\alpha - 1)^2 \omega^2 C^2]^{1/2}}{2R_0 (\alpha - 1) \omega^2 C^2}$$

Since  $4R_0^2 (\alpha - 1)^2 \omega^2 C^2 \ll 1$  we have rf resistance of a polar liquid.

$$R = \frac{1}{R_0 (\alpha - 1) \omega^2 C^2} \quad (2.34)$$

$$\text{Now } R = \rho \frac{d}{S} \quad (2.35)$$

where  $\rho$  is the specific resistance of the liquid,  $d$  is the distance between the electrodes of cross-sectional area  $S$ .

If  $\sigma'$  is the rf conductivity of the liquid, then

$$\sigma' = \frac{d}{R.S} \quad (2.36)$$

The capacity of the tuning condenser for the resonant current  $I_0$  is given by,

$$C_0 = \frac{S}{4\pi d} \quad (2.37)$$

From Eqs. (2.36) and (2.37) we get the working formula of  $\sigma'$  where

$$\sigma' = \frac{1}{4\pi R C_0} \quad (2.38)$$

## 2.7. Washing of Dielectric Cell and Purification of Dipolar Liquids

Before filling the cell with experimental liquid, the cell was cleaned with sodium hydroxide and chromic acid, then for several times with pure distilled water and finally with benzene. The cell was then dried by an electric drier.

The liquids under investigation were N, N dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), methanol ( $\text{CH}_3\text{OH}$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) n-propanol ( $\text{C}_3\text{H}_7\text{OH}$ ) 2-butanol ( $\text{C}_4\text{H}_9\text{OH}$ ) in solvents benzene ( $\text{C}_6\text{H}_6$ ) and carbon tetrachloride ( $\text{CCl}_4$ ). They were of Analar grade from Messrs BDH (London) and E. Merck (Germany). The liquids were distilled in vacuum and kept in a

desiccator before use. The temperature of the cell was controlled by a thermostat of accuracy  $\pm 0.5^\circ\text{C}$ .

## 2.8. Coefficient of Viscosity of Dipolar Liquids

The coefficient of viscosity  $\eta$  of the dielectric liquids was measured by Ostwald viscometer.

The volumes of distilled water and the experimental liquid flowing through the capillary tube of length  $l$  and radius  $r$  per unit time are

$$V_1 = \frac{\pi P_1 r^4}{8 \eta_1 l} = \frac{K \pi \rho_1 r^4}{8 \eta_1 l} \quad (2.39)$$

$$V_2 = \frac{\pi P_2 r^4}{8 \eta_2 l} = \frac{K \pi \rho_2 r^4}{8 \eta_2 l} \quad (2.40)$$

Here  $P_1$  and  $P_2$  are the pressure differences between the ends of capillary tube.  $\eta_1$  and  $\eta_2$  are the coefficient of viscosities of water and experimental liquid respectively.

Now,

$$\frac{V_1}{V_2} = \frac{\rho_1}{\rho_2} \cdot \frac{\eta_2}{\eta_1} \quad (2.41)$$

and since the times  $t_1$  and  $t_2$  of free fall of two liquids vary inversely as  $V_1$  and  $V_2$

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \cdot \frac{\rho_1}{\rho_2} \quad (2.42)$$

with the Known  $\eta_1$ ,  $\rho_1$ ,  $\rho_2$  [12],  $t_1$  and  $t_2$  by a digital timer stop watch  $\eta_2$ 's were estimated.

## 2.9. Formulations for $n$ , $\tau_j$ and $\mu_j$ Under Rf Electric Field

The equation of motion of a polar molecule through a viscous medium under rf electric field is

$$M \frac{dv}{dt} = eE_0 e^{j\omega t} - 6\pi\eta a v \quad (2.43)$$

It is solved by :

$$v = A e^{j\omega t} \quad (2.44)$$

The drift velocity of ion is

$$v = \frac{eE_0 e^{j\omega t}}{M(\gamma + j\omega)} \quad (2.45)$$

Where  $\gamma = 6\pi\eta a/M$  and  $j = \sqrt{-1}$ , a complex number. Hence

$$v = \frac{eE_0}{M} \left[ \frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right] e^{j\omega t}$$

and the mobility of ion

$$\mu = \frac{v}{E} = \frac{e}{M} \left[ \frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right]$$

If  $n$  be the number of ions per unit volume, the conduction current is

$$i = \frac{ne^2}{M} \left[ \frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right] E_0 e^{j\omega t} \quad (2.46)$$

The real part  $\sigma'_{ij}$  of complex hf conductivity  $\sigma_{ij}^*$  is [13]

$$\begin{aligned} \sigma' &= ne\mu = \frac{ne^2}{M} \cdot \frac{\gamma}{\gamma^2 + \omega^2} \\ &= \frac{ne^2}{M} \cdot \frac{6\pi\eta a/M}{(6\pi\eta a/M)^2 + \omega^2} \\ \sigma' &= \frac{ne^2}{6\pi\eta a} \end{aligned} \quad (2.47)$$

as 
$$\frac{6\pi\eta a}{M} \gg \omega$$

Again from Murphy – Morgan [14] relation  $\sigma_{ij}^*$  is given by

$$\sigma_{ij}^* = \sigma_{ij}' + j \sigma_{ij}'' \quad (2.48)$$

where  $\sigma_{ij}' = \frac{\omega}{4\pi} \epsilon_{ij}''$  and  $\sigma_{ij}'' = -\frac{\omega}{4\pi} \epsilon_{ij}'$  are the real and imaginary parts, of hf complex conductivity  $\sigma_{ij}^*$

From Eqs. (2.47) and (2.48)  $\sigma_{ij}'$  is

$$\sigma_{ij}' = \frac{\omega}{4\pi} \epsilon_{ij}'' + \left( \frac{ne^2}{6\pi a} \right) \cdot \frac{1}{\eta_{ij}} \quad (2.49)$$

Eq. (2.49) with Eq. (1.32) becomes

$$\sigma_{ij}' = \frac{\omega}{4\pi} \left( \frac{\epsilon_{oij} - \epsilon_{\infty ij}}{1 + \omega^2 \tau^2} \right) \omega \tau + \left( \frac{ne^2}{6\pi a} \right) \cdot \frac{1}{\eta_{ij}} \quad (2.50)$$

under rf electric field  $\omega^2 \tau^2 \ll 1$ , Eq (2.50) becomes :

$$\sigma_{ij}' = \frac{\omega^2 \tau}{4\pi} (\epsilon_{oij} - \epsilon_{\infty ij}) + \left( \frac{ne^2}{6\pi a} \right) \cdot \frac{1}{\eta_{ij}} \quad (2.51)$$

The Eq. (2.51) shows that  $\sigma_{ij}'$  varies linearly with  $1/\eta_{ij}$ . The slope  $(ne^2/6\pi a)$  is used to estimate n.

$$\text{Einstein - Stokes relation [15] is } D\eta/T = \frac{k}{6\pi a} \quad (2.52)$$

where  $D = \frac{\mu kT}{e}$ , the diffusion coefficient. Eq (2.52) with Eq (1.102) and (2.47) becomes

$$\tau_j = \frac{2na^2 e^2}{3\sigma_{ij}' kT} \quad (2.53)$$

where  $a$  = molecular radius,  $e$  = electronic charge =  $4.803 \times 10^{-10}$  e.s.u and  $k$  = Boltzmann constant =  $1.38 \times 10^{-16}$  erg mole $^{-1}$  K $^{-1}$ ,  $T$  = Temperature in Kelvin.

$$\text{Again } \sigma_{ij}' = \frac{\omega}{4\pi} \epsilon_{ij}'' \quad (2.54)$$

The  $\epsilon_{ij}''$  according to Smyth [4] is

$$\epsilon_{ij}'' = \frac{4\pi N d_{ij} w_j \mu_j^2 (\epsilon_{oij} + 2) (n_{Dij}^2 + 2) \omega \tau}{27 M_j kT (1 + \omega^2 \tau^2)} \quad (2.55)$$

In rf electric field  $\omega^2 \tau^2 \ll 1$

$$\therefore \sigma_{ij}' = \frac{4\pi^2 f^2 N \tau_j \mu_j^2 d_{ij} (\epsilon_{oij} + 2) (n_{Dij}^2 + 2) w_j}{27 M_j kT} \quad (2.56)$$

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

$$\left( \frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{4\pi^2 f^2 N \tau_j \mu_j^2 d_{ij} (\epsilon_{oi} + 2) (n_{Di}^2 + 2)}{27 M_j kT} \quad (2.57)$$

$(d\sigma_{ij}'/dw_j)_{w_j \rightarrow 0} = \beta$  is the linear coefficient of variation of  $\sigma_{ij}'$  with  $w_j$ .  $\mu_j$  is finally given by :

$$\mu_j = \left[ \frac{27 M_j kT \beta}{4\pi^2 f^2 N \tau_j d_{ij} (\epsilon_{oi} + 2) (n_{Di}^2 + 2)} \right]^{1/2} \quad (2.58)$$

where

$M_j$  = molecular weight of dipolar liquid

$f$  = frequency of applied electric field

$N$  = Avogadro's number =  $6.023 \times 10^{23}$

$d_{ij}$  = density of solvent

$\epsilon_{oi}$  = relative permittivity of solvent

$n_{Di}$  = refractive index of solvent.

The theoretical formulations thus derived are applied on some alcohols and interesting aprotic polar amides in the 9th and 10th chapter of the thesis.

## 2.10. Eyrings' Rate Theory

The thermodynamic energy parameters using Eyring's rate theory [16] were attempted from the temperature variation of  $\tau_j$  under hf electric field. The energy parameters  $\Delta H_\tau$ , the enthalpy of activation,  $\Delta S_\tau$ , the entropy of activation and  $\Delta F_\tau$ , the free energy of activation gives an insight into the stability or unstability [2,17-19] of the systems. However, the aspect of molecular association [2,17,19] could also be inferred from such study.

The radius 'a' of a rotating unit is [20-22].

$$a = \frac{\tau_j T}{\eta^\gamma} \quad (2.59)$$

where  $\gamma = \Delta H_\tau / \Delta H_\eta$ ,

$$\text{or, } \ln \tau_j T = \ln a + \gamma \cdot \ln \eta \quad (2.60)$$

establishing the linear relation between  $\ln \tau_j T$  and  $\ln \eta$ . The slope  $\gamma$  of Eq.(2.60) gives information of solute - solvent and solute-solute associations. If  $\gamma > 0.50$  the solute molecule behaves as solid phase rotator[2,17]. This fact has been discussed in the chapters 3, 5 and 10 of this thesis.

## 2.11. Structural Aspects of Dipolar Molecules From $\mu_{\text{theo}}$

Structure of a polar molecule is studied in terms of atomic orbitals which often overlaps to form hybridised orbitals. The phenomenon is known as hybridisation. When two atoms are linked by a covalent bond, the distance between the centre of the two atomic nuclei is called bond length. The bond due to overlap of two S orbitals is called  $\sigma$  - bond. The sidewise overlap of two half filled p-orbitals to have a nodal plane form a  $\pi$  - bond. The bond angle depends on the nature of hybridisation due to size and the electronegativity of atoms or groups attached to a molecule.

Available bond moments of flexible polar groups of a molecule are used to estimate  $\mu_{\text{theo}}$  by simple vector addition rules [2, 5, 6, 17, 23] on the planer molecule. The  $\mu_{\text{theo}}$ 's differ from measured hf  $\mu_j$  and static  $\mu_s$  due to inductive, electromeric and mesomeric effects [2, 5, 6] owing to their aromaticity or electronegativity.

### Inductive Effect

The different electronegativities of atoms produces a certain degree of polarity in the bond. The more or less electronegative atoms acquire a  $\delta^-$  or  $\delta^+$  charges. Such polarity in the bond is called I-effect.  $-\text{NO}_2$ ,  $-\text{OH}$ ,  $-\text{C}_6\text{H}_5$  etc. push electrons while  $(\text{CH}_3)\text{C}-$ ,  $(\text{CH}_3)_2\text{CH}-$ ,  $\text{CH}_3-$  etc pull electrons away from C – atom are said to have +I and – I effects.

### Electromeric Effect

It is a temporary effect involving the complete transfer of a shared pair of  $\pi$  electrons to one or other atoms joined by double or triple bonds. Thus it is a polarisability effect.

### Mesomeric (Resonance) Effect

Mesomeric effect refers to the polarity produced in a molecule as a result of interaction between two  $\pi$  bonds or a  $\pi$  bond and lone pair of electrons.

The groups i.e.  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{OCH}_3$  etc. loose electrons towards a C-atom are said to have +M effect. While  $-\text{NO}_2$ ,  $-\text{C}\equiv\text{N}$ ,  $-\text{C}=\text{O}$  etc draw electrons away from a C-atom are said to have a – M effect.

All these effects play the vital role in the measured  $\mu_j$ 's and  $\mu_s$ 's. These effects possibly may change the experimental parameters :  $\sigma_{ij}$ ,  $\chi_{ij}$ ,  $X_{ij}$  etc to a certain degree. The agreement of  $\mu_j$ 's or  $\mu_s$ 's with  $\mu_{\text{theo}}$  is, however accomplished by multiplying [5] the available bond moments with  $\mu_s / \mu_{\text{theo}}$  or  $\mu_j / \mu_{\text{theo}}$  as shown in this thesis.

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