

## CHAPTER 7

DIELECTRIC RELAXATION OF AROMATIC PARA SUBSTITUTED  
DERIVATIVE POLAR LIQUIDS FROM DISPERSION AND ABSORPTION  
PHENOMENA UNDER GIGA HERTZ ELECTRIC FIELD

## 7. DIELECTRIC RELAXATION OF AROMATIC PARA SUBSTITUTED DERIVATIVE POLAR LIQUIDS FROM DISPERSION AND ABSORPTION PHENOMENA UNDER GIGA HERTZ ELECTRIC FIELD

### 7.1. INTRODUCTION

Both aliphatic and aromatic polar liquid molecules having substituted polar groups attached to the parent ones are often characterized by more than one relaxation time  $\tau_j$ 's corresponding to rotations of over all molecule and flexible parts attached to it. In long chain compounds, the molecules having polar flexible parts at their ends may have multiple relaxation processes [1,2]. It is, of course, possible to measure these  $\tau$ 's while in some cases, the average  $\tau$ 's are, however, determined since the resolution of more than two distinct dispersive regions cannot often be detected. Para polar aromatic liquid molecules usually, attracted the attention of a large number of workers [3-5] to study their physico-chemical aspects from the dispersion and absorption phenomena.

Dhar et al [6] and Somevanshi et al [7] measured real  $\epsilon'_{ij}$  and imaginary  $\epsilon''_{ij}$  parts of hf complex relative permittivity  $\epsilon^*_{ij}$  under 10 GHz electric field, of some interesting para substituted derivative polar liquid molecules in solvent dioxane and benzene respectively in the temperature range of 17 to 40°C as collected in Table 7.1. p-hydroxypropiophenone, p-chloropropiophenone, p-benzyloxybenzaldehyde were available in the purest form from Aldrich Chemicals and p-acetamidobenzaldehyde from Central Drug Research Institute, Lucknow, India. The liquids dioxane, benzene, p-anisidine, p-phenitidine etc. were, however, obtained from M/S BDH. London. The liquids were purified through repeated fractional distillations. The physical constants of the solvents like density  $\rho$ , viscosity  $\eta$ , and the relative permittivity  $\epsilon_r$  at different temperatures in °C were collected from the literature [8].

Nowadays, the usual and conventional trend to study the dielectric relaxation phenomena of a polar liquid (DRL) is being advanced with the established symbols of dielectric terminology and parameter of hf, complex orientational susceptibility  $\chi^*_{ij}$  of which  $\chi'_{ij} (= \epsilon'_{ij} - \epsilon_{\infty ij})$  and  $\chi''_{ij} (= \epsilon''_{ij})$  are the

real and the imaginary parts in S.I. units. If 1 is subtracted from  $\varepsilon'_{ij}$  to get the real part  $\chi'_{ij}$  in which all operating processes result, while if infinitely *hf* permittivity  $\varepsilon_{\omega ij}$  is subtracted from *hf*  $\varepsilon'_{ij}$  and static  $\varepsilon_{0ij}$  one gets  $\chi'_{ij}$  and  $\chi_{0ij}$  due to only orientational polarisation process.  $\chi_{0ij}$  is a real quantity.

Ghosh et al [9] recently studied all these p-compounds in terms of the complex *hf* conductivity  $\sigma^*_{ij}$  [10] where

$$\sigma^*_{ij} = \sigma'_{ij} + j\sigma''_{ij} = \omega\varepsilon_0\varepsilon'_{ij} + j\omega\varepsilon_0\varepsilon''_{ij} \quad (7.1)$$

$\varepsilon'_{ij}$  and  $\varepsilon''_{ij}$  are the real and imaginary parts of the *hf* complex relative permittivity  $\varepsilon^*_{ij}$  related by

$$\varepsilon^*_{ij} = \varepsilon'_{ij} - j\varepsilon''_{ij} \quad (7.2)$$

$j = \sqrt{-1}$  is a complex number and  $\varepsilon_0 =$  permittivity of free space  $= 8.854 \times 10^{-12}$  Farad metre<sup>-1</sup>, to show that all these p-compounds obey Debye-relaxation mechanism. Both  $\sigma''_{ij}$  and  $\sigma'_{ij}$  are related by [11]

$$\sigma''_{ij} = \sigma_{\omega ij} + \frac{1}{\omega\tau_j} \sigma'_{ij} \quad (7.3)$$

$$\text{or, } \frac{d\sigma''_{ij}}{d\sigma'_{ij}} = \frac{1}{\omega\tau_j} \quad (7.4)$$

$\tau_j$ 's may, therefore, be determined by the slopes of  $\sigma''_{ij}$  against  $\sigma'_{ij}$  linear curves [11]. A better representation of eq (7.4) can, however, be given by

$$\left( \frac{d\sigma''_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} \bigg/ \left( \frac{d\sigma'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \frac{1}{\omega\tau_j} \quad (7.5)$$

to eliminate polar-polar interactions in the solution when  $\omega_j \rightarrow 0$  to measure  $\tau_j$ 's by Ghosh et al [12] by the conductivity method and known  $\omega = 2\pi f$  where  $f =$  frequency of the applied electric field = 10 GHz.. Hence Debye Pellat's equation. [13]

$$\varepsilon'_{ij} = \varepsilon_{\infty ij} + \frac{\varepsilon_{0ij} - \varepsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \quad (7.6)$$

$$\text{and } \varepsilon''_{ij} = \frac{\varepsilon_{0ij} - \varepsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \omega \tau_j \quad (7.7)$$

can be used to obtain the concentration variation of  $\varepsilon_{0ij}$  and  $\varepsilon_{\infty ij}$  of any polar liquid in close agreement with the experimentally measured data within  $\pm 1\%$  error as tested. The data are placed in Table 7.1 together with  $\chi'_{ij}$  ( $= \varepsilon'_{ij} - \varepsilon_{\infty ij}$ ),  $\chi''_{ij}$  ( $= \varepsilon''_{ij}$ ) to measure  $\tau_j$ 's and  $hf$   $\mu_j$ 's and the static parameters  $X_{ij}$  as a function of  $\omega_j$ 's to get the static  $\mu_s$ 's. The estimated value of  $\mu_s$  confirms the data are much more accurate. This indicates the very soundness of the method so far suggested. Thus a faithful measurement of  $\chi'_{ij}$  and  $\chi''_{ij}$  is possible to study the relaxation phenomena where the orientational polarisation alone plays the important role. In  $\sigma_{ij}$ 's measurements, the transfer of bound molecular charges are responsible to yield  $hf$   $\mu_j$ 's with an approximation that  $\sigma_{ij} \approx \sigma''_{ij}$  where  $\sigma_{ij}$  is the total  $hf$  conductivity  $\sigma_{ij} = \omega \varepsilon_0 (\varepsilon''_{ij}{}^2 + \varepsilon'_{ij}{}^2)^{1/2}$  as a function of  $\omega_j$  at each temperature.

Some sample curves of both  $\chi'_{ij}$  and  $\chi''_{ij}$  against  $\omega_j$ 's are shown in Figs. 7.1 and 7.2 respectively. The linear equations of  $\ln \tau_j T$  against  $1/T$  with  $\tau_j$ 's from the susceptibility measurements are shown graphically in Fig. 7.3 with the experimental points placed upon them. The values of intercepts and slopes are entered in the Table 7.3, to compute thermodynamic energy parameters like enthalpy  $\Delta H_\tau$ , entropy  $\Delta S_\tau$  and free energy  $\Delta F_\tau$  of activation due to dielectric relaxation from Eyring's rate process equations [14]. The enthalpy of activation  $\Delta H_\eta$  due to viscous flow was estimated from  $\Delta H_\tau$  and the slope  $\delta$  of the linear equations of  $\ln \tau_j T$  against  $\ln \eta_i$  where  $\eta_i$  is the coefficient of viscosity of the solvents used. The data as seen in Table 7.2 throw much light on the stability as well as on the physico-chemical properties of the systems. Kalman and Debye factors placed in the Table 7.3 reflect the applicability of Debye model of relaxation for such p-compounds [9].

The *hf*  $\mu_j$ 's of all the para liquid molecules due to orientational prolarization alone were carefully worked out from the linear coefficients  $\beta$ 's of  $\chi'_{ij} - \omega_j$  equations and the dimensionless parameters 'b' involved with estimated  $\mu_j$ 's at different temperatures and are placed in Table 7.2. They are compared with the reported *hf*  $\mu_j$ 's, static  $\mu_s$ 's obtained from linear coefficient  $a_1$  of static  $X_{ij} - \omega_j$  equations, and  $\mu_{theo}$ 's from the available infrared spectroscopic data of bond moments of the substituted polar groups attached to the parent molecules. The disagreement of measured *hf*  $\mu_j$  with  $\mu_{theo}$  establishes the existence of inductive and mesomeric moments which in excitd state offers the electromeric effects suffered by the polar groups of the molecules under GHz electric field. The close agreement between  $\mu_j$  and  $\mu_{theo}$  is, however, achieved when the bond moments are corrected by multiplying with  $\frac{\mu_j}{\mu_{theo}}$  and  $\frac{\mu_s}{\mu_{theo}}$  respectively as required.

## 7.2. THEORETICAL FORMULATONS TO MEASURE $\tau_j$ AND $\mu_j$ OF A POLAR

### UNIT

The real and imaginary parts of *hf* complex relative permittivity  $\epsilon^*_{ij}$  are related by

$$\epsilon'_{ij} = \epsilon_{\infty ij} + \frac{1}{\omega\tau_j} \epsilon''_{ij} \quad (7.8)$$

replacing  $\epsilon'_{ij} - \epsilon_{\infty ij}$  by  $\chi'_{ij}$  and  $\epsilon''_{ij}$  by  $\chi''_{ij}$  we have

$$\chi''_{ij} = (\omega\tau_j) \chi'_{ij}$$

$$\text{or } d\chi''_{ij} / d\chi'_{ij} = (\omega\tau_j) \quad (7.9)$$

$\chi''_{ij}$  varies linearly with  $\chi'_{ij}$ . The slope of eq. (7.9) which is used to measure  $\tau_j$  of a polar unit.

But for associative liquids like p-anisidine, p-phenitidine etc the variation of  $\chi''_{ij}$  with  $\chi'_{ij}$  is not strictly linear as claimed elsewhere [15]. The ratio of slopes of individual variations of  $\chi''_{ij}$  and  $\chi'_{ij}$  against  $w_j$ 's are found to be a better representation of the slope of eq. (7.9) in which polar - polar interactions are supposed to be almost eliminated [16].

$$\text{Thus } \frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (7.10)$$

The imaginary part  $\chi''_{ij}$  of hf  $\chi^*_{ij}$  is [17, 18].

$$\chi''_{ij} = \left( \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \right) (\varepsilon_i + 2)^2 \cdot \frac{\omega\tau_j}{1 + \omega^2\tau_j^2} w_j \quad (7.11)$$

which on differentiation w.r.t.  $w_j$  and in the limit  $w_j \rightarrow 0$  becomes :

$$\left( \frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \left( \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \right) (\varepsilon_i + 2)^2 \cdot \frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \quad (7.12)$$

From eqs (7.10) and (7.12) one obtains

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

which at once provides  $\mu_j$  as :

$$\mu_j = \left[ \frac{27\varepsilon_0 M_j k_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 b} \right]^{\frac{1}{2}} \quad (7.13)$$

to measure hf dipole moments  $\mu_j$ 's in terms of  $\tau_j$ 's obtained from eq.( 7.10) where  $\varepsilon_0$  = Permittivity of free space =  $8.854 \times 10^{-12}$  Farad. metre<sup>-1</sup>.

$M_j$  = Molecular weight of solute in Kg

$k_B$  = Boltzmann constant =  $1.38 \times 10^{-23}$  J mole<sup>-1</sup>K<sup>-1</sup>

$\beta$  = Linear coefficient of  $\chi'_{ij}-w_j$  curves of Fig.7.1 at  $w_j \rightarrow 0$

T= Temperature in Kelvin

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

$\epsilon_j = \text{Dielectric relative permittivity of the solvent and}$

$b = \frac{1}{1 + \omega^2 \tau_j^2}$ , a dimensionless parameter involved with estimated  $\tau_j$ 's.

Thus the eq. (7.13) can be employed to measure  $hf \mu_j$ 's of all para-polar liquid molecules under investigation, in benzene and dioxane at different experimental temperatures. They are presented in Table 7.2. The temperature variations of  $hf \mu_j$ 's are shown graphically in Fig. 7.4. It is evident from Fig 7.4 that the temperature variation  $\mu_j$ 's offers a valuable information about the structural aspects in addition to the physico chemical properties of the liquid molecules.

### 7.3. THEORETICAL FORMULATION OF STATIC PARAMETER $X_{ij}$ TO

#### ESTIMATE STATIC DIPOLE MOMENT $\mu_s$

The static dipole moment  $\mu_s$  of a polar solute (j) in a non-polar solvent (i) at TK is given in terms of  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  of Table 7.1, by [12, 13]

$$\frac{\epsilon_{0ij} - 1}{\epsilon_{0ij} + 2} - \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} = \frac{\epsilon_{0i} - 1}{\epsilon_{0i} + 2} - \frac{\epsilon_{\infty i} - 1}{\epsilon_{\infty i} + 2} + \frac{N \mu_s^2}{9 \epsilon_0 k_B T} c_j \quad (7.14)$$

The molar concentration  $c_j$  is expressed by  $w_j$  of the polar solute

$$c_j = \frac{\rho_{ij}}{M_j} w_j$$

The weight  $W_j$  and volume  $V_j$  of a polar solute is dissolved in a non-polar solvent of weight  $W_i$  and volume  $V_i$  to have the solution density  $\rho_{ij}$  where

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

$$\begin{aligned}
 &= \frac{\rho_i \rho_j}{\rho_j w_i + \rho_i w_j} = \rho_i (1 - \gamma w_j)^{-1} \\
 &= \rho_i (1 + \gamma w_j + \gamma w_j^2 + \dots) \quad (7.15)
 \end{aligned}$$

The weight fractions  $w_i$  and  $w_j$  of the solvent and solute are

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

such that  $w_i + w_j = 1$  and  $\gamma = \left(1 - \frac{\rho_i}{\rho_j}\right)$  where  $\rho_i$  and  $\rho_j$  are the densities of pure solvent and pure solute respectively in S.I. units.

Hence eq. (7.14) becomes:

$$\begin{aligned}
 \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{(\epsilon_{0ij} + 2)(\epsilon_{\infty ij} + 2)} &= \frac{\epsilon_{oi} - \epsilon_{\alpha i}}{(\epsilon_{oi} + 2)(\epsilon_{\alpha i} + 2)} + \frac{N \rho_i \mu_s^2}{27 \epsilon_0 M_j k_B T} \times w_j (1 + \gamma w_j + \dots) \\
 \text{or, } X_{ij} &= X_i + \frac{N \rho_i \mu_s^2}{27 \epsilon_0 M_j k_B T} w_j + \frac{N \rho_i \mu_s^2}{27 \epsilon_0 M_j k_B T} \gamma w_j^2 + \dots \quad (7.16)
 \end{aligned}$$

Since  $0 < w_j < 1$ , the above eq. (7.16) can be expressed by the polynomial equation of  $w_j$  upto the third term only like

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \dots \quad (7.17)$$

Comparing the coefficients of first power of  $w_j$  of eqs. (7.16) and (7.17) one gets the static  $\mu_s$  as:

$$\mu_s = \left[ \frac{27 \epsilon_0 M_j k_B T}{N \rho_i} a_1 \right]^{\frac{1}{2}} \quad (7.18)$$

where  $a_1$  is the linear coefficient of  $X_{ij} - w_j$  curves, a few of which are shown in Fig. 7.5 as for example.  $\mu_s$ 's from coefficient of higher powers of  $w_j$  of eq. (7.16) are not reliable as the term  $\gamma$  is involved with various effects like solute-solute interaction, relative density, macroscopic viscosity, internal field etc. The  $\mu_s$ 's thus obtained establish the very soundness of the methods so far advanced where

$\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  are not experimentally measured. The  $\mu_s$ 's thus estimated for the p-compounds are seen in Table 7.2 to compare with *hf*  $\mu_j$ 's from the orientational susceptibility measurements and theoretical  $\mu_{theo}$ 's from the available bond angles and bond moments of the substituted polar groups attached to the parent molecules.

#### 7.4. RESULTS AND DISCUSSION

The concentration variation of  $\chi'_{ij}$  and  $\chi''_{ij}$  of all the p-compounds in solvents dioxane and benzene respectively at different experimental temperatures in  $^{\circ}\text{C}$  are collected in Table 7.1 to show some variations of  $\chi'_{ij}$  and  $\chi''_{ij}$  with  $w_j$ 's in Figs.7.1 and 7.2 respectively as for example. The relaxation times  $\tau_j$ 's have been measured under 3 cm wave length electric field from eqs. (7.9) and (7.10) by using  $\chi'_{ij}$  and  $\chi''_{ij}$  of Table 7.1.  $\tau_j$ 's from eq. (7.10) are presented in the Table 7.2 to compare with those placed in the same Table 7.2 recalculated from eq.(7.5) by conductivity  $\sigma_{ij}$  method [9] and reported ones [6, 7]. The close agreement between all the  $\tau_j$ 's at once reflects the validity of eq.(7.10) derived from the susceptibility  $\chi_{ij}$ 's measurements. Thus the method of ratio of slopes of individual variations of  $\chi'_{ij}$  and  $\chi''_{ij}$  with  $w_j$ 's in the limit  $w_j = 0$  to get  $\tau_j$  from eq.(7.10) is superior one where the effects of fast polarization in addition to polar-polar interactions are reduced to a large extent [16]. Although not shown in Table 7.2, they were interesting to see that the direct slope of  $\chi''_{ij}$  against  $\chi'_{ij}$  gives rise to almost the same  $\tau_j$ 's with those obtained from the ratio of the individual slopes of  $\chi''_{ij}$  and  $\chi'_{ij}$  against  $w_j$ 's of eq. (7.10). The  $\tau_j$ 's at all the temperatures for p-hydroxypropiophenone, p-chloropropiophenone, p-acetamidobenzaldehyde, p-benzyloxy benzaldehyde are of high values probably due to their larger molecular sizes [9] while the reverse is true for p-anisidine, p-phenitidine, o-chloroparanitroaniline and p-bromonitrobenzene. The observation indicates that  $\tau_j$ 's of all the liquids decrease with the rise of temperature in  $^{\circ}\text{C}$  for the lower values of the coefficients of viscosity [6] of solution. The variation of some  $\tau_j$ 's with  $t^{\circ}\text{C}$  of all the p-liquids were found to be (see Table 7.2) irregular and in disagreement with the Debye relaxation [19]. This is, however, explained on the

basis of the fact that as the temperature rises the stretching of bond angles and distributions of bond moments of all the flexible polar groups attached to the parent ones lead to either symmetric or asymmetric shapes of the molecules [9].

The process of rotation of the rotating molecular dipole requires an activation energy sufficient to overcome the energy barrier between two equilibrium positions. Eyrings rate process equation [14] can be used with the known  $\tau_j$ 's, where

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

$$\text{or, } \ln \tau_j T = \ln A' + \frac{\Delta H_\tau}{RT} \quad (7.19)$$

$$\text{since } \Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad \text{and } A' = Ae^{-\Delta S_\tau / R}$$

to measure thermodynamic energy parameters like  $\Delta F_\tau$ ,  $\Delta H_\tau$  and  $\Delta S_\tau$  usually known as free energy, enthalpy and entropy of activations due to dielectric relaxation processes.

The linear eq.( 7.19) of  $\ln \tau_j T$  against  $1/T$  having intercept and slope are presented in Table 7.3 together with the values of  $\Delta F_\tau$ ,  $\Delta H_\tau$  and  $\Delta S_\tau$  as obtained from eq. (7.19). The least square fitted linear plots of  $\ln \tau_j T$  against  $1/T$  with the experimental points placed on them have been shown in Fig. 7.3. Some of the experimental points are found not to fall on the smooth curves of Fig. 7.3 due to irregular variations of  $\tau_j$ 's with temperature [9] probably due to the fact that the non spherical dipolar molecules are known to be non Debye in their relaxation behaviours. As seen in Table 7.3  $\Delta F_\tau$ 's for most of the systems are higher in comparison to  $\Delta H_\tau$ 's. This implies that a large number of flexible polar groups surrounding the parent molecules are rotating under GHz electric field [6]. The -ve  $\Delta S_\tau$  for all the systems except p-benzyloxybenzaldehyde and p-anisidine is due to co-operative orientations of the steric forces [20] indicating thereby that the activated states are more ordered [4,21] while the +ve  $\Delta S_\tau$ 's for other systems refers to the instability of the activated states. Enthalpy of activation due

to viscous flow  $\Delta H_\eta$ , has been estimated from slope  $\delta$  of  $\ln \tau_j T$  with  $\ln \eta_i$  fitted linear equation and known  $\Delta H_\tau$  in order to place them in Table 7.3.  $\delta (= \Delta H_\tau / \Delta H_\eta)$  for all the molecules  $> 0.50$  except p-hydroxypropiophenone and p-acetamidobenzaldehyde indicates the solvent environment around the solute molecules to behave as solid phase rotators [9]. Low value of  $\delta$  for systems as seen in Table 7.3 arises for the weak interaction of the solvent and solute [9]. Almost constant values of Debye factor  $\tau_j T / \eta_i$  rather than Kalman factor  $\tau_j T / \eta_i^\delta$  at all the temperatures for each molecule implies the applicability of Debye relaxation for such p-liquids [9,22].

This at once prompted us to recalculate *hf*  $\tau_j$ 's from conductivity, measurements in the GHz range. From eq.( 7.3) one gets

$$\beta = \frac{1}{\omega \tau_j} \left( \frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} \quad (7.20)$$

where  $\beta$  is the slope of  $\sigma_{ij} - w_j$  curve of a polar-nonpolar liquid mixture at  $w_j \rightarrow 0$

The real part of *hf* complex  $\sigma_{ij}^*$  is [12, 17]

$$\text{Now } \sigma'_{ij} = \frac{N\rho_i \mu_j^2}{27M_j k_B T} (\epsilon_{ij} + 2)^2 \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} w_j$$

$$\text{or, } \left( \frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{27M_j k_B T} (\epsilon_i + 2)^2 \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \quad (7.21)$$

Comparing eqs (7.20) and (7.21) the following formula is obtained to get *hf*  $\mu_j$  from  $\sigma_{ij}$  in  $\Omega^{-1}m^{-1}$  which takes into account of the contribution of bound molecular charge transfer among the solute molecules

$$\mu_j = \left[ \frac{27M_j k_B T}{N\rho_i (\epsilon_i + 2)^2} \cdot \frac{\beta}{\omega b} \right]^{\frac{1}{2}} \quad (7.22)$$

where  $b$  is a dimensionless parameter involved with  $\tau_j$ 's measured from eq. (7.5). The recalculated  $\tau_j$ 's are presented in Table 7.2 for comparison with those measured from eq. (7.10) and reported ones [6,7]. Estimation of  $\tau_j$  by eq. (7.5) is significant one, as it is useful to obtain  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  by Debye – Pellat's equation, to have static  $\mu_s$  as entered in Table 7.2.  $\mu_j$ 's by susceptibility measurements are shown in Table 7.2 to see how far they agree with  $\mu_{theo}$ 's of the bond moments of the flexible parts as calculated in Fig. 7.6 and the static  $\mu_s$  from eq. (7.18).  $\mu_s$ 's thus computed from  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  data of Table 7.1 show the fact that they are very close to hf  $\mu_j$ . Thus the frequency effect is almost nil in hf  $\mu_j$ 's obtained by susceptibility method. A comparison between hf  $\mu_j$  from eqs. (7.13) and (7.22) may, however, be interesting which is to be studied later on. The values of  $n_{Dij}^2$  ( $\approx \epsilon_{\infty ij}$ ) had been tested from the literature [8] where they were available.

$\mu_j - t$  of least square fitted curves of I, III, IV and V of p-hydroxypropiophenone, p-acetamidobenzaldehyde, p-benzyloxybenzaldehyde and p-anisidine initially increases with temperature and then attain the highest value to show maximum asymmetries at different temperatures as seen in Fig. 7.4.  $\mu_j$ 's of those compounds go on decreasing with temperature to attain symmetries. These curves are convex in nature showing  $\mu_j = 0$  at lower and higher temperatures due to strong symmetry attained at those temperatures [9]. The curve of VII for o-chloro-p-nitroaniline shows gradual decrease of  $\mu_j$  values with temperature. On the other hand the least square fitted curves of  $\mu_j$  against  $t$  in  $^{\circ}\text{C}$  of II, VI and VIII are concave in nature. The curve VI of p-phenitidine reaches the highest symmetry and then goes on increasing with the rise in temperature. The curve shows 0 (zero) values at lower and higher temperature, as shown by the dotted line to maintain the continuity of the curves. The above nature of  $\mu_j - t$  curves are explained by the rupture of solute-solvent (monomer) and solute-solute (dimer) associations due to stretching of bond angles and bond moments of substituted polar groups at different temperatures. [4,9].

Ghosh et al [9] obtained the  $\mu$ 's of p-compounds i.e. systems I – VIII as 8.27, 9.73, 13.12, 6.23, 6.82, 15.04, 15.93 & 8.40 each multiplied by  $10^{-30}$  in C.m. respectively. A special attention is to be paid to the contributions of the available bond moments and bond angles due to different substituent groups of parent molecules in calculating theoretical dipole moments  $\mu_{theo}$ 's. But  $\mu_{theo}$ 's as sketched elsewhere [9] are found to be slightly deviated from the measured hf  $\mu_j$ 's and  $\mu_s$ 's because of the existence of the inductive and the mesomeric moments for different flexible groups. The reduced or elongated bond moments of the substituted polar groups are calculated by multiplying the  $\mu_{theo}$ 's by the factor  $\mu_j / \mu_{theo}$  around  $20^0$  C. The results for systems I to VIII are 14.27, 7.27, 12.62, 10.22, 8.56, 29.36, 2.41 and 4.23 each multiplied by  $10^{-30}$  in C.m. respectively. They are placed in the last column of Table 7.2 and displayed in Fig. 7.6. The reduction or elongation in bond moments exhibits the presence of mesomeric, inductive and electromeric effects under static and hf electric fields.

## 7.5. CONCLUSION

Theoretical consideration in S.I units for the effective utilization of the established symbols of dielectric terminologies and parameters in terms of dielectric susceptibilities obtained from dielectric relative permittivities appears to be more topical, significant and useful one to have valuable information in the study of dispersion and absorption phenomena as they are directly linked with the molecular orientational polarisation. A convenient method is, therefore, suggested to calculate  $\tau_j$  and  $\mu_j$  under GHz electric field along with the static  $\mu_s$  in S.I units of some p-compounds. The ratio of slopes of individual variations of  $\chi''_{ij}$  and  $\chi'_{ij}$  with  $w_j$ 's is a better representation over the previous one of Murthy et al as it eliminates polar-polar interactions almost completely in a given solution. Thermodynamic energy parameters ; enthalpy  $\Delta H_r$ , entropy  $\Delta S_r$ , and free energy  $\Delta F_r$  of activation due to dielectric relaxation and enthalpy of 'activation due to viscous flow of solvent provides information about the stability or unstabilities of the states of polar-nonpolar liquid mixture in a given temperature range. The physico chemical properties could, also be studied in terms of conformations of such p-compounds. The temperature variation of measured  $\mu_j$ 's reveals that the

molecules may attain either symmetric or asymmetric shapes with the rise in temperature. The slight difference between experimental  $\mu_j$ 's and theoretical  $\mu_{theo}$ 's suggests the existence of inductive, mesomeric and electromeric effects of the polar flexible groups of the molecules due to their aromaticity. Theoretical formulations, so far developed, are in S.I. units because of its unified, coherent and rationalised nature. The experimental points in some cases are slightly deviated from the least squares fitted plots indicating that the highly nonspherical polar molecules are slightly non Debye in relaxation behaviour. However, the  $X_{ij} - \omega_j$  curves used to get  $\mu_s$ , can be used to test the accuracies of the measurements of static  $\epsilon_{0ij}$  and hf  $\epsilon_{\infty ij}$ .

The  $X_{ij}$ 's are involved with the low and infinitely hf permittivities  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  derived from Debye- pellet's equations in terms of measured concentration variation of  $\epsilon'_{ij}$  and  $\epsilon''_{ij}$  of polar-non polar liquid mixtures. The  $\mu_j$ 's and  $\mu_s$ 's are almost equal in some cases only to show that  $\mu_j$ 's are little affected by the applied electric field frequency. The computation of  $\tau_j$ ,  $\mu_j$  and  $\mu_s$  from  $\sigma_{ij}$ ,  $\chi_{ij}$  and  $X_{ij}$  measurements of a polar unit in a given solvent appears to be more simple, straight forward and topical one to locate the accuracies of  $\tau_j$ ,  $\mu_j$  and  $\mu_s$  which are claimed to be accurate within 10% and 5% respectively. The calculated results appear to be of more archival values to reveal some interest in the process of dielectric relaxation. The factors of  $\mu_i / \mu_{theo}$  and  $\mu_j / \mu_{theo}$  are almost constant for all the molecules revealing the material property of the systems [23]. The correlation between the conformational structures presented in Fig. 7.6 of the p-compounds with the observed results enhances the scientific content and adds a new horizon to understand the existing knowledge of dielectric relaxation from dispersion and absorption phenomena.

Table 7.1: Concentration variation of the real and imaginary parts of dielectric permittivity  $\epsilon^*_{ij}$ , static permittivity  $\epsilon_{0ij}$ , infinitely high frequency permittivity  $\epsilon_{\infty ij}$ , real and imaginary parts of dielectric susceptibilities  $\chi'_{ij}$  and  $\chi''_{ij}$  of hf complex susceptibility  $\chi^*_{ij}$  and static experimental parameters  $X_{ij}$ , of some parapolar liquids in non polar solvents at different experimental temperatures under 10 GHz electric field

System with Sl. No.	Temp in $^{\circ}\text{C}$	Weight fraction	Dielectric permittivities				Dielectric susceptibilities		static experimental parameter
			$\epsilon'_{ij}$	$\epsilon''_{ij}$	$\epsilon_{0ij}$	$\epsilon_{\infty ij}$	$\chi'_{ij}$	$\chi''_{ij}$	$X_{ij}$
1. p-hydroxy- propiophenone ( in dioxane )	17	0.0040	2.0930	0.0320	2.1316	2.0665	0.0265	0.0320	0.00388
		0.0066	2.0970	0.0420	2.1477	2.0622	0.0348	0.0420	0.00507
		0.0089	2.0980	0.0440	2.1511	2.0615	0.0365	0.0440	0.00531
		0.0107	2.0990	0.0470	2.1557	2.0601	0.0389	0.0470	0.00567
		0.0116	2.1210	0.0620	2.1958	2.0696	0.0514	0.0620	0.00739
	23	0.0040	2.1250	0.0310	2.1663	2.1018	0.0232	0.0310	0.00378
		0.0066	2.1330	0.0470	2.1957	2.0978	0.0352	0.0470	0.00570
		0.0090	2.1410	0.0590	2.2197	2.0968	0.0442	0.0590	0.00711
		0.0117	2.1560	0.0720	2.2520	2.1020	0.0540	0.0720	0.00860
	30	0.0041	2.1490	0.0360	2.2035	2.1252	0.0238	0.0360	0.00451
		0.0067	2.1550	0.0440	2.2216	2.1259	0.0291	0.0440	0.00549
		0.0091	2.1560	0.0470	2.2271	2.1249	0.0311	0.0470	0.00586
		0.0109	2.1570	0.0490	2.2312	2.1246	0.0324	0.0490	0.00610
		0.0118	2.1730	0.0710	2.2805	2.1261	0.0469	0.0710	0.00874
	37	0.0041	2.1580	0.0350	2.1896	2.1192	0.0388	0.0350	0.00408
		0.0068	2.1750	0.0440	2.2147	2.1263	0.0487	0.0440	0.00509
		0.0092	2.1780	0.0510	2.2241	2.1215	0.0565	0.0510	0.00589
		0.0110	2.1840	0.0560	2.2346	2.1220	0.0620	0.0560	0.00645
		0.0119	2.1860	0.0590	2.2393	2.1207	0.0653	0.0590	0.00679
	2. p-chloro- propiophenone ( in dioxane )	19	0.0050	2.1100	0.0280	2.1301	2.0709	0.0391	0.0280
0.0068			2.1200	0.0320	2.1429	2.0754	0.0446	0.0320	0.00400
0.0080			2.1220	0.0340	2.1464	2.0746	0.0474	0.0340	0.00425
0.0093			2.1270	0.0400	2.1557	2.0712	0.0558	0.0400	0.00499
0.0112			2.1330	0.0450	2.1653	2.0702	0.0628	0.0450	0.00561
0.0123			2.1430	0.0490	2.1781	2.0746	0.0684	0.0490	0.00608
25		0.0051	2.1230	0.0290	2.1581	2.0990	0.0240	0.0290	0.00347
		0.0069	2.1250	0.0320	2.1637	2.0986	0.0264	0.0320	0.00382
		0.0081	2.1280	0.0340	2.1692	2.0999	0.0281	0.0340	0.00405
		0.0094	2.1290	0.0390	2.1762	2.0968	0.0322	0.0390	0.00464
		0.0113	2.1340	0.0430	2.1861	2.0985	0.0355	0.0430	0.00510
		0.0124	2.1410	0.0500	2.2015	2.0997	0.0413	0.0500	0.00591
31		0.0051	2.1350	0.0290	2.1817	2.1170	0.0180	0.0290	0.00376
		0.0069	2.1380	0.0330	2.1911	2.1175	0.0205	0.0330	0.00427
		0.0082	2.1390	0.0340	2.1937	2.1179	0.0211	0.0340	0.00439
		0.0095	2.1480	0.0390	2.2108	2.1238	0.0242	0.0390	0.00501
		0.0114	2.1490	0.0410	2.2150	2.1235	0.0255	0.0410	0.00526
		0.0125	2.1510	0.0630	2.2524	2.1119	0.0391	0.0630	0.00804
37		0.0052	2.1450	0.0270	2.1574	2.0861	0.0589	0.0270	0.00419
		0.0070	2.1680	0.0290	2.1813	2.1048	0.0632	0.0290	0.00446
	0.0083	2.1730	0.0330	2.1881	2.1011	0.0719	0.0330	0.00507	
	0.0115	2.1740	0.0360	2.1905	2.0955	0.0785	0.0360	0.00553	
	0.0126	2.1790	0.0400	2.1974	2.0918	0.0872	0.0400	0.00615	

System with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities				Dielectric susceptibilities		static experimental parameter
			$w_j$	$\epsilon'_{ij}$	$\epsilon''_{ij}$	$\epsilon_{oij}$	$\epsilon_{\infty ij}$	$\chi'_{ij}$	$\chi''_{ij}$
3. p-acetamido benzaldehyde ( in dioxane )	17	0.0023	2.1530	0.0290	2.2024	2.1360	0.0170	0.0290	0.00382
		0.0042	2.1540	0.0380	2.2187	2.1317	0.0223	0.0380	0.00499
		0.0073	2.1600	0.0530	2.2503	2.1289	0.0311	0.0530	0.00692
		0.0078	2.1690	0.0610	2.2729	2.1332	0.0358	0.0610	0.00791
		0.0112	2.1750	0.0670	2.2891	2.1357	0.0393	0.0670	0.00865
	23	0.0023	2.1580	0.0340	2.2031	2.1324	0.0256	0.0340	0.00407
		0.0043	2.1650	0.0440	2.2233	2.1318	0.0332	0.0440	0.00524
		0.0073	2.1710	0.0480	2.2346	2.1348	0.0362	0.0480	0.00570
		0.0078	2.1740	0.0560	2.2482	2.1318	0.0422	0.0560	0.00664
		0.0113	2.1820	0.0670	2.2708	2.1315	0.0505	0.0670	0.00790
	30	0.0154	2.1840	0.0680	2.2741	2.1327	0.0513	0.0680	0.00801
		0.0074	2.1750	0.0350	2.2275	2.1517	0.0233	0.0350	0.00432
		0.0079	2.1860	0.0430	2.2505	2.1573	0.0287	0.0430	0.00527
		0.0098	2.1870	0.0530	2.2665	2.1517	0.0353	0.0530	0.00648
		0.0114	2.1950	0.0590	2.2835	2.1557	0.0393	0.0590	0.00718
37	0.0155	2.2010	0.0710	2.3075	2.1537	0.0473	0.0710	0.00860	
	0.0075	2.2110	0.0370	2.2600	2.1831	0.0279	0.0370	0.00432	
	0.0080	2.2210	0.0470	2.2832	2.1855	0.0355	0.0470	0.00545	
	0.0099	2.2320	0.0550	2.3048	2.1905	0.0415	0.0550	0.00634	
	0.0115	2.2410	0.0730	2.3377	2.1859	0.0551	0.0730	0.00836	
4. p- benzyloxy- benzaldehyde ( in dioxane )	20	0.0157	2.2420	0.0760	2.3426	2.1846	0.0574	0.0760	0.00870
		0.004	2.1450	0.027	2.1910	2.1292	0.0158	0.0270	0.00358
		0.0066	2.1500	0.029	2.1994	2.1330	0.0170	0.0290	0.00383
		0.0089	2.1520	0.031	2.2049	2.1338	0.0182	0.0310	0.00409
		0.0104	2.1530	0.035	2.2127	2.1325	0.0205	0.0350	0.00461
	25	0.0116	2.1540	0.036	2.2154	2.1329	0.0211	0.0360	0.00473
		0.0153	2.1560	0.045	2.2327	2.1296	0.0264	0.0450	0.00590
		0.0041	2.167	0.028	2.1947	2.1387	0.0283	0.0280	0.00323
		0.0067	2.172	0.034	2.2057	2.1377	0.0343	0.0340	0.00391
		0.009	2.174	0.038	2.2117	2.1357	0.0383	0.0380	0.00436
	30	0.0105	2.175	0.039	2.2136	2.1356	0.0394	0.0390	0.00448
		0.0117	2.18	0.044	2.2236	2.1356	0.0444	0.0440	0.00504
		0.0154	2.187	0.047	2.2336	2.1396	0.0474	0.0470	0.00536
		0.0041	2.1780	0.0310	2.2151	2.1521	0.0259	0.0310	0.00360
		0.0067	2.1920	0.0350	2.2339	2.1627	0.0293	0.0350	0.00404
35	0.009	2.1930	0.0390	2.2397	2.1604	0.0326	0.0390	0.00449	
	0.0106	2.1940	0.0400	2.2419	2.1606	0.0334	0.0400	0.00461	
	0.0118	2.1960	0.0440	2.2486	2.1592	0.0368	0.0440	0.00506	
	0.0155	2.2060	0.0620	2.2802	2.1542	0.0518	0.0620	0.00709	
	0.0041	2.2030	0.0320	2.2290	2.1636	0.0394	0.0320	0.00371	
35	0.0091	2.2090	0.036	2.2382	2.1647	0.0443	0.0360	0.00417	
	0.0119	2.2160	0.042	2.2501	2.1643	0.0517	0.0420	0.00485	
	0.0156	2.2190	0.0450	2.2556	2.1636	0.0554	0.0450	0.00519	

System with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities				Dielectric susceptibilities		static experimental parameter
			$\epsilon'_{ij}$	$\epsilon''_{ij}$	$\epsilon_{oij}$	$\epsilon_{\infty ij}$	$\chi'_{ij}$	$\chi''_{ij}$	$X_{ij}$
5. p-anisidine ( in benzene )	20	0.0071	2.1700	0.0300	2.1854	2.1117	0.0583	0.0300	0.00428
		0.0098	2.1900	0.0350	2.2080	2.1220	0.0680	0.0350	0.00496
		0.0121	2.2000	0.0400	2.2206	2.1223	0.0777	0.0400	0.00565
		0.0165	2.2000	0.0440	2.2227	2.1146	0.0854	0.0440	0.00622
		0.0198	2.2100	0.0480	2.2347	2.1168	0.0932	0.0480	0.00676
	30	0.0071	2.1800	0.0300	2.1919	2.1041	0.0759	0.0300	0.00510
		0.0098	2.1900	0.0350	2.2038	2.1014	0.0886	0.0350	0.00594
		0.0121	2.2000	0.0400	2.2158	2.0987	0.1013	0.0400	0.00677
		0.0165	2.2100	0.0450	2.2278	2.0961	0.1139	0.0450	0.00760
		0.0198	2.2200	0.0450	2.2378	2.1061	0.1139	0.0450	0.00757
	40	0.0071	2.1900	0.0400	2.1997	2.0247	0.1653	0.0400	0.01035
		0.0098	2.2000	0.0420	2.2102	2.0265	0.1735	0.0420	0.01084
		0.0121	2.2100	0.0440	2.2206	2.0282	0.1818	0.0440	0.01132
		0.0165	2.2200	0.0460	2.2311	2.0299	0.1901	0.0460	0.01180
		0.0198	2.2300	0.0500	2.2421	2.0234	0.2066	0.0500	0.01281
6. p-phenitidine ( in benzene )	20	0.0132	2.3100	0.0300	2.3296	2.2642	0.0458	0.0300	0.00355
		0.0149	2.3200	0.0500	2.3527	2.2436	0.0764	0.0500	0.00591
		0.0168	2.3400	0.0700	2.3858	2.2330	0.1070	0.0700	0.00823
		0.0199	2.3800	0.0800	2.4324	2.2577	0.1223	0.0800	0.00925
		0.0231	2.3900	0.0900	2.4489	2.2525	0.1375	0.0900	0.01038
	30	0.0132	2.3200	0.0300	2.3373	2.2681	0.0519	0.0300	0.00374
		0.0149	2.3700	0.0400	2.3931	2.3008	0.0692	0.0400	0.00489
		0.0168	2.3800	0.0500	2.4089	2.2935	0.0865	0.0500	0.00610
		0.0199	2.4100	0.0600	2.4447	2.3061	0.1039	0.0600	0.00724
		0.0231	2.4100	0.0800	2.4562	2.2715	0.1385	0.0800	0.00970
	40	0.0132	2.3400	0.0400	2.3604	2.2615	0.0785	0.0400	0.00532
		0.0149	2.3400	0.0500	2.3655	2.2419	0.0981	0.0500	0.00668
		0.0168	2.3600	0.0600	2.3906	2.2422	0.1178	0.0600	0.00796
		0.0199	2.3900	0.0700	2.4257	2.2526	0.1374	0.0700	0.00920
		0.0231	2.4100	0.0800	2.4508	2.2530	0.1570	0.0800	0.01045
7. o-chloro-p- nitro aniline ( in benzene )	20	0.0251	2.0700	0.0200	2.0832	2.0398	0.0302	0.0200	0.00264
		0.0293	2.0800	0.0200	2.0932	2.0498	0.0302	0.0200	0.00262
		0.0331	2.0900	0.0300	2.1098	2.0446	0.0454	0.0300	0.00392
		0.0652	2.1000	0.0300	2.1198	2.0546	0.0454	0.0300	0.00390
		0.0851	2.1000	0.0400	2.1265	2.0395	0.0605	0.0400	0.00522
	30	0.0251	2.1000	0.0200	2.1100	2.0600	0.0400	0.0200	0.00300
		0.0293	2.1000	0.0200	2.1100	2.0600	0.0400	0.0200	0.00300
		0.0331	2.1100	0.0250	2.1225	2.0600	0.0500	0.0250	0.00373
		0.0652	2.1100	0.0250	2.1225	2.0600	0.0500	0.0250	0.00373
		0.0851	2.1200	0.0300	2.1350	2.0600	0.0600	0.0300	0.00447
	40	0.0251	2.1200	0.0300	2.1344	2.0575	0.0625	0.0300	0.00459
		0.0293	2.1200	0.0300	2.1344	2.0575	0.0625	0.0300	0.00459
		0.0331	2.1300	0.0325	2.1456	2.0623	0.0677	0.0325	0.00495
		0.0652	2.1300	0.0325	2.1456	2.0623	0.0677	0.0325	0.00495
		0.0851	2.1300	0.0350	2.1468	2.0571	0.0729	0.0350	0.00533

System with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities				Dielectric susceptibilities		static experimental parameter
			$\epsilon'_{ij}$	$\epsilon''_{ij}$	$\epsilon_{oij}$	$\epsilon_{\infty ij}$	$\chi'_{ij}$	$\chi''_{ij}$	$X_{ij}$
8. p-bromo- nitro benzene ( in benzenè )	20	0.0162	2.2100	0.0263	2.2267	2.1686	0.0415	0.0263	0.00330
		0.0202	2.2313	0.0302	2.2504	2.1837	0.0476	0.0302	0.00375
		0.0342	2.2352	0.0350	2.2574	2.1801	0.0551	0.0350	0.00434
		0.0375	2.2423	0.0375	2.2661	2.1832	0.0591	0.0375	0.00464
		0.0416	2.2540	0.0400	2.2794	2.1910	0.0630	0.0400	0.00493
	30	0.0162	2.2483	0.0270	2.2634	2.2003	0.0480	0.0270	0.00353
		0.0202	2.2621	0.0320	2.2801	2.2051	0.0570	0.0320	0.00416
		0.0342	2.2670	0.0351	2.2867	2.2044	0.0625	0.0351	0.00456
		0.0375	2.2739	0.0441	2.2987	2.1953	0.0786	0.0441	0.00573
		0.0416	2.2880	0.0460	2.3138	2.2061	0.0819	0.0460	0.00594
	40	0.0162	2.2756	0.0276	2.2898	2.2218	0.0538	0.0276	0.00375
		0.0202	2.2931	0.0332	2.3101	2.2283	0.0648	0.0332	0.00449
		0.0342	2.2982	0.0353	2.3162	2.2294	0.0688	0.0353	0.00476
		0.0375	2.3056	0.0463	2.3293	2.2153	0.0903	0.0463	0.00625
		0.0416	2.3220	0.0478	2.3465	2.2287	0.0933	0.0478	0.00641

Table-7.2:- Measured  $\tau_j$ 's from ratio of slopes of individual variations of  $\chi'_{ij}$  and  $\chi''_{ij}$  with  $\omega_j$ , estimated relaxation time  $\tau_i$ , reported  $\tau_i$  all are in pico second, estimated dipole moments ( $\mu_j$ ) using  $\tau_j$  of eq. (7.10), estimated  $\mu_s$ , reported  $\mu_j$  and theoretical dipole moment  $\mu_{theo}$  using bond moments in Coulomb - metre of some para compounds in non-polar solvents at different experimental temperatures under 10 GHz electric field.

System with Sl.no. & molecular weight (Mj) in Kg	Temp. in $^{\circ}\text{C}$	Measured $\tau_j$ in p-sec using eq.(7.10)	$\tau_j$ in p-sec by eq.(5)	Reported $\tau_j$ in p-sec	Estimated hf $\mu_j \times 10^{30}$ in C.m.	Estimated $\mu_s \times 10^{30}$ in C.m.	Reported $\mu \times 10^{30}$ in C.m.	Corrected $\mu_{theo} \times 10^{30}$ in C.m.
1. p-hydroxy propiophenone Mj = 0.150 Kg	17	19.20	19.20	-	-	-		
	23	21.21	21.21	25.40	14.28	14.65	10.20	14.27
	30	24.08	24.08	24.20		-		
	37	14.37	14.37	23.10	10.25	10.16		
2. P-chloro propiophenone Mj = 0.1685 Kg	19	11.40	11.40	20.80	5.33	5.61	9.84	7.27
	25	19.26	19.26	19.20	-	-		
	31	25.60	25.60	18.20	-	-		
	37	7.30	7.30	17.10	7.28	6.46		
3. P-acetamido benzaldehyde Mj = 0.163 Kg	17	27.10	27.10	21.80	15.96	16.07		
	23	21.09	21.09	20.80	12.62	12.60	10.37	12.62
	30	23.86	23.86	19.00	20.57	20.40		
	37	21.07	21.06	18.60	26.85	26.12		
4. P-benzyloxy benzaldehyde Mj = 0.212 Kg	20	27.13	27.12	20.00	-	-		
	25	15.77	15.77	19.40	10.22	10.34	10.63	10.22
	30	19.03	19.03	18.00	-	-		
	35	12.92	12.92	16.90	6.12	6.05		
5. P-anisidine Mj = 0.123 Kg	20	8.19	9.21	3.89	9.29	9.38	5.20	8.56
	30	6.28	10.86	3.67	12.43	12.78	10.33	
	40	3.85	11.34	3.17	4.84	4.47	8.87	
6. P-phenitidine Mj = 0.0.137 Kg	20	10.41	9.82	11.08	29.35	29.22	7.47	29.36
	30	9.19	10.17	10.63	11.06	9.55	9.27	
	40	8.10	9.91	9.95	20.32	20.26	10.47	
7. O-chloro p-nitro aniline Mj = 0.1725 Kg	20	10.52	10.52	10.57	2.41	2.33	8.13	2.41
	30	7.95	20.47	9.89	1.87	1.97	10.93	
	40	7.64	30.59	9.18	1.38	1.17	13.10	
8. P-bromo nitrobenzene Mj = 0.202 kg	20	10.10	8.40	-	4.23	4.36	-	4.23
	30	8.93	8.93	-	-	-	-	
	40	8.15	8.16	-	-	-	-	

Table-7.3 :The intercepts and slopes of  $\ln\tau_j T$  against  $1/T$  curves of Fig. 7.3, thermodynamic energy parameters like enthalpy of activation  $\Delta H_\tau$  in Kilo Joule mole<sup>-1</sup>, the entropy of activation  $\Delta S_\tau$  in Joule mole<sup>-1</sup> K<sup>-1</sup>, free energy of activation  $\Delta F_\tau$  in Kilo Joule mole<sup>-1</sup> for dielectric relaxation process, enthalpy of activation  $\Delta H_\eta$  in kilo Joule mole<sup>-1</sup> due to viscous flow,  $\delta$  as the ratio of  $\Delta H_\tau$  and  $\Delta H_\eta$ , kalman factor  $(\tau_j T/\eta^\delta)$ , Debye factor  $(\tau_j T/\eta)$  at different experimental temperatures in °C and the coefficients of  $\mu_j - t$  equations  $\mu_j = a + bt + ct^2$  of different para compounds in dioxane and benzene under 10 GHz electric field frequency.

System with Sl.no. & mole ular weight (Mj) in Kg	Tem p in °C	Intercept & slope of $\ln\tau_j T$ Vs $1/T$ equation		$\Delta H_\tau$ i n KJ mole <sup>-1</sup>	$\Delta S_\tau$ in J mole <sup>-1</sup> K <sup>-1</sup>	$\Delta F_\tau$ in KJ mole <sup>-1</sup>	$\gamma =$ ( $\Delta H_\tau /$ $\Delta H_\eta$ )	$\Delta H_\eta$ in KJ mole <sup>-1</sup>	Kalman factor ( $\tau_j T/\eta^\delta$ )	Debye factor ( $\tau_j T/\eta$ ) $\times 10^6$	Coefficients in the eqs $\mu_j$ $\times 10^{30} = a + bt + ct^2$ equation		
		Intercept	slope								a	b	c
p-hydroxy propionophenone Mj = 0.150 Kg	17				-19.29	11.50			$1.40 \times 10^{-7}$	3.88			
	23	-21.33	708.00	5.91	-20.71	12.03	0.49	11.99	$1.66 \times 10^{-7}$	4.83	-0.02	1.15	-11.49
	30				-22.42	12.70			$2.06 \times 10^{-7}$	6.40			
	37				-18.74	11.72			$1.30 \times 10^{-7}$	4.52			
P-chloro propionophenone Mj = 0.1685 g	19				-1.59	10.33			$1.48 \times 10^{-6}$	2.40			
	25	-23.20	1182.4	9.86	-6.81	11.89	0.92	10.68	$2.81 \times 10^{-6}$	4.57	0.0875	-4.8	65.11
	31				-10.01	12.90			$4.22 \times 10^{-6}$	6.95			
	37				-0.33	9.96			$1.38 \times 10^{-6}$	2.30			
P- acetamido benzaldehyde Mj = 0.163 Kg	17				-27.27	12.33			$5.48 \times 10^{-8}$	5.48			
	23	-20.56	530.45	4.42	-25.66	12.02	0.30	14.92	$4.48 \times 10^{-8}$	4.80	0.0595	-2.06	35.89
	30				-27.23	12.68			$5.40 \times 10^{-8}$	6.34			
	37				-26.71	12.71			$5.09 \times 10^{-8}$	6.63			
P-benzyloxy benzaldehyde Mj = 0.212 Kg	20				53.72	12.49			$1.50 \times 10^{-3}$	5.81			
	25	-30.30	3384.2	28.23	56.49	11.39	1.84	15.32	$1.04 \times 10^{-3}$	3.74	-0.041	2.42	30.10
	30				53.21	12.10			$1.53 \times 10^{-3}$	5.06			
	35				54.79	11.35			$1.31 \times 10^{-3}$	3.94			
P-anisidine Mj = 0.123 Kg	20				56.96	9.56			$2.78 \times 10^{-4}$	3.89			
	30	-30.55	3147.2	26.25	55.93	9.30	4.07	6.45	$3.24 \times 10^{-4}$	3.39	-0.054	3.00	29.22
	40				56.98	8.42			$2.73 \times 10^{-4}$	2.30			
P- phenitidine Mj 0.0.137 Kg	20				-10.58	10.15			$2.44 \times 10^{-5}$	4.94			
	30	-22.49	844.99	7.05	-10.62	10.26	1.11	6.37	$2.08 \times 10^{-5}$	4.96	0.1377	-8.71	148.55
	40				-10.58	10.36			$2.48 \times 10^{-5}$	4.85			
O-chloro p- nitro aniline Mj = 0.1725 g	20				-1.22	10.17			$4.22 \times 10^{-4}$	5.00			
	30	-23.65	1177.0	9.82	-0.26	9.90	1.60	6.14	$3.85 \times 10^{-4}$	4.29	0.0002	-0.06	3.575
	40				-1.24	10.21			$4.27 \times 10^{-4}$	4.57			
P-bromo nitrobenzene Mj = 0.202 kg	20				-15.07	10.07			$1.95 \times 10^{-6}$	4.79			
	30	-21.96	678.44	5.66	-14.96	10.19	0.90	6.32	$1.94 \times 10^{-6}$	4.82	0.0211	-1.48	25.35
	40				-15.07	10.38			$1.95 \times 10^{-6}$	4.88			

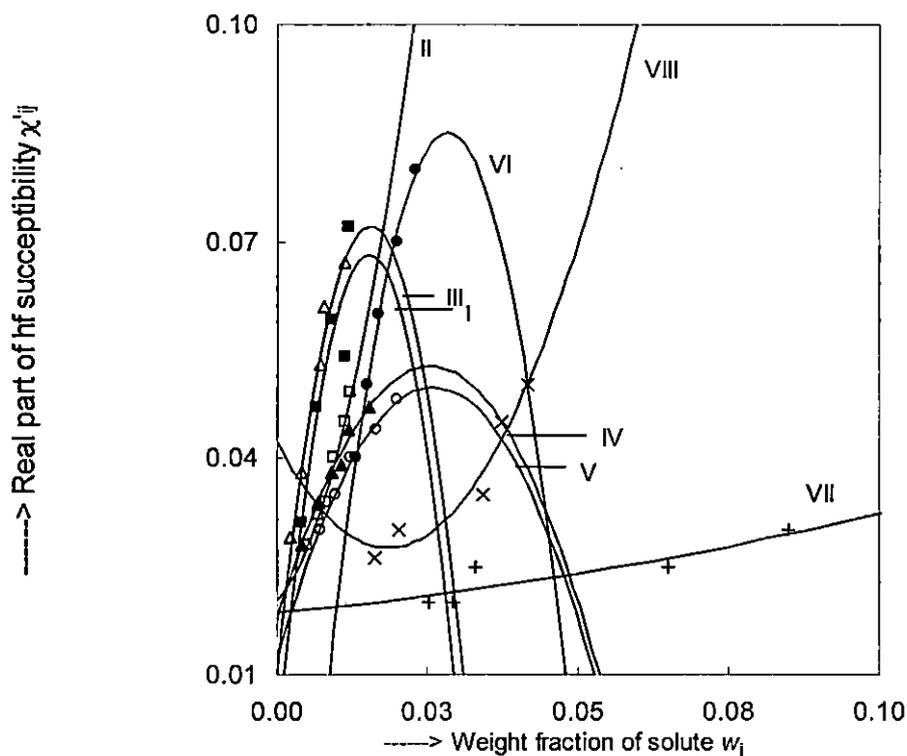


Fig-7.1: Variation of real part  $\chi'_{ij}$  of hf complex orientational susceptibility against weight fraction  $w_1$  of solute of some para compounds at selected temperatures in nonpolar solvents ( dioxane and benzene ) under 10 GHz electric field frequency I. p-hydroxypropiofenone (-- ■ --) at 23<sup>o</sup> C, II.p-chloropropiofenone (-- □ --) at 19<sup>o</sup> C, III.P-acetamidobenzaldehyde (-- △ --) at 17<sup>o</sup> C, IV .p-benzyloxybenzaldehyde (-- ▲ - -) at 25<sup>o</sup> C, V. p-anisidine (-- o-- ) at 20<sup>o</sup> C, VI. p-phenitidine (-- • --) at 40<sup>o</sup> C, VII. o-chloro-p-nitroaniline (-- + --) at 30<sup>o</sup> C, VIII. p-bromonitrobenzene (-- x --) at 20<sup>o</sup> C .

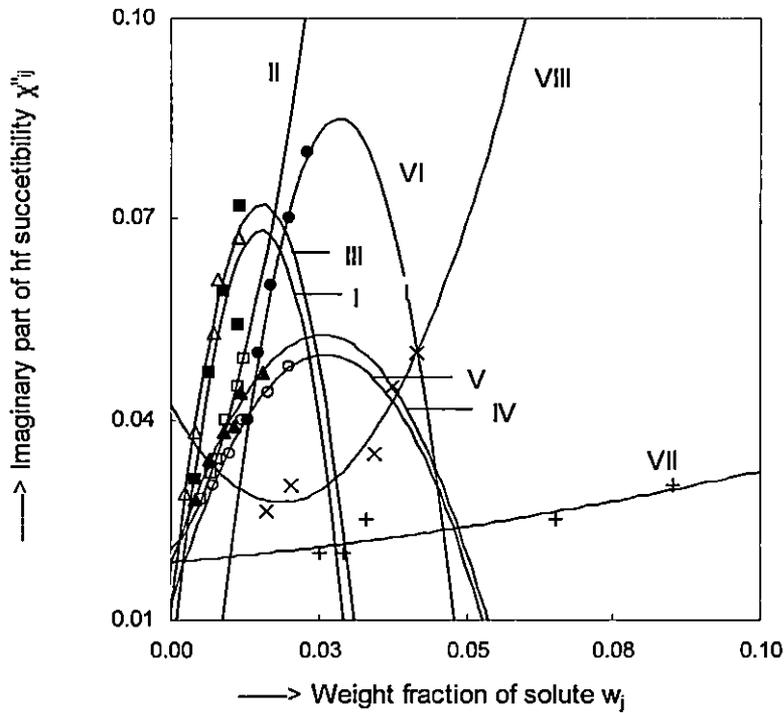


Fig.7.2: Variation of imaginary part  $\chi''_{ij}$  of hf complex orientational susceptibility against weight fraction  $w_j$  of solute of some para compounds at selected temperatures in nonpolar solvents ( dioxane and benzene ) under 10 GHz electric field frequency. I. p-hydroxypopiophenone (-- ■ --) at 23<sup>o</sup> C, II.p-chloropropiophenone (-- □ --) at 19<sup>o</sup>C, III.P-acetamidobenzaldehyde (-- △ --) at 17<sup>o</sup>C, IV .p-benzyloxybenzaldehyde (-- ▲ --) at 25<sup>o</sup>C, V. p-anisidine (-- o-- ) at 20<sup>o</sup>C, VI. p-phenitidine (-- • --) at 40<sup>o</sup>C, VII. o-chloro-p-nitroaniline (-- + --) at 30<sup>o</sup>C, VIII. p-bromonitrobenzene (-- x --) at 20<sup>o</sup>C .

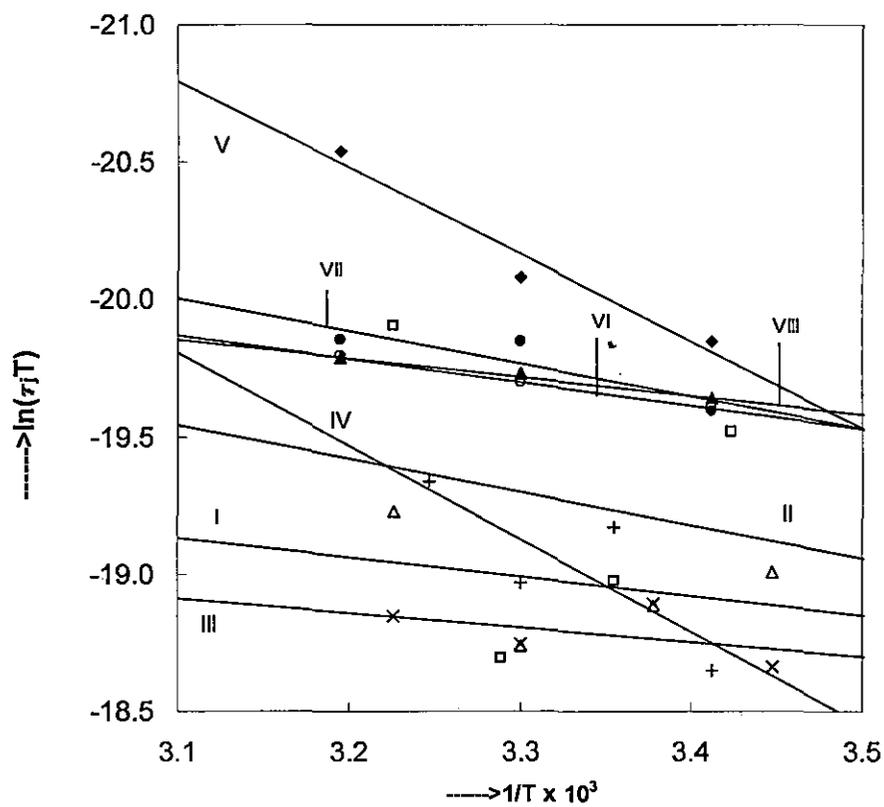


Fig. 7.3 .Straight line plots of  $\ln(\tau_i T)$  against  $1/T$  I. p-hydroxypropiophenone ( $-\Delta-$ ). II. P-chloroprolohenone ( $-\square-$ ). III. P-acetamidobenzaldehyde ( $-\times-$ ). IV. P-benzyloxybenzaldehyde ( $-\+-$ ). V. P-anisidine ( $-\blacklozenge-$ ). VI. P-phenitidine ( $-\circ-$ ). VII. o-chloro-p-nitroaniline ( $-\bullet-$ ). VIII. P-bromonitrobenzene ( $-\blacktriangle-$ ).

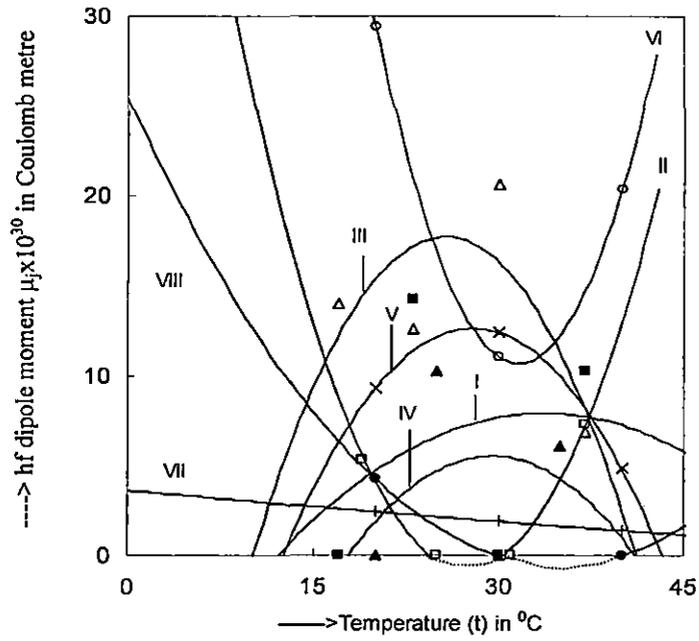


Fig. 7.4 Variation of estimated hf dipole moments  $\mu_j \times 10^{30}$  in Coulomb metre against  $t$  in  $^{\circ}\text{C}$ . I. p-hydroxy propiophenone (—■—) II. p-chloropropiophenone (—□—) III. p-acetamidobenzaldehyde (—△—) IV. p-benzyloxybenzaldehyde (—▲—) V. p-anisidine (—x—) VI. p-phenitidine (—o—) VII. o-chloro-p-nitroaniline (—+—) VIII. p-bromonitrobenzene (—•—)

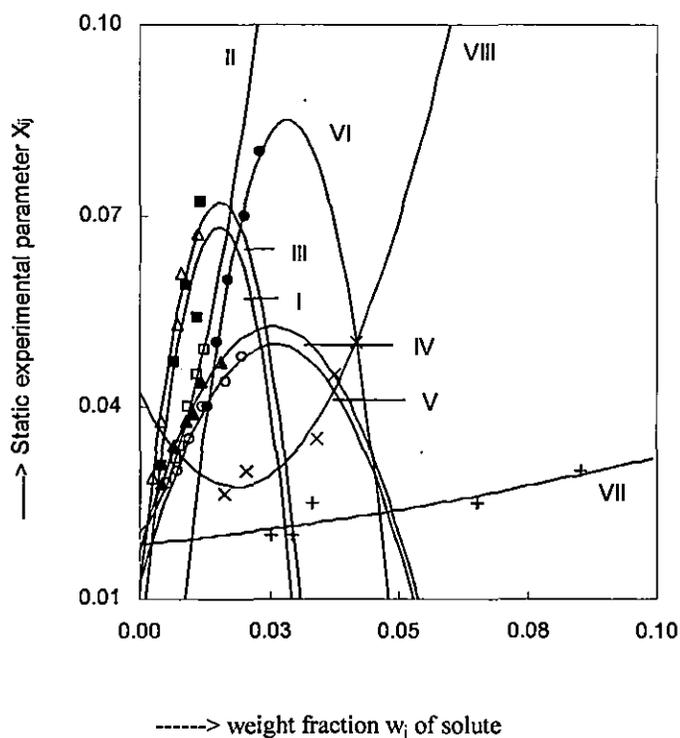


Fig. 7.5 Variation of static experimental parameter  $X_j$  against weight fraction  $w_1$  of solute of some para compounds at temperatures in nonpolar solvents ( dioxane 7 benzene ) under 10 GHz electric field frequency. I. p-hydroxypropiphenone (—■—) at 23°C, II. p-chloropropiphenone (—□—) at 19°C III. P-acetamidobenzaldehyde (—△—) at 17°C, IV. P-benzyloxybenzaldehyde (—▲—) at 5°C, V p-anisidine (—○—) at 20°C, VI.p-phenitidine (—●—) at 40°C, VII.o-chloro p-nitroaniline (—+—) at 30°C,VIII.p-bromonitrobenzene (—x—) at 20°C

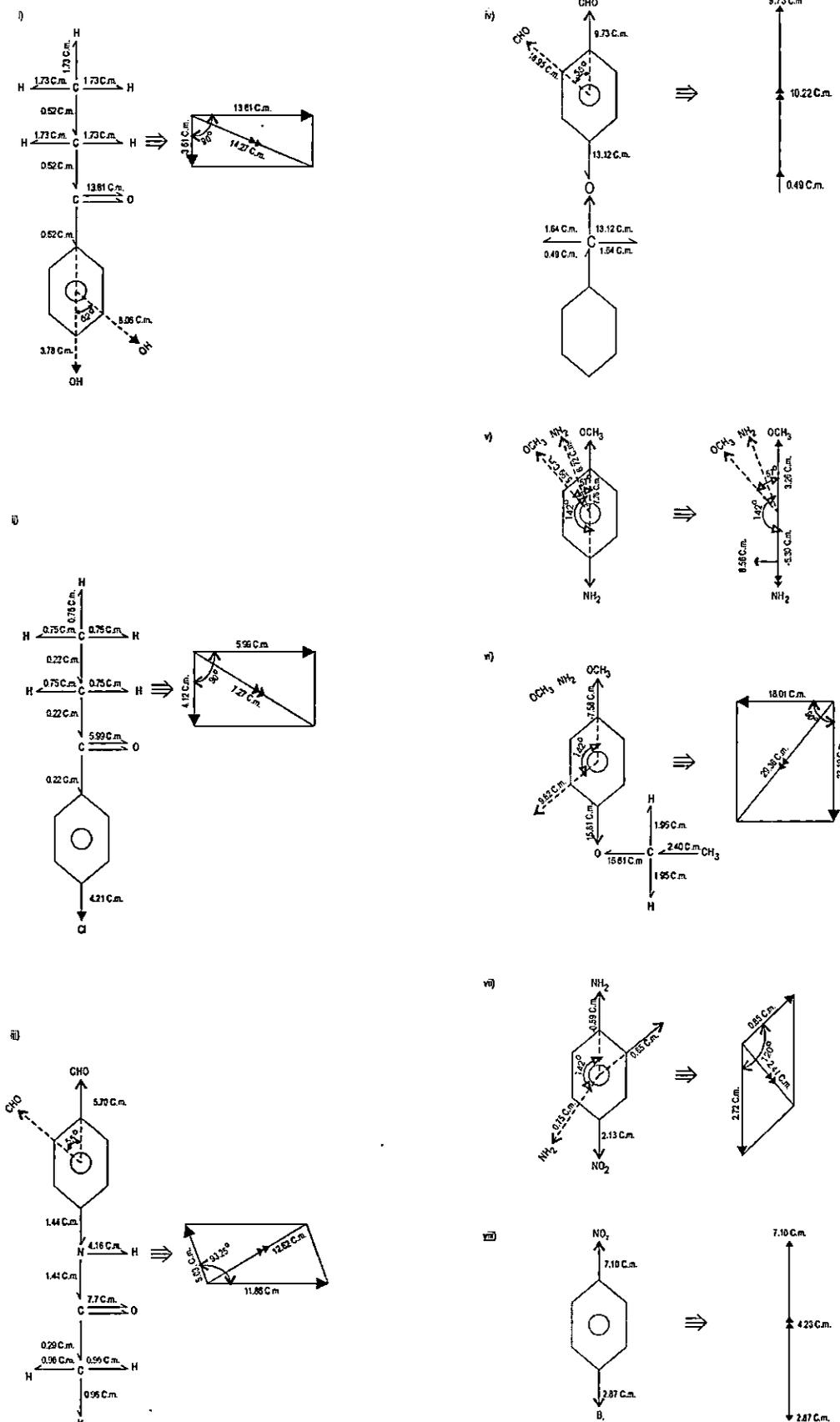


Fig. 7.6 Confrontational structures from available bond moments and bond angles of para compounds: (i) para-hydroxypropiophenone (ii) para-chloropropiophenone (iii) para-acetamidobenzaldehyde (iv) para-benzyloxybenzaldehyde (v) para-anisidine (vi) para-phenitidine (vii) ortho-chloroparanitroaniline and (viii) para-bromonitrobenzene

## REFERENCES

- [1] H D Purohit, and H S Sharma, *Bull. Chem. Soc. Japan.* **50** (1977) 2606
- [2] F L Mopisk and R H Cole, *J Chem.Phys* **44** (1966) 1015
- [3] S Acharyya, A K Chatterjee , P Acharyya and I L Saha , *Ind J Phys* **56** (1982) 291
- [4] S K Sit , N Ghosh, U Saha and S Acharyya , *Indian J Phys* **71B** (1997) 533
- [5] N Paul , K P Sharma and S Chattopadhyay, *Indian J Phys* **71B** (1997 ) 711
- [6] R L Dhar , A Mathur , J P Shukla and M C Saxena , *Indian J Pure & Appl Phys* **11** (1973) 568
- [7] S K S Somevanshi, S B I Misra and N K Mehrotra , *Indian J Pure & Appl Phys* **16** (1978) 57
- [8] *Hand Book of Chemistry and Physics*. CRC Press 58th Edition 1977-78
- [9] N Ghosh, R C Basak, S K Sit and S Acharyya, *J Mol Liquids (Germany)* **85** (2000) 375
- [10] F J Murphy and S O Morgan , *Bell Syst Tech J* **18** (1939) 502
- [11] M B R Murthy, R L Patil and D K Deshpande, *Indian J Phys* **63B** (1980) 491
- [12] N Ghosh, A Karmakar, S K Sit and S Acharyya, *Indian J Pure & Appl Phys* **38** (2000 ) 574
- [13] P Debye '*Polar Molecules*' (Chemical Catalogue) 1929
- [14] H Eyring, S Glasstone and K J Laidler '*The Theory of Rate Process*' ( Mc Graw Hill: New York) 1941
- [15] K Dutta, A Karmakar, L Dutta, S K Sit and S Acharyya, *Indian J Pure & Appl Phys* **40** (2002 ) 801
- [16] N Ghosh, S K Sit, A K Bothra and S Acharyya, *J Phys D : Appl Phys* **34** (2001) 379
- [17] C P Smyth, '*Dielectric Behaviour and Structure*' ( Mc Graw Hill: New York) 1955
- [18] N Ghosh, S K Sit, and S Acharyya , *J Mol Liquids (Germany)* **102** (2003) 29
- [19] S C Srivastava and S Chandra, *Indian J Pure & Appl Phys* **13** (1975) 101
- [20] F H Branin (Jr) and C P Smyth J., *Chem Phys* **02** (1952) 1120
- [21] S K Garg and C P Smyth, *J Phys Chem* **69** (1965) 1294
- [22] K Dutta, S K Sit and S Acharyya, *J Mol liquids* **92** (2001) 263
- [23] K Dutta, A Karmakar, S K Sit, and Acharyya, *Pramana J phys* (communicated) 2004