

# *Chapter 2*

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

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### 2.1. INTRODUCTION

The present position of the investigation of dielectric relaxation process of a polar-nonpolar liquid mixture under high frequency electric field is very encouraging. It provides one with the information of structural configuration of a polar molecule.

The method of study so far developed is based on measurements of conductivity of polar-nonpolar liquid mixture under a hf electric field of microwave or radio frequency range at a suitable temperature. Later on, the concept of single Debye-like dispersion is replaced by the fact that the polar molecule may possess two discrete relaxation times at a temperature under hf electric field. The substituent polar groups of a polar molecule exhibit mesomeric and inductive moments. Under such context, it is worthwhile to study the relaxation mechanism in terms of SI units because of its coherent, unified and rationalised nature.

### 2.2. ESTIMATION OF $\tau$ FROM REAL PART OF HIGH FREQUENCY CONDUCTIVITY

Dutta et al<sup>1</sup> used the real part of hf conductivity  $K'_{ij}$  of polar-nonpolar liquid mixture of  $w_j$  of a polar liquid at any temperature  $T$  K as deduced by Ghosh and Acharyya<sup>2</sup> based on Debye model<sup>3</sup>. The expression of  $K'_{ij}$  is given by :

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT} \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) w_j \quad \dots\dots\dots (2.1)$$

where  $\mu_j$  is the dipole moment of the polar solute of molecular weight  $M_j$ ,  $N$  and  $k$  are the Avogadro's number and Boltzmann constant respectively.  $F_{ij}$  is the local field given by  $F_{ij} = [(\epsilon_{ij} + 2)/3]^2$ ,  $\epsilon_{ij}$  being the dielectric constant of the solution of density  $\rho_{ij}$ .

At infinite dilution (i.e.  $w_j \rightarrow 0$ ) the relaxation time  $\tau$  becomes  $\tau_s$  of a polar solute in a given solvent.

The eq. (2.1) on being differentiated with respect to  $w_j$  and making  $w_j \rightarrow 0$  yields that

$$\left(\frac{dK'_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2}\right) \dots\dots\dots (2.2)$$

which is equal to  $\beta$ , the slope of the experimental  $K'_{ij}$  with  $w_j$  curve at T K. Hence

$$\frac{\omega \tau_s}{1 + \omega^2 \tau_s^2} = \frac{\beta}{R' \omega} = b \text{ (say)} \dots\dots\dots (2.3)$$

where  $R' = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT} = \text{a constant.}$

Now, eq. (2.3) is a quadratic equation in  $\omega \tau_s$  having roots

$$\tau_s = \frac{1}{\omega} \cdot \frac{1 \pm \sqrt{1 - 4b^2}}{2b} \dots\dots\dots (2.4)$$

The  $\tau_s$  of eq. (2.4) depends mainly upon the values of  $b$  for a given frequency of the applied electric field. It is single valued for  $b=0.5$ . When  $b>0.5$   $\tau_s$  has two values which are complex conjugate to each other. This is practically impossible because  $\tau_s$  of a polar liquid is a real physical quantity. Hence, eq. (2.4) becomes,

$$\tau_s = \frac{1}{2b\omega} \dots\dots\dots (2.5)$$

giving a single value of  $\tau_s$  for  $b \geq 0.5$ . But both the values of  $\tau_s$  will be real and different for  $b < 0.5$ .

The  $K'_{ij}$  of large number of systems like p-anisidine, p-bromonitrobenzene, (Fig. 2.1), 1-2 dinitrochlorobenzene, 2-4 dinitrochlorobenzene, o-nitroaniline (Fig.2.2), 3-5 dichloronitrobenzene (Fig. 2.3) and 3-6 dichloro aniline (Fig. 2.4) had already been studied by Dutta et al<sup>1</sup> to estimate  $\tau_s$ . Figures 2.1 to 2.4 show the variation of  $K'_{ij}$  at different  $w_j$ 's of solutes.

The procedure to get slope  $\beta$  of  $K'_{ij} - w_j$  curve was to draw a tangent to each curve of  $K'_{ij} - w_j$  at  $w_j \rightarrow 0$ . The value of  $b (= \beta/R'\omega)$  was calculated from  $\beta$  and placed in Table 2.1 along with  $\tau_s$ .

For the systems in which  $-NO_2$  group is rigidly fixed with the parent benzene molecule there are two values of  $\tau_s$  i.e.

$$\tau_1 = \tau_0 e^{-E_{\tau_1}/2kt} \quad \text{and} \quad \tau_2 = \tau_0 e^{-E_{\tau_2}/2kt} \text{ as indicated by Higasi et al}^4$$

$E_{\tau_1}$  and  $E_{\tau_2}$  are the activation energies due to relaxation of molecules in heat units. They also calculated the effective molecular diameter of units rotating under hf electric field from the Debye relation :

$$\sigma = \left( \frac{2kT}{\pi \eta} \tau_s \right)^{1/3} \quad \text{.....(2.6)}$$

which are placed in Table 2.1. The diameters are more or less of the order of the gas kinetic values for all systems. The molecular parameters needed to compute  $R'$  are shown in Table 2.2.

### 2.3. EYRING'S RATE THEORY

By considering Eyring's rate theory<sup>5</sup> it can be shown that

$$\ln(\tau_s T) = \ln A + \Delta H_{\tau_s}/RT, \quad \text{.....(2.7)}$$

which is a straight line equation of  $\ln(\tau_s T)$  with  $1/T$ . Since the solution is purely a mechanical mixture and there is no evolution or absorption of heat energy due

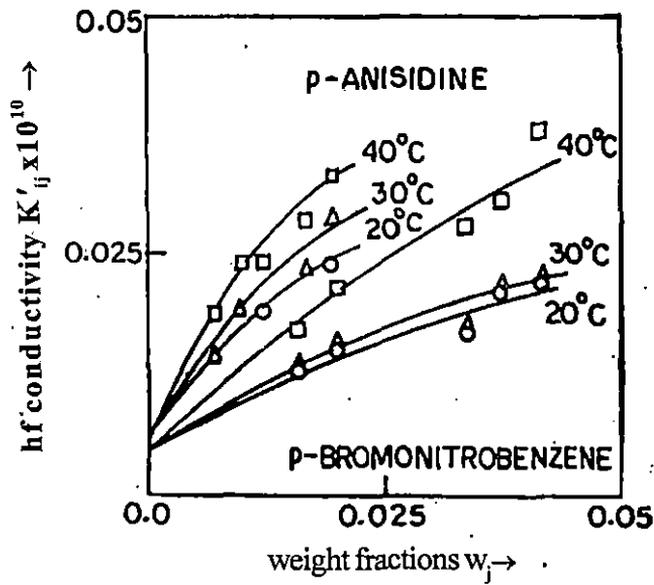


Figure 2.1. hf conductivity  $K'_{ij}$  against weight fractions  $w_j$  of solute.  
 —o—o— at 20°C, —Δ—Δ— at 30°C, —□—□— at 40°C

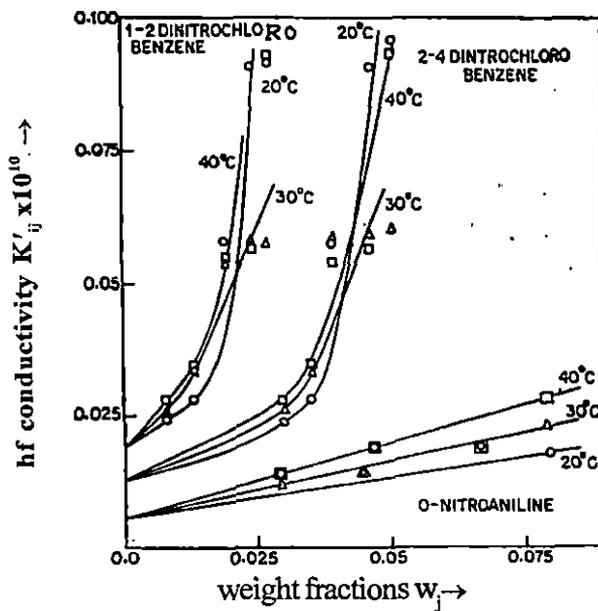


Figure 2.2. hf conductivity  $K'_{ij}$  against weight fractions  $w_j$  of solute.  
 —o—o— at 20°C, —Δ—Δ— at 30°C, —□—□— at 40°C

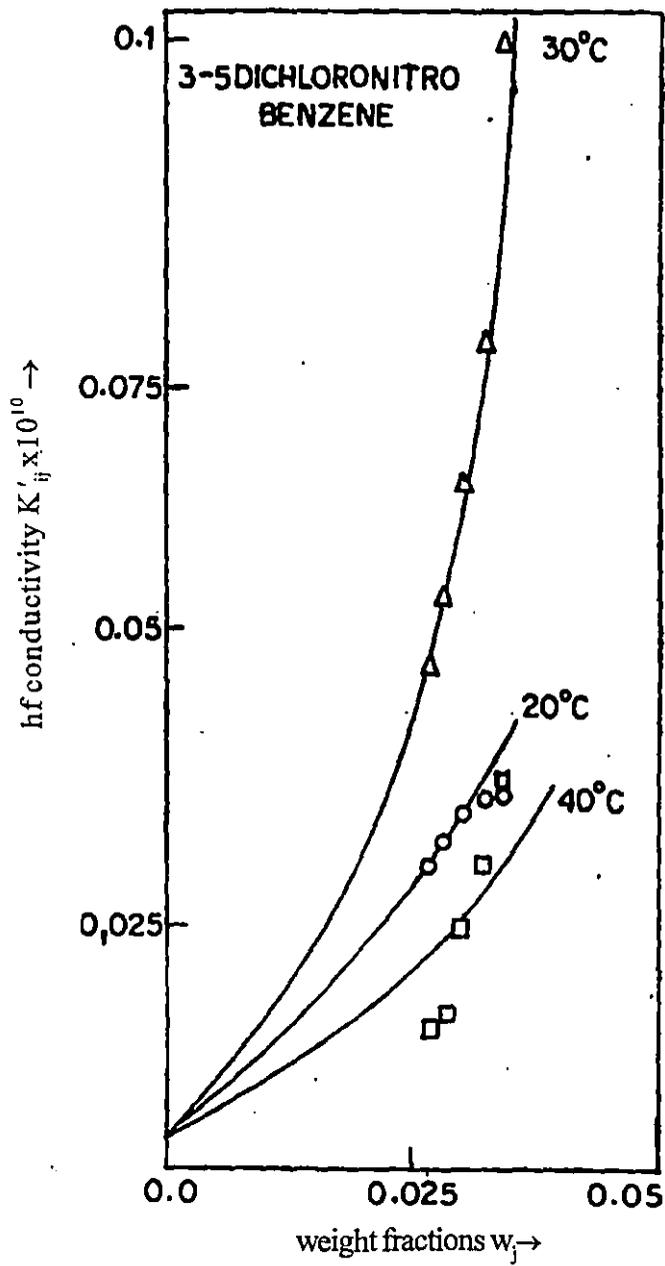
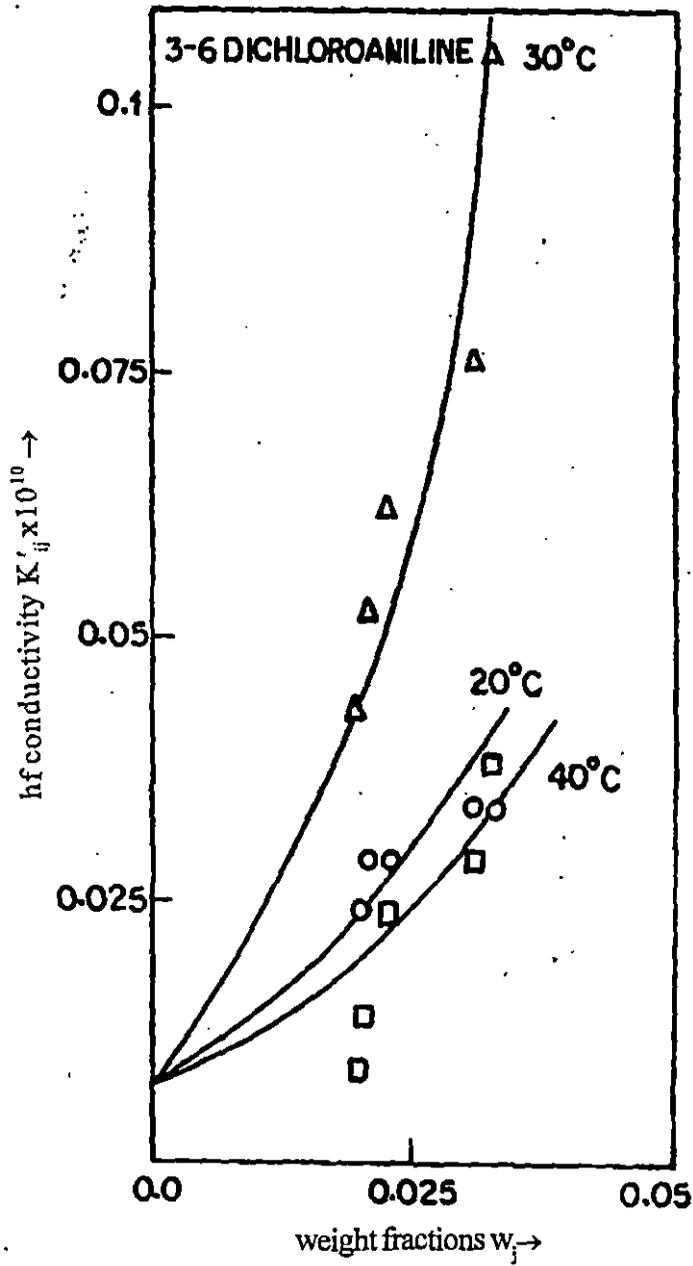


Figure 2.3. hf conductivity  $K'_{ij}$  against weight fractions  $w_j$  of solute.  
 —○—○— at 20°C, —△—△— at 30°C, —□—□— at 40°C



**Figure 2.4.** hf conductivity  $K'_{ij}$  against weight fractions  $w_j$  of solute.  
 —○—○— at 20°C, —Δ—Δ— at 30°C, —□—□— at 40°C

**Table 2.1 : Relaxation time, activation energy and radii of the rotating units at different temperatures.**

| System                     | Temp. in °C | Estimated $b = \beta/R'\omega$ values | $\tau_1$ calc in sec.   | $\tau_1 \times 10^{12}$ reported in sec. | $\sigma \times 10^9$ in cm Diameter of the unit | $E_a$ in K cal calc. | $\Delta H_a$ in K cal calc. |
|----------------------------|-------------|---------------------------------------|-------------------------|--|---|----------------------|-----------------------------|
| p-anisidine                | 20          | 1.1879                                | $6.99 \times 10^{-12}$  | 3.89                                     | 3.022   | 6.297                | 5.715                       |
|                            | 30          | 1.5268                                | $5.44 \times 10^{-12}$  | 3.67                                     | 2.950   | 6.317                |                             |
|                            | 40          | 2.3656                                | $3.51 \times 10^{-12}$  | 3.17                                     | 2.677   | 6.337                |                             |
| 3-6 dichloroaniline        | 20          | 0.7454                                | $11.14 \times 10^{-12}$ | 12.51                                    | 3.540   | 0.483                | -0.099                      |
|                            | 30          | 1.7972                                | $4.62 \times 10^{-12}$  | 11.24                                    | 2.799   | 0.503                |                             |
|                            | 40          | 0.4733                                | $11.89 \times 10^{-12}$ | 10.52                                    | 3.969   | 0.523                |                             |
| o-nitroaniline             | 20          | 0.0214                                | $23.21 \times 10^{-12}$ | 9.33                                     | 4.962   | 6.821                | 6.239                       |
|                            |             |                                       | $7.76 \times 10^{-10}$  |  | 14.524  |                      |                             |
|                            | 30          | 0.0326                                | $3.55 \times 10^{-13}$  | 8.99                                     | 1.229   | -6.859               |                             |
|                            |             |                                       | $5.08 \times 10^{-10}$  |  | 13.387  | 6.841                |                             |
|                            | 40          | 0.0433                                | $5.42 \times 10^{-13}$  | 8.28                                     | 1.368   | -6.839               |                             |
|                            |             |                                       | $3.66 \times 10^{-10}$  |  | 12.598  | 6.861                |                             |
| p-bromonitro-benzene       | 20          | 0.3364                                | $7.54 \times 10^{-12}$  | 8.28                                     | 1.603   | -6.820               |                             |
|                            |             |                                       | $4.29 \times 10^{-11}$  |  | 5.535   | 11.755               |                             |
|                            | 30          | 0.4204                                | $6.42 \times 10^{-12}$  | 7.32                                     | 2.937   | -5.679               | 11.172                      |
| 3-5 dichloronitro-benzene  | 20          | 0.6666                                | $3.04 \times 10^{-11}$  | 8.28                                     | 5.237   | 11.775               | 0.036                       |
|                            |             |                                       | $9.06 \times 10^{-12}$  |  | 3.497   | -5.659               |                             |
|                            | 40          | 0.6941                                | $11.96 \times 10^{-12}$ | 6.25                                     | 4.029   | 11.794               |                             |
| 2-4 dinitrochloro-benzene. | 20          | 0.0906                                | $6.42 \times 10^{-12}$  | 15.42                                    | 2.937   | -5.679               | 5.840                       |
|                            |             |                                       | $1.82 \times 10^{-10}$  |  | 8.953   | 6.422                |                             |
|                            | 30          | 0.1221                                | $1.52 \times 10^{-12}$  | 14.58                                    | 1.816   | -6.462               |                             |
| 1-2 dinitrochloro benzene  | 20          | 0.0751                                | $1.34 \times 10^{-10}$  | 17.53                                    | 8.582   | 6.442                | 5.461                       |
|                            |             |                                       | $2.06 \times 10^{-12}$  |  | 2.134   | -6.442               |                             |
|                            | 30          | 0.1058                                | $0.90 \times 10^{-10}$  | 13.67                                    | 7.890   | 6.462                |                             |
| 1-2 dinitrochloro benzene  | 20          | 0.0751                                | $3.07 \times 10^{-12}$  | 17.53                                    | 2.560   | -6.422               | 5.461                       |
|                            |             |                                       | $2.20 \times 10^{-10}$  |  | 9.538   | 6.043                |                             |
|                            | 30          | 0.1058                                | $1.25 \times 10^{-12}$  | 16.46                                    | 1.705   | -6.082               |                             |
| 1-2 dinitrochloro benzene  | 20          | 0.0751                                | $1.55 \times 10^{-10}$  | 17.53                                    | 9.014   | 6.063                | 5.461                       |
|                            |             |                                       | $1.78 \times 10^{-12}$  |  | 2.032   | -6.063               |                             |
|                            | 30          | 0.1058                                | $1.13 \times 10^{-10}$  | 16.46                                    | 8.516   | 6.083                |                             |
| 1-2 dinitrochloro benzene  | 40          | 0.1439                                | $1.13 \times 10^{-10}$  | 15.39                                    | 8.516   | 6.083                | -6.665                      |
|                            |             |                                       | $2.44 \times 10^{-12}$  |  | 2.372   | -6.043               |                             |

to mixing, we have  $\Delta F_{\tau} = \Delta H_{\tau}$ , where  $\Delta F_{\tau}$  and  $\Delta H_{\tau}$  are the free energy and enthalpy of activation due to relaxation respectively. The corresponding energy of activation,  $E_{\tau}$  in heat units at any temperature is also calculated from the relation<sup>6</sup>

$$E_{\tau} = \Delta H_{\tau} + RT \quad \dots\dots\dots(2.8)$$

and are listed in Table 2.1. The prescribed method for obtaining  $\tau_s$  in terms of  $\mu_j$  is a very simple one because the dielectric constant and the density of the solvent are only needed.

#### 2.4. HIGH FREQUENCY CONDUCTIVITY OF POLAR-NONPOLAR LIQUID MIXTURE

In recent years Acharyya et al<sup>7</sup>, Acharyya and Chatterjee<sup>8</sup> and Acharyya et al<sup>9</sup> showed that total hf  $K_{ij}$  of a polar-nonpolar binary liquid mixture is usually given by :

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon'_{ij}{}^2 + \epsilon''_{ij}{}^2)^{1/2} \quad \dots\dots\dots (2.9)$$

where  $\epsilon'_{ij}$  and  $\epsilon''_{ij}$  are the real and the imaginary parts of the complex dielectric constant  $\epsilon^*_{ij}$  of a solution. In the electric field of microwave region  $\epsilon'_{ij}$  of a solution is usually very small and often equals to optical dielectric constant of the solution, but still  $\epsilon'_{ij} \gg \epsilon''_{ij}$ , where  $\epsilon''_{ij}$  is responsible for the absorption of electrical energy by the dielectric medium to offer resistance to polarisation. Hence the real part  $K'_{ij}$  of the complex hf conductivity  $K^*_{ij}$  of solution of  $w_j$  of a polar solute at TK is

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT} \left( \frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \right) w_j$$

which is similar to eq. (2.1). Since for the hf region of the electric field, the total conductivity becomes  $K_{ij} = (\omega/4\pi) \epsilon'_{ij}$  ..... (2.10)

It can also be shown that  $\epsilon'_{ij} = \epsilon_{ij\infty} + \epsilon''_{ij}/\omega\tau_s$

$$\text{or, } \frac{\omega}{4\pi} \epsilon'_{ij} = \frac{\omega}{4\pi} \epsilon_{ij\infty} + \frac{\omega}{4\pi} \epsilon''_{ij}/\omega\tau_s \quad \dots\dots\dots(2.11)$$

The above eq. (2.11) could, however, be written as

$$K''_{ij} = K_{\infty ij} + K'_{ij} / \omega\tau_s \quad \dots\dots\dots (2.12)$$

The eq. (2.12) was used to estimate  $\tau_s$  of a polar unit by Murthy et al<sup>10</sup>, Acharyya et al<sup>11</sup>) and Acharyya and Chartterjee<sup>8</sup>. In the low concentration, since the Debye's relation is valid, the variation of  $K''_{ij}$  and  $K'_{ij}$  with  $w_j$  will be linear<sup>11</sup>.

Using the value of  $\tau_s$  and the slope of  $K_{ij}$  against  $w_j$  curve the value of  $\mu_j$  can be determined. Now, in eq. (2.11) or (2.12),  $K_{ij\infty}$  is a constant conductivity and  $\tau_s$  is the relaxation time of a polar liquid in a given solvent. Since  $K_{ij}$  or  $K''_{ij}$  is a function of  $w_j$  we have from eq. (2.11).

$$\left(\frac{dK'_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \omega\tau_s \left(\frac{dK_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \omega\tau_s\beta \quad \dots\dots\dots(2.13)$$

where  $\beta$  is the slope of  $K_{ij}$ -  $w_j$  curve at  $w_j \rightarrow 0$ . Comparing eq. (2.13) with eq.(2.2) we can have

$$b = \beta / \left( \frac{\mu_j^2 N \rho_i F_i \omega}{3M_j kT} \right)$$

$$\text{or } \mu_j = \left( \frac{27M_j kT}{N \rho_i (\epsilon_i + 2)^2} \cdot \frac{\beta}{b\omega} \right)^{1/2} \quad \dots\dots\dots(2.14)$$

as a required formula to evaluate  $\mu_j$  of a single polar molecule dissolved in a non-polar solvent, provided the value of  $b$  is estimated from the relation :

$$b = \frac{1}{1 + \omega^2 \tau_s^2} \quad \dots\dots\dots(2.15)$$

in terms of the reported or predetermined  $\tau_s$

With the help of the theories as mentioned above a few systems were already studied and shown graphically in Figs. 2.5 to 2.6 for  $K_{ij}$  against  $w_j$ . Similar studies were also made in high concentration regions and shown graphically in Figs. 2.7 to 2.8 for  $K_{ij}$  against  $w_j$ . The results of the studies were presented in tabular form in Tables 2.3 and 2.4 respectively in the lower as well as in the higher concentrations.

When the measurements on  $K_{ij}$  of polar-nonpolar liquid mixtures are made in the high concentration regions of particularly aromatic polar compounds as solutes all  $K_{ij}$ 's have a tendency to meet at a common point on  $K_{ij}$ -axis at  $w_j \rightarrow 0$ . These are illustrated graphically in Fig. 2.5 to 2.7 for  $K_{ij}$  against  $w_j$  for the systems namely 2-5 dichloronitrobenzene, 3-nitro-o-anisidine, 2-chloro-p-nitroaniline, (Fig. 2.5) p-phenitidine, 2-5 dibromonitrobenzene, o-nitroaniline (Fig.2.6). The temperature variation of dipole moments  $\mu$ 's of seven systems as mentioned above is shown in Fig. 2.9.

## 2.5. DOUBLE RELAXATION PHENOMENON

Under hf electric field a polar solute dissolved in nonpolar solvent may exhibit double relaxation phenomena by showing  $\tau_2$  and  $\tau_1$  due to end-over-end rotation and the rotation of the flexible part of the molecule. Assuming a molecule possessing two discrete relaxation times  $\tau_2$  and  $\tau_1$ , the Bergmann equation<sup>12)</sup> can, however, be written as

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \dots\dots\dots(2.16)$$

and

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots\dots\dots(2.17)$$

where  $c_1$  and  $c_2$  are the relative contributions towards dielectric dispersions due to  $\tau_1$  and  $\tau_2$  such that  $c_1 + c_2 = 1$ .

**Table 2.2 : Molecular parameters needed to compute R'**

| System                    | Molecular weight $M_r$ | Dipole moment in Debye | Reference |
|---------------------------|------------------------|------------------------|-----------|
| p-anisidine               | 123                    | 1.87                   | a         |
| 3-6 dichloroaniline       | 161                    | 1.69                   | a         |
| o-nitroaniline            | 138                    | 4.25                   | a         |
| p-bromonitro-benzene      | 202                    | 2.40                   | b         |
| 3-5 dichloronitro-benzene | 192                    | 2.20                   | b         |
| 2-4 dinitrochloro-benzene | 192                    | 3.39                   | b         |
| 1-2 dinitrochloro-benzene | 192                    | 5.35                   | b         |

a Somevanshi *et al* (1978)

b Calculated from the vector model assuming the molecules to be planar.

**Table 2.3 : Computed dipole moment  $\mu_{j\text{compt}}$ , rept. dipole moment  $\mu_{j\text{rept}}$ , relaxation times  $\tau_s$  and b at temperatures : 20<sup>o</sup>, 30<sup>o</sup> and 40<sup>o</sup>C.**

| System                       | Temp. C | b compt. | $\tau_s \times 10^{12}$ rept in sec. | $\mu_{j\text{compt}}$ in D | $\mu_{j\text{rept}}$ in D | $\mu_{j\text{theo}}$ in D |
|------------------------------|---------|----------|--------------------------------------|----------------------------|---------------------------|---------------------------|
| (i) 2-5 dichloronitrobenzene | 20      | 0.6620   | 11.87**                              | 3.29                       |                           | 4.23***                   |
|                              | 30      | 0.7060   | 10.72                                | 3.48                       |                           |                           |
|                              | 40      | 0.7477   | 9.65                                 | 3.77                       |                           |                           |
| (ii) 2-5 dibromonitrobenzene | 20      | 0.3736   | 21.51**                              | 5.72                       |                           | 4.23***                   |
|                              | 30      | 0.4090   | 19.97                                | 5.93                       |                           |                           |
|                              | 40      | 0.4369   | 18.86                                | 6.11                       |                           |                           |
| (iii) 3-nitro-o-anisidine    | 20      | 0.6165   | 13.27*                               | 3.93                       | 2.76                      | 4.93***                   |
|                              | 30      | 0.6793   | 11.56                                | 5.88                       | 3.11                      |                           |
|                              | 40      | 0.7282   | 10.28                                | 8.53                       | 3.76                      |                           |
| (iv) 2-chloro p-nitroaniline | 20      | 0.7170   | 10.57*                               | 2.13                       | 2.44                      | 2.39***                   |
|                              | 30      | 0.7432   | 9.89                                 | 2.72                       | 3.28                      |                           |
|                              | 40      | 0.7706   | 9.18                                 | 3.07                       | 3.93                      |                           |
| (v) p-phenetidine            | 20      | 0.6975   | 11.08*                               | 2.82                       | 2.24                      | 1.53***                   |
|                              | 30      | 0.7147   | 10.63                                | 3.09                       | 2.78                      |                           |
|                              | 40      | 0.7409   | 9.95                                 | 3.22                       | 3.14                      |                           |
| (vi) o-nitroaniline          | 20      | 0.7648   | 9.33*                                | 2.02                       | 3.95                      | 4.25***                   |
|                              | 30      | 0.7779   | 8.99                                 | 2.38                       | 2.19                      |                           |
|                              | 40      | 0.8050   | 8.28                                 | 2.68                       | 2.24                      |                           |
| (vii) p-anisidine            | 20      | 0.9493   | 3.89**                               | 1.81                       | 1.56                      | 1.87***                   |
|                              | 30      | 0.9546   | 3.67                                 | 2.54                       | 3.10                      |                           |
|                              | 40      | 0.9657   | 3.17                                 | 2.67                       | 2.66                      |                           |

\* Somevanshi *et al* (1978)

\*\* Pant *et al* (1977)

\*\*\* Calculated from the vector model assuming molecule to be planar.

**Table 2.4 :** Values of  $(\mu_j)_{\text{comput}}$ ,  $(\mu_j)_{\text{rept}}$ ,  $(\mu_j)_{\text{theo}}$ ,  $(\tau_s)_{\text{rept}}$  and  $b(\text{compute})$  at different temperatures.

| System  | Temp. C | b (compt) | $\tau \times 10^{12}$ rept in sec. | $\mu_j$ compt. in D | $\mu_j$ corr in D | $(\mu_j)_\lambda$ D | $(\mu_j)_\lambda$ rept. in D |
|---|---------|-----------|------------------------------------|---------------------|-------------------|---------------------|------------------------------|
| n-methyl acetamide in benzene                       | 25      | 0.6334    | 12.13                              | 3.882               | 4.135             | 4.30                | 3.69                         |
|   | 35      | 0.7068    | 10.27                              | 4.008               | 4.262             |                     | 3.78                         |
|   | 45      | 0.7637    | 8.87                               | 4.064               | 4.313             |                     | 3.80                         |
|   | 55      | 0.8065    | 7.81                               | 4.216               | 4.467             |                     | 3.82                         |
| n-methyl acetamide in dioxane                       | 25      | 0.7185    | 9.88                               | 3.647               | 3.862             |                     | 3.66                         |
|   | 35      | 0.7824    | 8.41                               | 3.886               | 4.109             |                     | 3.69                         |
|   | 45      | 0.8252    | 7.34                               | 3.830               | 4.043             |                     | 3.78                         |
|   | 55      | 0.8631    | 6.35                               | 3.907               | 4.117             |                     | 3.83                         |
| n-methyl acetamide in benzene in high concentration | 25      | 0.6987    | 10.47                              | 2.236               | 2.383             | 2.48                | 1.87                         |
| p-bromonitrobenzene in benzene                      | 20      | 0.7905    | 8.21                               | 3.456               | 3.687             | 3.658               |                              |
|   | 30      | 0.8259    | 7.32                               | 4.013               | 4.272             |                     |                              |
|   | 40      | 0.8657    | 6.28                               | 4.494               | 4.774             |                     |                              |

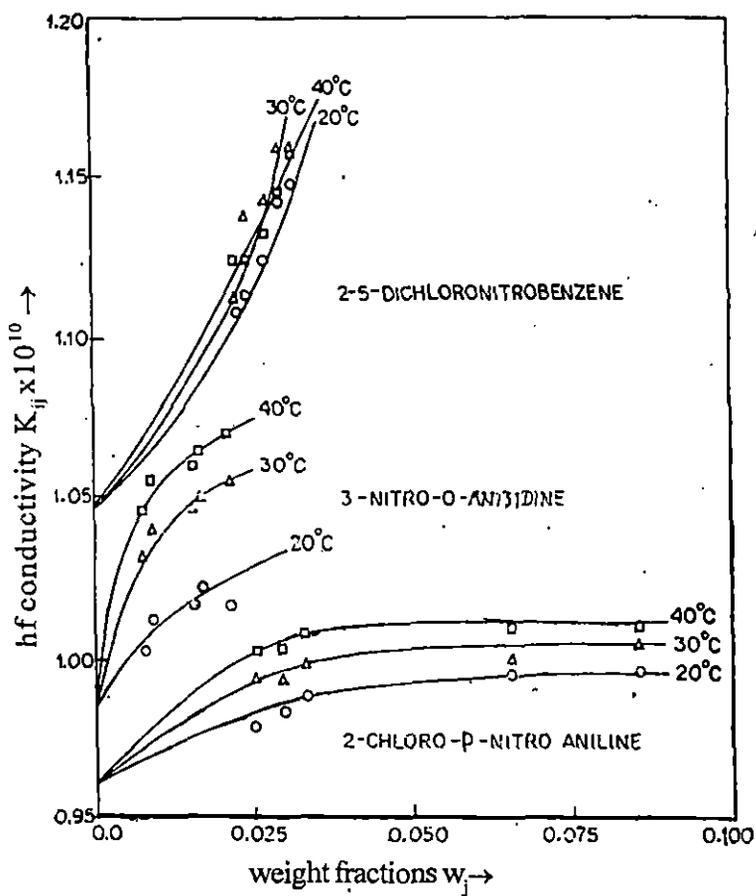


Figure 2.5. hf conductivity  $K_{ij}$  against weight fractions  $w_j$  of solute  
 —○—○— at 20°C, —△—△— at 30°C, —□—□— at 40°C

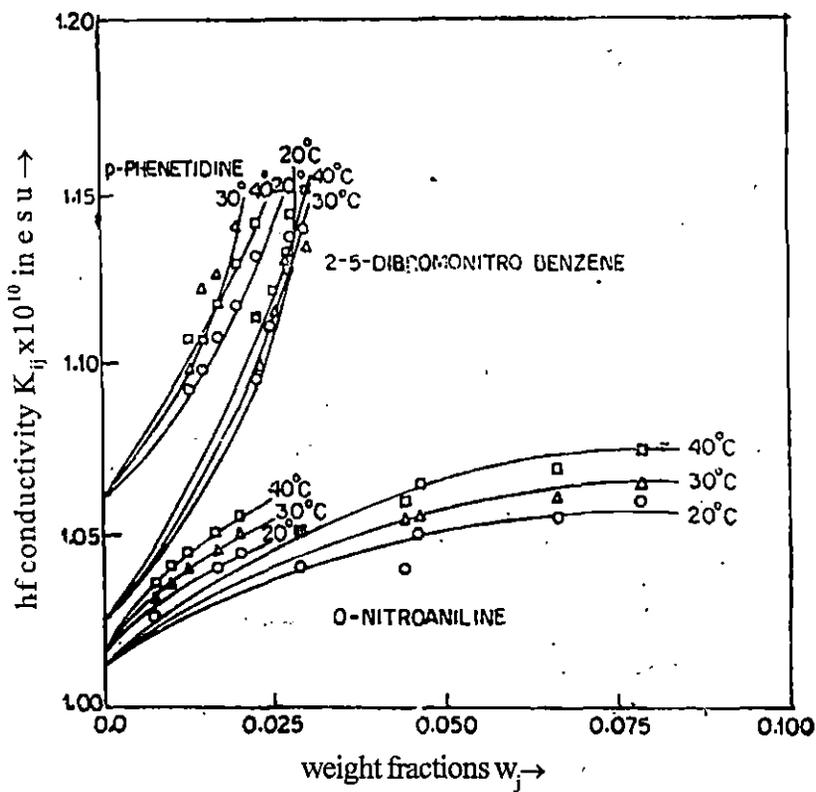


Figure 2.6. hf conductivity  $K_{ij}$  against weight fractions  $w_j$  of solute  
 —○—○— at 20°C, —△—△— at 30°C, —□—□— at 40°C

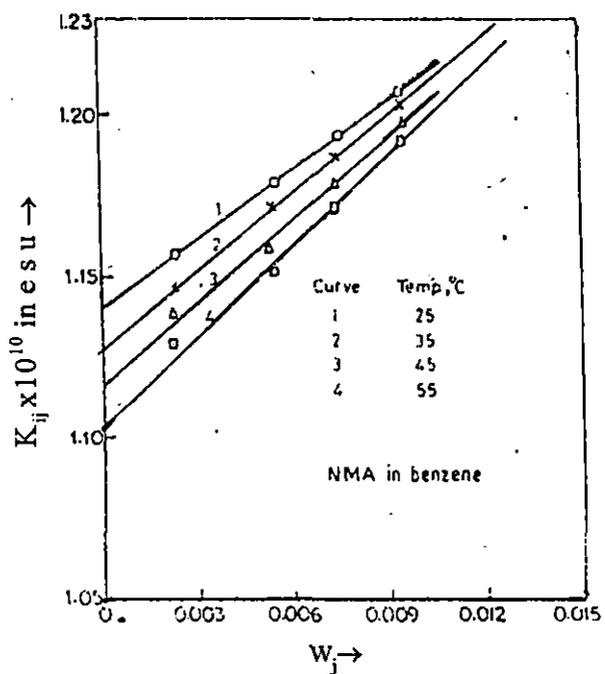
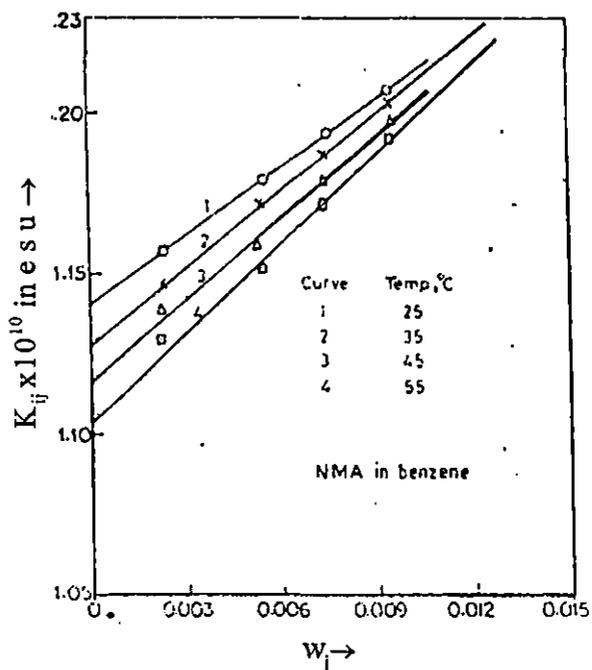


Figure 2.7. Concentration variation of  $K_{ij}$  of NMA in benzene and in dioxane at different temperatures.

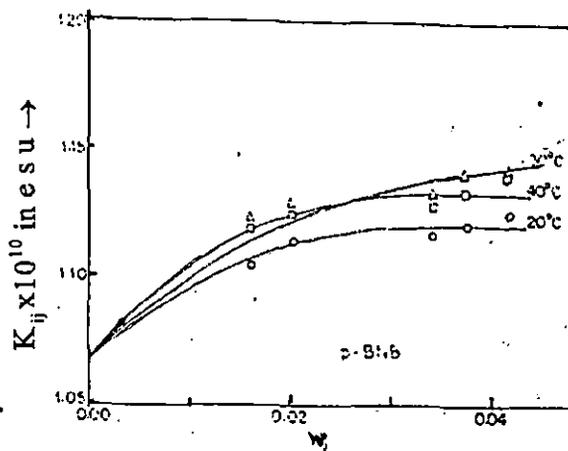
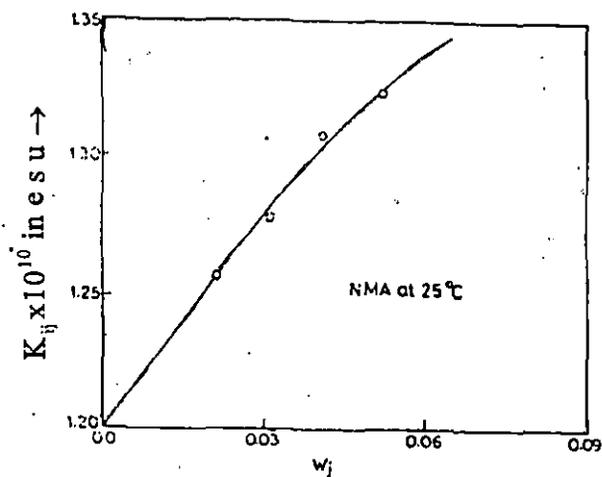
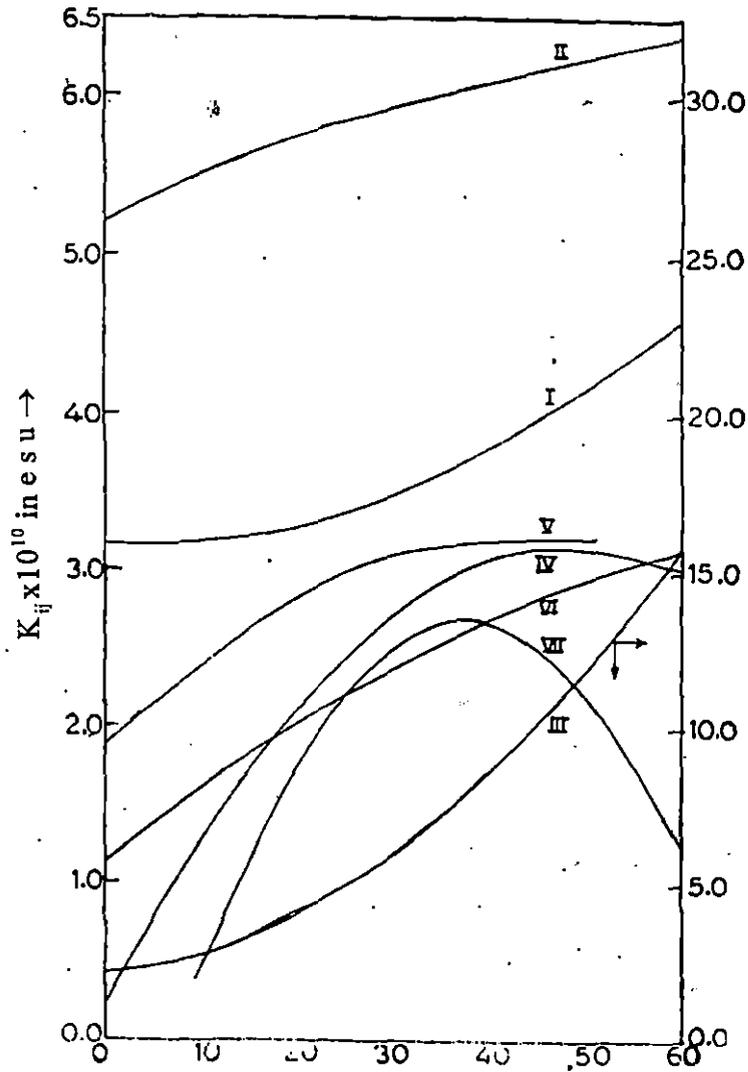


Figure 2.8. Concentration variation of  $K_{ij}$  of NMA in benzene at 25°C and p-BNB in benzene at different temperatures.



**Figure 2.9.** Dipole moments  $\mu_j$  (computed) of seven polar liquids are plotted against temperature in  $^{\circ}\text{C}$ .  
 For system III :  $\mu_j$  (0 – 15D) is shown on the right side of the graph while for other six systems :  $\mu_j$  (0 – 6.5D) on the left side of the graph.

Substituting  $(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{oij} - \epsilon_{\infty ij}) = x$ ,  $\epsilon''_{ij} / (\epsilon_{oij} - \epsilon_{\infty ij}) = y$ ,  $\omega\tau_1 = \alpha_1$  and  $\omega\tau_2 = \alpha_2$  in eqs. (2.16) and (2.17) one gets

$$x = c_1 a_1 + c_2 a_2 \quad \dots\dots\dots (2.18)$$

$$y = c_1 b_1 + c_2 b_2 \quad \dots\dots\dots (2.19)$$

where  $a = 1/(1+\alpha^2)$  and  $b = \alpha/(1+\alpha^2)$  and suffices 1 and 2 with  $a$  and  $b$  are related to  $\tau_1$  and  $\tau_2$  respectively. Solving eqs. (2.18) and (2.19) for  $c_1$  and  $c_2$  one can write :

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots\dots\dots (2.20)$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots\dots\dots (2.21)$$

provided  $\alpha_2 \neq \alpha_1$  and  $\alpha_2 > \alpha_1$ .

The eqs. (2.20) and (2.21) when are added in order to get after simplification

$$\frac{\epsilon_{oij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2\tau_1\tau_2 \quad \dots\dots\dots(2.22)$$

as a simple straight line equation (eq. 2.22) having intercept  $-\omega^2\tau_1\tau_2$  and slope  $\omega(\tau_1 + \tau_2)$ , where  $\omega (=2\pi f)$  is the angular frequency of electric field of frequency  $f$  in GHz range. The slopes and intercepts are, however, obtained by least square fitting the measured relaxation parameters like  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  at different  $\omega_s$ 's of a polar solute. The relaxation times  $\tau_1$  and  $\tau_2$  are obtained from the estimated slopes and intercepts respectively of eq. (2.22).

The relative contributions  $c_1$  and  $c_2$  towards dielectric dispersions due to  $\tau_1$  and  $\tau_2$  are estimated from the  $x$  and  $y$  of Fröhlich's method<sup>13</sup> as :

$$x = \frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{oij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left( \frac{e^{2A} \omega^2 \tau_s^2 + 1}{1 + \omega^2 \tau_s^2} \right) \quad \dots\dots\dots (2.23)$$

$$y = \frac{\epsilon''_{ij}}{\epsilon_{oij} - \epsilon_{\infty ij}} = \frac{1}{A} [\tan^{-1}(e^A \omega \tau_s) - \tan^{-1}(\omega \tau_s)] \quad \dots\dots\dots (2.24)$$

where  $\tau_s$  = small limiting relaxation time =  $\tau_1$  and  $A$  = Fröhlich parameter =  $\ln(\tau_2/\tau_1)$ . Substituting the values of  $x$  and  $y$  in eq. (2.20) and (2.21) from the measured  $\tau_1$  and  $\tau_2$  one may get the theoretical values of  $c_1$  and  $c_2$ .

The experimental values of  $c_1$  and  $c_2$  can again, be obtained from the graphical method. It consists of plotting the measured values of  $x$  and  $y$  against  $w_j$  in order to get the values at infinite dilution i.e., at  $w_j \rightarrow 0$ . The variation of  $x = (\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{oij} - \epsilon_{\infty ij})$  and  $y = \epsilon''_{ij} / (\epsilon_{oij} - \epsilon_{\infty ij})$  with different  $w_j$ 's of polar solute are usually concave and convex for a number of disubstituted benzenes and anilines.

The method seems to be superior in comparison to other existing methods because the data of polar-nonpolar liquid mixture at a single frequency is enough to predict the double relaxation mechanism.

The technique so far developed is tested on a number of non spherical polar liquids dissolved in nonpolar solvents under different hf electric fields. This has been elaborately discussed in Chapter 5 and 6.

## 2.6. DIELECTRIC RELAXATION IN S.I. UNIT

It is better to express the dielectric relaxation parameters in terms of dimensionless dielectric constants like  $k'_{ij}$  and imaginary  $k''_{ij}$  parts of complex dielectric constant  $k^*_{ij}$ .  $k_{oij}$  and  $k_{\infty ij}$  are the static and infinite frequency dielectric constant in S.I. unit,

where  $k'_{ij} (= \epsilon'_{ij} / \epsilon_o)$ ,  $k''_{ij} (= \epsilon''_{ij} / \epsilon_o)$ ,  $k_{oij} (= \epsilon_{oij} / \epsilon_o)$  and  $k_{\infty ij} (= \epsilon_{\infty ij} / \epsilon_o)$ .

where  $\epsilon_o$  = permittivity of free space =  $8.854 \times 10^{-12}$  F.m<sup>-1</sup>. The expression of any physical equation in S.I. unit is widely accepted because of its unified, rationalised and coherent nature.

## 2.7. STATIC DIPOLE MOMENT $\mu_s$ IN S.I. UNIT

Under static or low frequency electric field  $\mu_s$  of a polar liquid (j) in a non-polar solvent (i) may be written from Debye's equation<sup>13</sup> as :

$$\frac{(\epsilon_o k_{oj} - 1)}{(\epsilon_o k_{oj} + 2)} - \frac{(\epsilon_o k_{\infty j} - 1)}{(\epsilon_o k_{\infty j} + 2)}$$

$$= \frac{(\epsilon_o k_{oi} - 1)}{(\epsilon_o k_{oi} + 2)} - \frac{(\epsilon_o k_{\infty i} - 1)}{(\epsilon_o k_{\infty i} + 2)} + \frac{N\mu_s^2}{3\epsilon_o k_B T} c_j \quad \dots\dots\dots (2.25)$$

where  $c_j$  is the molar concentration of the solute and is given by  $c_j = \rho_j w_j / M_j$  and other symbols carry usual meanings<sup>14</sup>. Again,  $\rho_j$  as defined in the section 1.6 of Chapter -1, is

$$\rho_j = \rho_i (1 - \gamma w_j)^{-1} \quad \dots\dots\dots (2.26)$$

where  $w_j$  is weight fraction of solute dissolved in a solvent liquid. The eq. (2.25) after simplification becomes :

$$\frac{(k_{oj} - k_{\infty j})}{(\epsilon_o k_{oj} + 2)(\epsilon_o k_{\infty j} + 2)} = \frac{(k_{oi} - k_{\infty i})}{(\epsilon_o k_{oi} + 2)(\epsilon_o k_{\infty i} + 2)} + \frac{N\rho_i \mu_s^2}{9\epsilon_o^2 M_j k_B T} w_j (1 - \gamma w_j)^{-1}$$

$$X_{ij} = X_i + \frac{N\rho_i \mu_s^2}{9\epsilon_o^2 M_j k_B T} w_j + \frac{N\rho_i \mu_s^2}{9\epsilon_o^2 M_j k_B T} \gamma w_j^2 + \quad \dots\dots\dots (2.27)$$

where  $X_{ij}$  and  $X_i$ 's carry usual significance.

The L.H.S. of eq. (2.27) is a function of  $\epsilon_{\infty j}$  and  $\epsilon_{oj}$  and depends on  $w_j$  of a polar solute. Hence one can write

$$X_{ij} = a_o + a_1 w_j + a_2 w_j^2 + \quad \dots\dots\dots (2.28)$$

The above equation is often found to be parabolic in nature. Equating the linear

coefficients of  $w_j$  of eqs. (2.27) and (2.28) one gets static  $\mu_s$  in S.I. unit by

$$\mu_s = \left( \frac{9\epsilon_0^2 M_j k_B T}{N\rho_i} a_i \right)^{1/2} \dots\dots\dots (2.29)$$

## 2.8. MESOMERIC AND INDUCTIVE MOMENTS

It is a common observation that the estimated static and hf dipole moments do not tally with the theoretical dipole moment  $\mu_{theo}$  from available bond angles and bond moments. This is probably due to the fact that mesomeric and inductive moments are playing a vital role. These moments come into existence in the substituent polar groups of the solute molecule due to their difference in electron affinity which act as pusher or puller. This type of property arises out of aromaticity of the polar molecule. As a result, the bond moments are reduced by a factor  $\mu_{obs} / \mu_{theo}$  to get the actual dipole moment of the polar molecule. The fact is observed in different temperatures too<sup>15</sup>.

## 2.9. HF DIPOLE MOMENT $\mu_j$ IN S.I. UNIT

Murphy - Morgan<sup>16</sup> relation for hf complex conductivity  $\sigma^*_{ij}$  of solution of  $w_j$  is given by

$$\sigma^*_{ij} = \omega \epsilon_0 k''_{ij} + j\omega \epsilon_0 k'_{ij} \dots\dots\dots (2.30)$$

where  $\sigma'_{ij} = \omega \epsilon_0 k''_{ij}$  and  $\sigma''_{ij} = \omega \epsilon_0 k'_{ij}$  are real and imaginary parts of conductivity. Again, total conductivity  $\sigma_{ij}$  is given by

$$\sigma_{ij} = \omega \epsilon_0 \sqrt{k''_{ij}{}^2 + k'_{ij}{}^2} \dots\dots\dots (2.31)$$

The imaginary part of the hf conductivity  $\sigma''_{ij}$  is written as

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

$$\text{or } \left( \frac{d\sigma''_{ij}}{d\sigma'_{ij}} \right) = \frac{1}{\omega\tau} \dots\dots\dots (2.32)$$

In the hf region  $\sigma''_{ij} \simeq \sigma_{ij}$ , so eq. (2.32) yields :

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

or,  $\beta = \frac{1}{\omega\tau} \left( \frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0}$  ..... (2.33)

The real part of conductivity  $\sigma'_{ij}$  at TK is given by

$$\sigma'_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_o k_B TM_j} \left( \frac{\omega^2\tau}{1+\omega^2\tau^2} \right) (\epsilon_o k_{oij} + 2) (\epsilon_o k_{\infty ij} + 2) w_j$$
 .....(2.34)

Differentiation of the above equation with respect to  $w_j$  and at  $w_j \rightarrow 0$  yields

$$\left( \frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{3\epsilon_o k_B TM_j} \left( \frac{\epsilon_i + 2}{3} \right)^2 \left( \frac{\omega^2\tau}{1+\omega^2\tau^2} \right)$$
 .....(2.35)

The symbols used in above eq. (2.35) are of usual meanings.

From eq. (2.33) and (2.35) we get

$$\mu_j = \left( \frac{27\epsilon_o k_B TM_j}{N\rho_{ij}(\epsilon_i + 2)^2} \cdot \frac{\beta}{\omega b} \right)^{1/2}$$
 .....(2.36)

## 2.10. DOUBLE RELAXATION PHENOMENON IN S.I. UNIT

Bergmann's equation for a polar-nonpolar liquid mixture possessing two separate Debye-type dispersions at a fixed angular frequency  $\omega$  is written as<sup>17</sup>

$$\frac{k'_{ij} - k_{\infty ij}}{k_{oij} - k_{\infty ij}} = \frac{c_1}{1 + \omega^2\tau_1^2} + \frac{c_2}{1 + \omega^2\tau_2^2}$$

$$\frac{k''_{ij}}{k_{oij} - k_{\infty ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2}$$
 .....(2.37)

where  $c_1$  and  $c_2$  are the relative weight factors of dielectric dispersion due to  $\tau_1$  and  $\tau_2$  such that  $c_1 + c_2 = 1$ .

Solving eq. (2.37) for  $c_1$  and  $c_2$  after simplification yields :

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \dots\dots\dots(2.38)$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \dots\dots\dots(2.39)$$

where the significance of all the symbols have been mentioned in eq.(2.20) and (2.21). Now using the condition  $c_1 + c_2 = 1$ ; one gets,

$$\frac{k_{oij} - k'_{ij}}{k'_{ij} - k_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{k''_{ij}}{k'_{ij} - k_{\infty ij}} - \omega^2 \tau_1 \tau_2 \dots\dots\dots(2.40)$$

From slope  $\omega(\tau_1 + \tau_2)$  and intercept  $-\omega^2 \tau_1 \tau_2$  of the above straight line equation one may get  $\tau_1$  and  $\tau_2$ .

The relative contributions  $c_1$  and  $c_2$  can be had in S.I. unit from

$$\frac{k'_{ij} - k_{\infty ij}}{k_{oij} - k_{\infty ij}} = 1 - \frac{1}{2A} \ln \left( \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \dots\dots\dots(2.41)$$

$$\frac{k''_{ij}}{k_{oij} - k_{\infty ij}} = \frac{1}{A} [\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)] \dots\dots\dots(2.42)$$

The L.H.S. of the above equations are functions of  $\omega\tau_j$ . The usual variations of the curves of eq.(2.41) and (2.42) are presented in chapters 5 and 6.

## PART B : EXPERIMENTAL PART

### 2.11. RADIO FREQUENCY MEASUREMENT

The principle used in the experimental arrangement is the resonance method of measuring the dielectric constants of some experimental liquids <sup>18-21</sup> under the radio frequency (rf) electric field. The block diagram of the experimental arrangement is shown by a simple network circuit of Fig. 2.10 (a). The dielectric cell used is a cylindrical glass tube having an extended but narrow inlet closed by a piece of cork. It is fitted with two circular metal electrodes each of diameter 0.015 metre and separated by a distance of 0.01 metre. All of these are presented in Fig. 2.11 (a) and (2.11(b)). The cell is connected in parallel to a tuning condenser as shown in Fig. 2.11 - (a).

The expression of the equivalent impedances for parallel and series combinations in the circuit (Fig. 2.10(b) and 2.10 (c) are given by :

$$Z_p = \frac{R}{1+j\omega CR} \dots\dots\dots(2.43)$$

and

$$Z_p = R' + \frac{1}{1+j\omega CR'} \dots\dots\dots(2.44)$$

respectively, where  $j$  is a complex number  $= \sqrt{-1}$ . From eqs. (2.43) and (2.44) and considering only real parts one gets

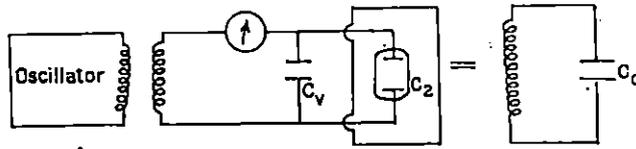
$$R' = \frac{R}{1+\omega^2 C^2 R^2} \dots\dots\dots(2.45)$$

Further, the resonant current  $I_o$  without glass cell is

$$I_o = E/R_o \dots\dots\dots(2.46)$$

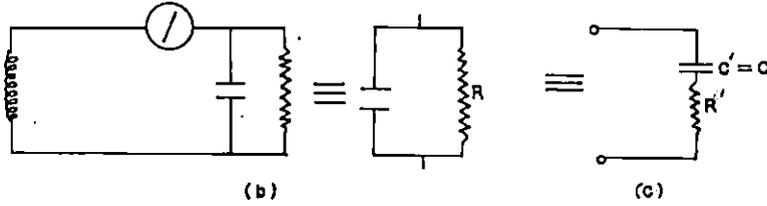
where  $R_o$  is the rf resistance of the secondary tuning circuit. At resonance condition  $R_o$  is :

$$R_o = \frac{C_2 - C_1}{2\omega C_1 C_2} \sqrt{\frac{I_1^2}{I_o^2 - I_1^2}} \dots\dots\dots(2.47)$$



(d)

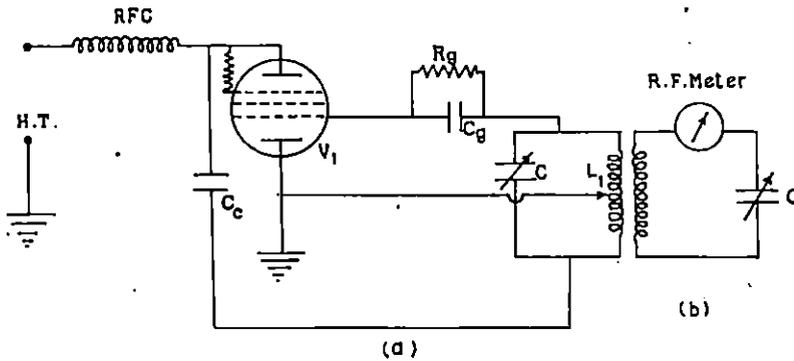
Fig. 2-10 (d). Circuit arrangement.



(b)

(c)

Fig. 2-10(b)&(c). Equivalent circuits.



(a)

(b)

Fig. 2-11(a). Radio frequency oscillator .

Fig. 2-11(b).Secondary tuning circuit .

**List of components**

$V_2 = 6L6$

$R_g = 30 \text{ K}\Omega$

$C_g = 350 \text{ pF}$

$C = 0 - 500 \text{ pF}$

$C_c = 0.01 \text{ }\mu\text{F}$

RFC = Radio frequency Choke

R.F. Meter - Radio frequency milliammeter (0-300mA)

where  $I_1$  is the resonant current with empty cell,  $C_1$  and  $C_2$  are the capacities for reducing the resonant current  $I_0$  by  $\frac{1}{\sqrt{2}}$ . The capacitance of the dielectric cell used in the experiment were measured with the help of a LCR bridge (Model No. VLCR.7, Basabi Electronics; Digital LCR Meter).

Again, when the cell is filled with the dielectric liquid, the resonant current becomes  $I_2$  where

$$I_2 = E / (R_0 + R')$$

$$\text{or, } I_2 = \frac{E}{R_0 + \frac{R}{1 + \omega^2 C^2 R^2}} \quad \dots\dots\dots (2.48)$$

Putting  $I_1 / I_2 = \alpha$ , from eqs. (2.46) and (2.48) the rf resistance becomes

$$R = \frac{1 \pm \sqrt{1 - 4R_0^2 (\alpha - 1)^2 \omega^2 C^2}}{2R_0 (\alpha - 1) \omega^2 C^2} \quad \dots\dots\dots (2.49)$$

In the present experimental arrangement, since  $4R_0^2 (\alpha - 1)^2 \omega^2 C^2 \ll 1$ , rf resistance of the dielectric liquid from eq. (2.48) can be written as :

$$R = \frac{1}{R_0 \omega^2 C^2 (\alpha - 1)} \quad \dots\dots\dots (2.50)$$

We know that resistance  $R$  is directly proportional to  $L$  and inversly proportional to  $S$ , where  $L$  is the distance between the electrodes and  $S$  is the cross sectional area of the electrodes,  $\rho$  is the specific resistance i.e.

$$R = \rho L / S \quad \dots\dots\dots (2.51)$$

If  $K'$  is the rf conductivity of the dielectric liquid, we have

$$K' = 1 / \rho = L / SR \quad \dots\dots\dots (2.52)$$

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

$$C_0 = S / 4 \pi L \quad \dots\dots\dots (2.53)$$

Therefore, the rf conductivity can be expressed as

$$K' = 1/4\pi RC_0 \dots\dots\dots(2.54)$$

The eq. (2.54) is a formula for measuring the rf conductivity of the dielectric liquid under investigation.

## 2.12. WASHING AND CLEANING OF THE DIELECTRIC CELL

The dielectric cell used was a cylindrical glass tube fitted with two circular electrodes separated by a distance 0.01 metre. Initially the glass cell, tube and glass wares were thoroughly washed with dilute chromic acid and then with NaOH solution. After washing several times with distilled water, the washed glass wares and instruments were kept inside the thermostat for some hours in order to remove the traces of water. The dried glass instruments and wares were again washed with dehydrated pure benzene and then dried for use.

## 2.13. PURIFICATION OF EXPERIMENTAL LIQUIDS

The purity of dielectric liquids is very important factor for the study of their molecular behaviour and structure under hf electric field. Analer grade pure quality liquids were usually collected from reputed manufacturing companies viz. E. Mark, British Drug House (BDH), etc. for use. The liquids were distilled in vacuum and put in a decicator before it was finally used in the dielectric cell.

## 2.14. DETERMINATION OF COEFFICIENT OF VISCOSITY

The coefficient of viscosity of liquids at different temperatures were measured with the help of Ostwald's Viscometer. The viscosity  $\eta_1$  of the liquid at a desired temperature was calculated from the relation:

$$\frac{\eta_1}{\eta_2} = \frac{\pi P_1 r^4 t_1}{8LV} \times \frac{8LV}{\pi P_2 r^4 t_2} = \frac{P_1 t_1}{P_2 t_2}$$

Since pressure  $P_1$  and  $P_2$  are proportional to the densities  $\rho_1$  and  $\rho_2$  of the experimental liquid and water it is written as

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

or,  $\eta_1 = \eta_2 \frac{\rho_1 t_1}{\rho_2 t_2}$  ..... (2.55)

where  $\eta_2$  was the coefficient of viscosity of standard liquid (water). The time of fall  $t_1$  and  $t_2$  of the experimental liquids or liquid mixtures and the standard liquid (water) were conveniently measured with a high precision-type stop-watch at the desired temperature.

A few systems of binary liquids were used to measure the concentration and temperature variation of their rf conductivities in order to throw much light on their structures, shapes and sizes. The data thus obtained and underlying results are presented in chapter 9.

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