

*Chapter 7*

**RELAXATION PHENOMENA IN METHYL  
BENZENES AND KETONES FROM ULTRA HIGH  
FREQUENCY CONDUCTIVITY**

## 7.1. Introduction :

Relaxation processes in dielectric polar liquid or solid material (DRL or DRS) are very encouraging to study the molecular behaviours and structures through various experimental techniques [7.1-7.2]. The methods are involved with the high frequency conductivity [7.3] or susceptibility measurements [7.4], thermally stimulated depolarisation current [7.5] (TSDC) and time or frequency domain dielectric AC spectroscopy [7.6] etc. The latter two methods consist of a tedious computer simulated calculation in comparison to others, which are very simple and straightforward within the framework of Debye and Smyth model of dielectric liquid molecule.

Vaish and Mehrotra [7.7-7.8] measured real and imaginary parts  $\epsilon_{ij}'$  and  $\epsilon_{ij}''$  of complex dielectric relative permittivity  $\epsilon_{ij}^*$  of some methyl benzenes and ketones (j) in benzene (i) under 3.13 cm wavelength electric field at 25 °C. They attempted to correlate dielectric relaxation times with those of nuclear magnetic resonance spin lattice relaxation times by using the theory of Bloembergen et al [7.9] in terms of measured relaxation parameters. The relaxation times  $\tau$  of the molecules were calculated on the assumption that dipole-dipole (dimer) interaction occurs between the nuclear spins. The spin lattice relaxation times were obtained to compare with the Gopalakrishna, Debye and other methods. The experimental value differs significantly from those of theoretical one. This study reveals that  $\tau$  plays the main role in inter and intra molecular motions and nuclear magnetic resonance (NMR) spin lattice relaxation etc.

The values of  $\tau$  and dipole moment  $\mu$  of these polar molecules by the conductivity technique have been calculated in the present paper. The procedures employed to get  $\tau$  are those of Murthy et al [7.10] from the direct slope of the linear equation of imaginary  $\sigma_{ij}'' (= \omega \epsilon_0 \epsilon_{ij}'')$  in  $\Omega^{-1} \text{ m}^{-1}$  and real  $\sigma_{ij}' (= \omega \epsilon_0 \epsilon_{ij}')$  in  $\Omega^{-1} \text{ m}^{-1}$  parts of the hf complex conductivity  $\sigma_{ij}^*$  (Fig.7.1) and the ratio of the individual slopes of  $\sigma_{ij}'' - w_j$  and  $\sigma_{ij}' - w_j$  curves [7.11] (Figs.5.2 & 5.3) at  $w_j \rightarrow 0$  respectively. The use of the ratio of individual slopes to estimate  $\tau$  seems to be better as it eliminates the polar-polar interaction almost completely. Hence the purpose of the present paper is to study the success or otherwise of the proposed theory with the existing ones to infer molecular structures and associations. The graphs of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  with  $w_j$ 's in Figs.7.2 & 7.3 are found to be nonlinear to indicate the presence of solute-

Table 7.1 : Slope and intercepts of Eq.(7.2), correlation coefficient  $r$ , ratio of the individual slopes of  $\sigma_{ij}''-w_j$  and  $\sigma_{ij}'-w_j$  curves at  $w_j \rightarrow 0$ , relaxation time  $\tau_j$  from Eqs (7.3) and (7.4) and from Gopalakrishna's method of some methyl benzenes and ketones in benzene at 25°C under 9.585 GHz electric field.

System with sl.no.	Slope and intercepts of Eq.(7.3)		Corrl. coeff. $r$	Ratio of individual slopes of $\sigma_{ij}''-w_j$ and $\sigma_{ij}'-w_j$ at $w_j \rightarrow 0$	Relaxation times $\tau_j$ ( $\times 10^{12}$ ) in sec.		
					$\tau_j^a$	$\tau_j^b$	$\tau_j^g$
(I) toluene	1.8468	1.1385	0.9527	4.3891	8.99	3.78	8.24
(II) 1,3,5 tri methylbenzene	0.7897	1.1844	0.9755	2.8782	21.03	5.77	19.93
(III) 1,2,3,4 tetra methyl benzene	8.3666	1.1992	0.9678	6.5797	1.98	2.52	1.94
(IV) 1,2,4,5 tetra methyl benzene	1.9531	1.1854	0.9890	1.6133	8.50	10.29	8.06
(V) penta methyl benzene	1.3836	1.1770	0.9948	3.8814	12.00	4.28	11.02
(VI) <i>p</i> -fluorotoluene	4.8910	1.2071	0.9941	8.2548	3.39	2.01	3.12
(VII) butyl ethyl ketone	1.0070	1.1878	0.9481	40.3859	16.48	0.41	15.84
(VIII) methyl hexyl ketone	0.8452	1.1737	0.9993	0.6003	19.65	27.66	18.13
(IX) ethyl pentyl ketone	0.8640	1.1713	0.9686	0.6928	19.22	23.97	18.40
(X) heptyl methyl ketone	0.8203	1.1838	0.9859	1.8590	20.24	8.93	19.01

$\tau_j^a$  = Relaxation time from Eq. (7.3)

$\tau_j^b$  = Relaxation time from Eq. (7.4)

$\tau_j^g$  = Relaxation time from Gopalakrishna's method of Eq. (7.9)

solute associations in the mixture.  $\tau$ 's from linear slope are found to agree with the reported  $\tau$ 's from Gopalakrishna's fixed frequency method of Fig.7.4 and are presented in Table 7.1 together with all the measured  $\tau$ 's by different procedures. Further, the polar molecules under investigation are methyl substituted aromatic and ketone substituted aliphatic compounds of highly nonspherical nature. Methyl substituted benzenes and ketones have almost similar characteristics. Some of the methyl benzenes are supposed to have apparently zero dipole moment from bond moment calculation. Moreover, these molecules are supposed to absorb electric energy much more strongly in the effective dispersive region of nearly 10 GHz at which peak of the absorption curve occurs. The ketones, on the other hand, are pleasant smelling liquids and widely used in petroleum industry. These liquids are

used, as good solvents of synthetic rubber, wax etc. The study of the variation of  $\tau$  with respect to various substituted polar groups attached to different positions of the parent molecules may throw much light on the structural conformations of the methyl benzene and ketone molecules. We had already made a detailed investigation on some polysubstituted benzenes [7.12] at various temperatures to get molecular structures by conductivity technique. Dielectric parameters are very much temperature dependent. Calculations at some other temperature may reveal a better picture. Nevertheless, from these studies it may be clear as to what theory is valid for such highly nonspherical aliphatic and aromatic compounds. A systematic comparison of  $\tau$  and  $\mu$  can thus be made from the measured data at 25°C.

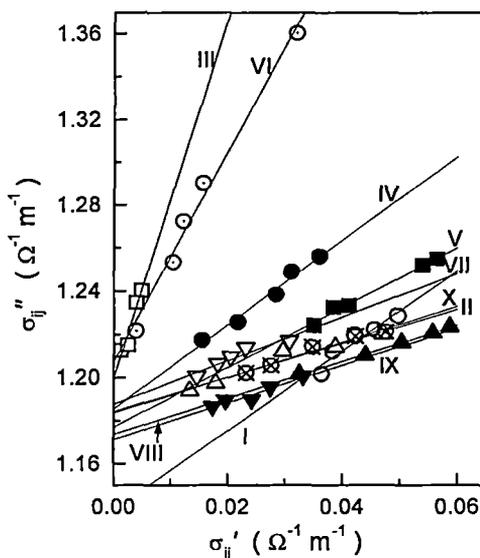


Figure.7.1 : The linear variation of imaginary part  $\sigma_{ij}''$  against real part  $\sigma_{ij}'$  of complex  $hf$  conductivity  $\sigma_{ij}$  at 25°C under 9.585 GHz electric field :

- (I) Toluene (-O-) (II) 1,3,5 tri methyl benzene (-Δ-) (III) 1,2,3,4 tetra methyl benzene (-□-) (IV) 1,2,4,5 tetra methyl benzene (-●-) (V) penta methyl benzene (-■-) (VI) *p*-fluoro toluene (-⊙-) (VII) Butyl ethyl ketone (-▽-) (VIII) Methyl hexyl ketone (-▲-) (IX) Ethyl pentyl ketone (-▼-) (X) heptyl methyl ketone (-⊗-)

The corresponding dipole moments  $\mu_j$ 's of these liquids are obtained from the linear coefficient  $\beta$  of  $uhf$  conductivity  $\sigma_{ij}$  curves against  $w_j$ 's of Fig.7.5. All the  $\beta$ 's and  $\mu$ 's are tabulated in Table 7.2 with those from Gopalakrishna and theoretical conformational

calculation of Fig.7.6. The inductive, mesomeric and electromeric effects under 3 cm wavelength electric field play the vital role in determining the theoretical  $\mu_{\text{theo}}$ 's of the molecules of Fig.7.6 in agreement with estimated  $\mu_j$ 's.

## 7.2. High Frequency Conductivity Technique to Estimate $\tau$ and $\mu$ :

The ultra high frequency (uhf) complex conductivity [7.13]  $\sigma_{ij}^*$  is :

$$\sigma_{ij}^* = \sigma'_{ij} + j\sigma''_{ij} \quad \dots (7.1)$$

where  $\sigma'_{ij} = \omega \epsilon_0 \epsilon_{ij}''$  and  $\sigma''_{ij} = \omega \epsilon_0 \epsilon_{ij}'$  are the real and imaginary parts of  $\sigma_{ij}^*$ ,  $\epsilon_0 =$  absolute permittivity of free space  $= 8.854 \times 10^{-12} \text{ F.m}^{-1}$  and  $\omega (= 2\pi f)$  is the angular frequency of the applied electric field of frequency,  $f = 9.585 \times 10^9 \text{ Hz}$ .

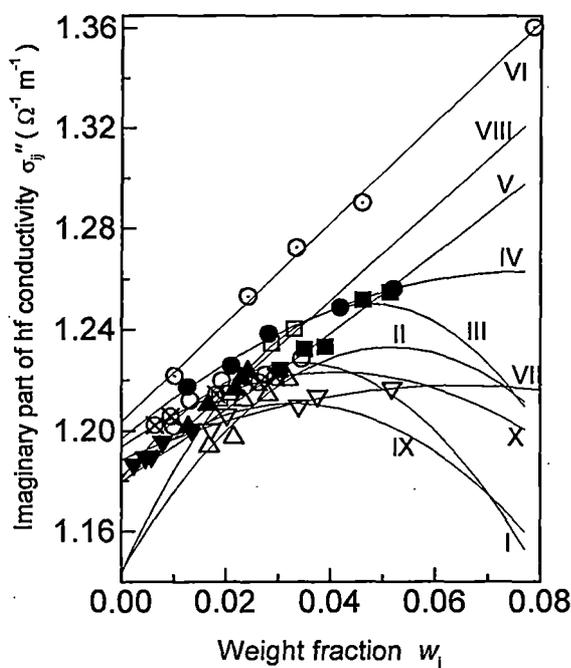


Figure.7.2: Variation of imaginary part of conductivity  $\sigma_{ij}''$  against  $w_1$  at  $25^\circ\text{C}$  under 9.585 GHz electric field :

- (I) Toluene (-O-), (II) 1,3,5 tri methyl benzene (-Δ-), (III) 1,2,3,4 tetra methyl benzene (-□-), (IV) 1,2,4,5 tetra methyl benzene (-●-), (V) penta methyl benzene (-■-), (VI) p-fluoro toluene (-⊙-), (VII) Butyl ethyl ketone (-∇-), (VIII) Methyl hexyl ketone (-▲-), (IX) Ethyl pentyl ketone (-▼-), (X) heptyl methyl ketone (-⊗-)

Table 7.2 : Coefficients of  $\sigma_{ij}-w_j$  curves, dimensionless parameter  $b [=1/(1+\omega^2\tau^2)]$ , dipole moment  $\mu_j$  in Coulomb.metre from  $\tau$ 's of Eq.(7.3), (7.4) and Gopalakrishna's method and the theoretical dipole moment  $\mu_{theo}$  from the available bond angles and bond moments of some methyl benzenes and ketones in benzene at 25°C under 9.585 GHz electric field.

System with sl.no.and mol.wt.	Coefficients of $\sigma_{ij} = \alpha + \beta w_j + \xi w_j^2$			Values of b by using $\tau$ of		Dipole moment ( $\times 10^{-30}$ ) C.m			
	$\alpha$	$\beta$	$\xi$	Eq.(7.3)	Eq.(7.4)	$\mu_j^a$	$\mu_j^b$	$\mu_j^g$	$\mu_{theo}$
(I) toluene $M_j=0.092$ Kg	1.1811	2.7545	-40.2180	0.7733	0.9507	7.93	7.15	7.80	1.23
(II) 1,3,5 tri methylbenzene $M_j= 0.120$ Kg	1.1446	3.4010	-31.2102	0.3840	0.8923	14.27	9.36	13.94	0.00
(III) 1,2,3,4 tetra methyl benzene $M_j=0.134$ Kg	1.1436	4.4952	-47.2133	0.9860	0.9775	10.82	10.87	10.82	0.00
(IV) 1,2,4,5 tetra methyl benzene $M_j=0.134$ Kg	1.1969	1.7313	-11.2125	0.7924	0.7225	7.49	7.84	7.39	0.00
(V) penta methyl benzene $M_j=0.148$ Kg	1.1798	1.4009	2.2168	0.6569	0.9377	7.78	6.51	7.63	1.23
(VI) p- fluoro toluene $M_j=0.110$ Kg	1.2039	1.9329	0.7021	0.9600	0.9856	6.52	6.43	6.53	6.23
(VII) butyl ethyl ketone $M_j=0.114$ Kg	1.1885	0.9115	-6.8748	0.5038	0.9994	6.29	4.46	6.19	8.09
(VIII) methyl hexyl ketone $M_j=0.128$ Kg	1.1790	1.8073	2.1902	0.4166	0.2649	10.32	12.94	10.05	8.14
(IX) ethyl pentyl ketone $M_j=0.128$ Kg	1.1820	1.7921	-27.0543	0.4274	0.3243	10.14	11.64	10.01	8.14
(X) heptyl methyl ketone $M_j=0.142$ Kg	1.1939	1.4569	-17.0797	0.4023	0.7757	9.93	7.15	9.60	8.20

$\mu_j^a$  = Dipole moment from Eq.(7.7) by using  $\tau_j$  of Eq. (7.3)

$\mu_j^b$  = Dipole moment from Eq. (7.7) by using  $\tau_j$  of Eq. (7.4)

$\mu_j^g$  = Dipole moment by Gopalakrishna's method of Eq. (7.10)

$\mu_{theo}$  = Theoretical dipole moment from the available bond angles and bond moments.

Debye equation [7.14] in the GHz region yields:

$$\sigma''_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau} \sigma'_{ij} \quad \dots (7.2)$$

$$\left( \frac{d\sigma''_{ij}}{d\sigma'_{ij}} \right) = \frac{1}{\omega\tau} \quad \dots (7.3)$$

Both  $\sigma''_{ij}$  and  $\sigma'_{ij}$  are functions of  $w_j$ . Their variations are nonlinear in the higher concentration region as seen in Figs.7.2 and 7.3. In this case one can write Eq.(7.2) as:

$$\left( \frac{d\sigma''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{1}{\omega\tau} \left( \frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} \quad \dots (7.4)$$

$\tau$ 's from both the Eqs.(7.3) and (7.4) were computed and are listed in Table 7.1 for comparison with the reported  $\tau$  recalculated from Gopalakrishna's method.

Since  $\epsilon_{ij} > \epsilon''_{ij}$ , but in hf region of GHz range  $\epsilon_{ij} \approx \epsilon''_{ij}$  where  $\epsilon''_{ij}$  offers resistance to polarisation and uhf conductivity  $\sigma_{ij}$  is  $\sigma_{ij} = \omega\epsilon_o (\epsilon'_{ij}{}^2 + \epsilon''_{ij}{}^2)^{1/2}$ . We can thus write Eq.(7.2) in the following form:

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

$$\left( \frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega\tau\beta \quad \dots (7.5)$$

$\beta$  is the slope of  $\sigma_{ij}$ - $w_j$  curve in the limit  $w_j = 0$  as observed in Fig.7.5 and listed in Table 7.2.

The real part  $\sigma'_{ij}$  of hf complex conductivity  $\sigma_{ij}^*$  is given by [7.12]

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

$$\left( \frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\mu_j^2 \rho_i}{27M_j k_B T} \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) (\epsilon_i + 2)^2 \quad \dots (7.6)$$

where density  $\rho_{ij}$  and local field  $F_{ij}$  of the solution become  $\rho_i$  and  $F_i = (\epsilon_i + 2)^2 / 9$  of the solvent in the limit  $w_j = 0$ .

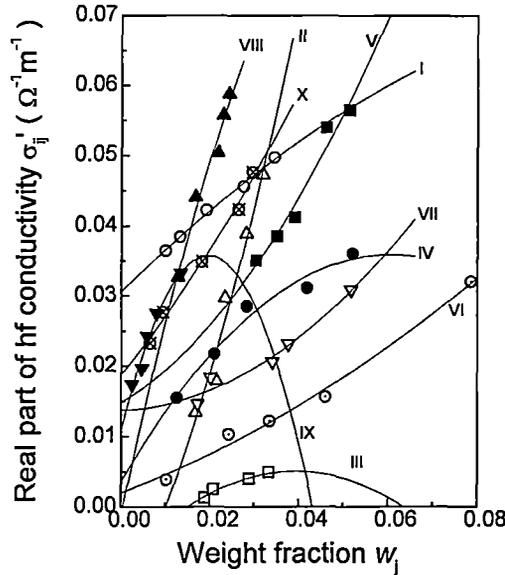


Figure 7.3 : Variation of real part of conductivity  $\sigma'_{ij}$  against  $w_j$  at  $25^\circ\text{C}$  under 9.585 GHz electric field :

(I) Toluene (-○-) (II) 1,3,5 tri methyl benzene (-△-) (III) 1,2,3,4 tetra methyl benzene (-□-) (IV) 1,2,4,5 tetra methyl benzene (-●-) (V) penta methyl benzene (-■-) (VI) p-fluoro toluene (-⊙-) (VII) Butyl ethyl ketone (-▽-) (VIII) Methyl hexyl ketone (-▲-) (IX) Ethyl pentyl ketone (-▼-) (X) heptyl methyl ketone (-⊗-)

From Eqs.(7.5) and (7.6) one gets hf dipole moment  $\mu_j$  as:

$$\mu_j = \left( \frac{27M_j k_B T \beta}{N \rho_i (\epsilon_i + 2)^2 \omega b} \right)^{\frac{1}{2}} \quad \dots (7.7)$$

where,

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

$\rho_i$  = density of solvent benzene at  $25^\circ\text{C}$  =  $874.3 \text{ Kg.m}^{-3}$

$\epsilon_i$  = relative permittivity of solvent benzene at 25°C = 2.274

$M_j$  = molecular weight of solute in Kg.

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

$b$  is the dimensionless parameter involved with measured  $\tau$  where  $b=1/(1+\omega^2\tau^2)$

Both the dipole moments  $\mu_j$ 's and dimensionless parameters  $b$ 's are presented in Table 7.2.

### 7.3. Results and Discussion :

The imaginary  $\sigma_{ij}'' (= \omega \epsilon_0 \epsilon_{ij}') \Omega^{-1} m^{-1}$  are plotted against real  $\sigma_{ij}' (= \omega \epsilon_0 \epsilon_{ij}'') \Omega^{-1} m^{-1}$  parts of hf complex conductivity  $\sigma_{ij}^*$  for different weight fractions  $w_j$ 's of solute according to Eq.(7.2) to get  $\tau$  of polar liquid molecules as shown in Fig.7.1. The variables are found to be almost linearly correlated as evident from the correlation coefficient 'r' of the straight line of Eq.(7.3). It appears from Fig.5.1 that the systems like (I), (II), (III) and (VII) show low values of r (Table 7.1) indicating their departure from perfect linearity of the variables. Perfect linearity is said to be achieved for  $-1 \leq r \leq 1$ . In such cases, the proposed method to determine  $\tau$  from the ratio of the individual slopes of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  against  $w_j$  according to Eq.(7.4) seems to be a better choice and is claimed to be the best improvement over the other two because polar-polar interaction is avoided almost completely in the limit  $w_j = 0$ . The estimated  $\tau$ 's for systems (III), (IV), (VI) and (IX) from Eq.(7.4) are in agreement with those of Murthy et al [7.10] and reported  $\tau$ . For the rest of the systems,  $\tau$ 's are lower from the ratio of individual slopes except methyl hexyl ketone. All the plots of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  against  $w_j$ 's as sketched in Figs.7.2 and 7.3 are parabolic in nature indicating the occurrence of associational aspect of polar liquid molecules in a non-polar solvent. The systems I(-○-), II(-△-), III(-□-), IV(-●-), VII(-▽-), IX(-▼-) and X(-⊗-) exhibit monotonic increase of  $\sigma_{ij}''$  with  $w_j$  like  $\sigma_{ij}-w_j$  curves of Fig.7.5 in order to attain maximum value at a certain concentration ( $w_j$ ) to show the convex nature. This is perhaps due to phase transition occurring in the polar-nonpolar liquid mixture as observed elsewhere [7.12]. Similar variation  $\sigma_{ij}''$  and  $\sigma_{ij}$  in  $\Omega^{-1} m^{-1}$  with  $w_j$  as displayed graphically in Figs.7.2 and 7.5 indicates the validity of the approximation of  $\sigma_{ij}'' \cong \sigma_{ij}$  of Eq.(7.5). All the curves of Figs.7.2 and 7.5 have a tendency to cut a point on the  $\sigma_{ij}$ -axis in the limit  $w_j=0$  except systems (II) and (III) probably due to solvation effect [7.15] of the polar-nonpolar liquid mixture. The plots of  $\sigma_{ij}'-w_j$  curves of Fig.7.3 are also parabolic in nature. The variation of  $\sigma_{ij}'$  against  $w_j$ 's for the

III(-□-), IV(-●-) and IX(-▼-) systems show convex shape indicating the maximum absorption of hf electric energy at  $w_j=0.04, 0.06$  and  $0.02$  respectively. The rest systems, display gradual increase of  $\sigma_{ij}'$  with  $w_j$  probably due to the fact that absorption of electric energy increases at the higher concentration. This is authenticated by the positive coefficient of the quadratic term in the fitted equations of  $\sigma_{ij}'-w_j$  curves of Fig.7.3. All the  $\tau$ 's of the polar liquid molecules of Table 7.1 agree well with those of Murthy et al [7.10] from Eq.(7.3) and reported value. The reported  $\tau$ 's based on the standard method of Gopalakrishna were found to be much higher [7.7-7.8] which prompted us to recalculate  $\tau$ 's from the following expression [7.16]:

$$x = \frac{\epsilon_{ij}'^2 + \epsilon_{ij}' + \epsilon_{ij}''^2 - 2}{(\epsilon_{ij}' + 2)^2 + \epsilon_{ij}''^2}; y = \frac{3\epsilon_{ij}''}{(\epsilon_{ij}' + 2)^2 + \epsilon_{ij}''^2} \quad \dots (7.8)$$

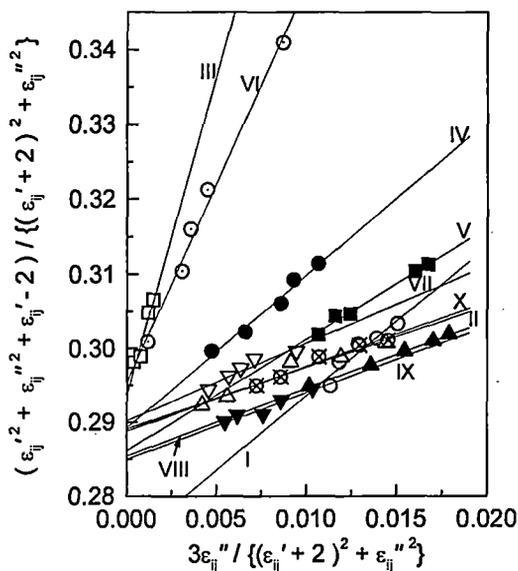


Figure 7.4: Linear plots of  $x$  against  $y$  for some methyl benzenes and ketones at  $25^{\circ}\text{C}$  under  $9.585$  GHz electric field:

- (I) Toluene (-○-), (II) 1,3,5 tri methyl benzene (-△-), (III) 1,2,3,4 tetra methyl benzene (-□-), (IV) 1,2,4,5 tetra methyl benzene (-●-), (V) penta methyl benzene (-■-), (VI) p-fluoro toluene (-⊙-), (VII) Butyl ethyl ketone (-▽-), (VIII) Methyl hexyl ketone (-▲-), (IX) Ethyl pentyl ketone (-▼-), (X) heptyl methyl ketone (-⊗-)

The variation of x against y of Eq.(7.8) are linear as seen in Fig.7.4. One can obtain  $\tau$  from:

$$\tau = \frac{1}{\omega(dx/dy)} \quad \dots (7.9)$$

$\mu_j$ 's are recalculated by using Gopalakrishna's equation [7.16] as:

$$\mu = \left[ \frac{9k_B T M_j}{4\pi N \rho_i} \left\{ 1 + \left( \frac{dy}{dx} \right)^2 \right\} \left( \frac{dx}{dw_j} \right)_{w_j \rightarrow 0} \right]^{\frac{1}{2}} \quad \dots (7.10)$$

$\tau$ 's from the ratio of the individual slopes of Eq.(7.4), on the other hand, are found to be in better agreement for the systems: 1,2,3,4 tetramethyl benzene (III); 1,2,4,5 tetramethyl benzene (IV); p-fluoro toluene (VI) and ethyl pentyl ketone (IX) respectively. The other systems exhibit low values of  $\tau$  from the ratio of individual slopes of  $\sigma_{ij}''$  and  $\sigma_{ij}'$  against  $w_j$ 's except methyl hexyl ketone (VIII). This behaviour can be explained on the basis of the fact that the methods of Murthy et al [7.10] and Gopalakrishna yield  $\tau$ 's of either a quasi isolated polar or a dimer (solute-solute association) molecule. The ratio of the individual slopes, on the other hand, takes into account both the processes in addition to  $\tau$  of a dimer molecule. The smaller value of  $\tau$  may be due to formation of monomer supported by low values of r of the systems under investigation.

Dipole moments  $\mu_j$ 's are computed from the slope  $\beta$  of uhf conductivity  $\sigma_{ij}$  against  $w_j$  curves of Fig.7.5 and dimensionless parameters b's of Eq.(7.7) to compare with the results of Eq.(7.10) of Gopalakrishna [7.16]. The  $\mu$ 's are now found to agree well as seen in Table 7.2 with Murthy et al [7.10] and recalculated values of Gopalakrishna for all the systems like  $\tau$ 's indicating the applicability of the methods for such systems under investigation.  $\sigma_{ij}$ 's of polar-nonpolar liquid mixtures are, however, concerned with the bound molecular charges which may be counted by  $\beta$  ( Table 7.2) of  $\sigma_{ij}-w_j$  curves of Fig.7.5. The agreement is better from Eqs.(7.4) and (7.7) with the use of the ratio of individual slopes for systems (I), (III), (IV), (VI) and (IX) respectively unlike other polar liquids where  $\mu$ 's are slightly lower except for methyl hexyl ketone. Low values of  $\mu$ 's may

be due to formation of monomer while high values are responsible for dimer formations. The slight difference between reported and estimated  $\mu$ 's may occur due to existence of steric hindrances among the substituted polar groups.

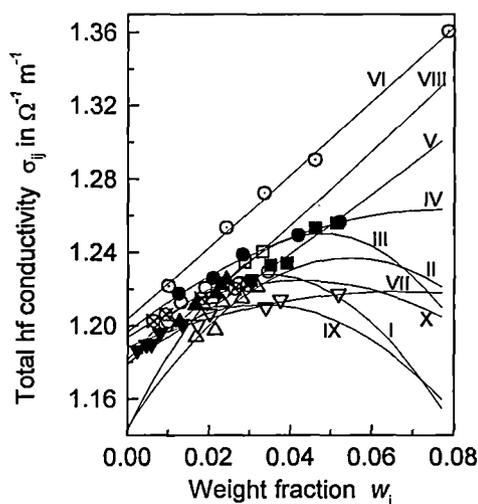


Figure 7.5 : The plot of uhf conductivity  $\sigma_{ij}$  against  $w_j$  :

(I) Toluene (-○-), (II) 1,3,5 tri methyl benzene (-△-), (III) 1,2,3,4 tetra methyl benzene (-□-), (IV) 1,2,4,5 tetra methyl benzene (-●-), (V) penta methyl benzene (-■-), (VI) p-fluoro toluene (-⊙-), (VII) Butyl ethyl ketone (-▽-), (VIII) Methyl hexyl ketone (-▲-), (IX) Ethyl pentyl ketone (-▼-), (X) heptyl methyl ketone (-⊖-)

The theoretical dipole moments  $\mu_{\text{theo}}$ 's are calculated on the basis of planar structures for the molecules from the available bond moments of  $\text{CH}_3 \rightarrow \text{C}$ ,  $\text{C} \leftarrow \text{O}$ ,  $\text{C} \leftarrow \text{C}$ ,  $\text{C} \rightarrow \text{F}$  and  $\text{C} \rightarrow \text{H}$  of  $1.23 \times 10^{-30}$ ,  $8 \times 10^{-30}$ ,  $0.3 \times 10^{-30}$ ,  $5.23 \times 10^{-30}$  and  $1 \times 10^{-30}$  in Coulomb-metre (C.m) respectively.  $\text{CH}_3 \rightarrow \text{C}$  makes an angle  $180^\circ$  with the bond axis. The direction of  $\text{C} \leftarrow \text{C}$  bond moment is taken in the reverse direction of bond axis [7.17]. All the substituted polar groups have the usual nature of either pushing or pulling electrons from the adjacent atoms of the parent molecules. Thus there exists a difference in electron affinity within each atom of the substituted polar groups causing inductive, mesomeric and electromeric effects in them, which play a role in the structure of the polar molecules of Fig.7.6. The solvent  $\text{C}_6\text{H}_6$  due to its aromaticity is a cyclic planar compound having three alternate single and double bonds

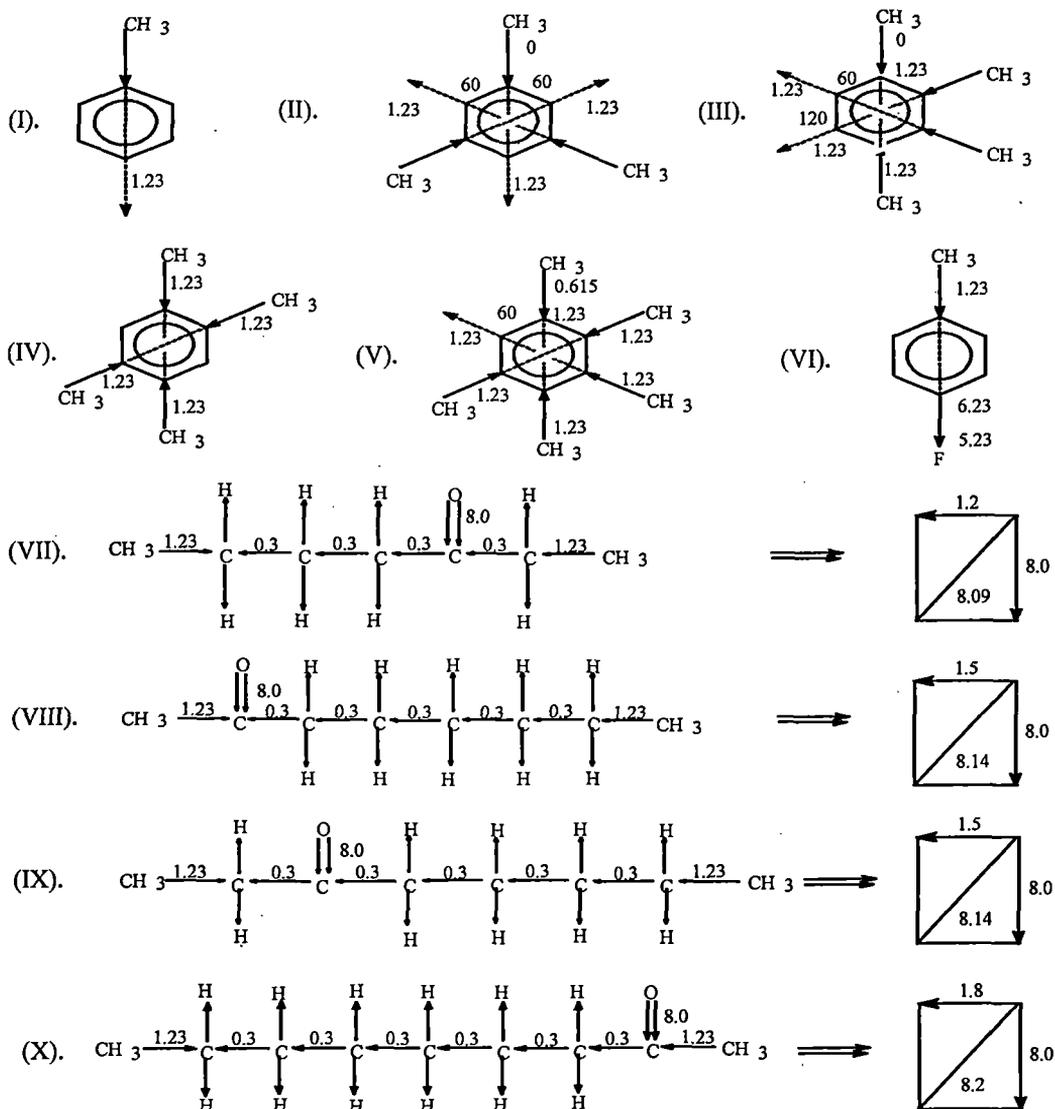


Figure 7.6: Conformational structures of polar molecules in terms of bond angles and bond moments ( $\times 10^{-30}$  Coulomb. metre) of the substituent groups.

(I) Toluene, (II) 1,3,5 tri methyl benzene, (III) 1,2,3,4 tetra methyl benzene (IV), 1,2,4,5 tetra methyl benzene, (V) penta methyl benzene, (VI) p-fluoro toluene, (VII) Butyl ethyl ketone, (VIII) Methyl hexyl ketone, (IX) Ethyl pentyl ketone, (X) heptyl methyl ketone.

and six p-electrons on six C-atoms. The  $sp^2$  hybridised electrons provide delocalised  $\pi$ -electrons to each atom of the substituted polar groups of the molecules.  $CH_3^{\delta+} \rightarrow C^{\delta-}$  is a strong electron pushing (+I effect) while  $>C^{\delta+} \leftarrow O^{\delta-}$  is responsible for both the mesomeric ( $-M$  effect) and electromeric effect. Thus all the substituted polar groups may be

responsible to form either solute-solvent (monomer) or solute-solute (dimer) association to yield lower and higher  $\mu_j$ 's respectively depending upon the solvent used. The difference  $\Delta\mu$  between  $\mu_j$ 's and  $\mu_{\text{theo}}$ 's of Fig.7.6 for the methyl substituted benzenes are 5.92, 9.36, 8.74, 7.84, 5.28 and 0.2 which are multiplied by  $10^{-30}$  C.m for the six systems while the rest of the four ketones have -3.63, 4.8, 3.5 and -1.05 which are multiplied by  $10^{-30}$  C.m respectively. This indicates the mesomeric and electromeric effects which are maximum for 1,3,5 trimethyl benzene and methyl hexyl ketone probably due to presence of strong electron repelling character of  $\text{CH}_3 \rightarrow \text{C}$  group. The  $\mu_{\text{theo}}$  of 1,3,5 tri methyl benzene, 1,2,3,4 tetra methyl benzene and 1,2,4,5 tetra methyl benzene are found to be of zero. The bond moment of  $\text{CH}_3 \rightarrow \text{C}$  group acts in opposite direction in a plane to yield zero value. The molecules may have considerable  $\mu_{\text{theo}}$  values if they are three dimensional structure. All these effects may be taken into account to get exact  $\mu_j$ 's of Table 7.2 from  $\mu_{\text{theo}}$  by the factor  $\mu_{\text{expt}}/\mu_{\text{theo}}$  (5.81, 5.29, 1.03, 0.55, 1.59, 1.43, 0.87 ) except for three molecules.

#### 7.4. Conclusions :

The structural information of some aromatic methyl benzenes and aliphatic ketones are obtained from the conductivity measurement at  $25^\circ\text{C}$  under the most effective dispersive region of 9.585 GHz electric field. Modern internationally accepted symbols of dielectric relaxation terminologies and parameters in SI units seem to be more topical, significant and useful contribution to obtain  $\tau$  and  $\mu$  of a dipolar liquid dissolved in nonpolar solvent.  $\tau_j$ 's measured from the slope of the linear  $\sigma_{ij}'' - \sigma_{ij}'$  curves are not in agreement for all cases with those from the ratio of the individual slopes of  $\sigma_{ij}'' - w_j$  and  $\sigma_{ij}' - w_j$  in the limit  $w_j = 0$  for all cases. The latter method is more significant because in this case one polar molecule is surrounded by a large number of non-polar molecules and thus polar-polar interactions are supposed to be completely eliminated. This method is thus supposed to yield monomeric or often dimeric structure of polar molecules.  $\mu_j$ 's are measured from the linear coefficient  $\beta$  of  $\sigma_{ij} - w_j$  curve at  $w_j \rightarrow 0$ .  $\sigma_{ij}$  or  $\sigma_{ij}''$  in  $\Omega^{-1} \text{ m}^{-1}$  for some systems increase gradually in order to attain the maximum value for a certain concentration of solute and then decrease. This indicates the change of phase of the systems under investigation. Similar nature of variation of  $\sigma_{ij}''$  with  $w_j$  indicates maximum absorption of hf electric energy for some systems.  $\tau_j$ 's and  $\mu_j$ 's claimed to be accurate within 10% and 5% are also compared with those from Gopalakrishna's fixed frequency method. The slight disagreement between experimental  $\mu_j$

with the theoretical dipole moment  $\mu_{\text{theo}}$  for some molecules reveals different associational aspects of dipolar liquid molecules in a non-polar solvent from the frequency dependence of relaxation parameters. This study also exhibits the presence of mesomeric, inductive and electromeric effects of the substituent polar groups of the molecules. The theoretical  $\mu_{\text{theo}}$  for systems II, III and IV are zero although they possess a considerable  $\mu_j$ . This invariably rules out the planar structure of the molecules and establish a three dimensional formation.

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