CHAPTER 4

DIELECTRIC RELAXATION PHENOMENA OF POLYSUBSTITUTED BENZENES UNDER HIGH FREQUENCY ELECTRIC FIELD

4.1. Introduction :

The dielectric relaxation phenomena of polysubstituted dielectropolar benzenes in benzene under high frequency (*hf*) electric field are of much importance to yield the structural aspect of a polar molecule. There exist several methods [4.1-4.2] to measure relaxation time τ_j and dipole moment μ_j of a polar molecule (j) from the measured real ε_{ij}' and imaginary ε_{ij}'' parts of the relative *hf* complex permittivity ε_{ij}^* of the solution (ij). However, such investigation on the relaxation phenomena of polysubstituted benzenes has not yet been made from the conductivity measurement [4.3-4.4]. Moreover, the most effective dispersive region for such polar liquids may exist at ~10 GHz (X-band) electric field [4.5]. Recently, Paul *et al* [4.6] had measured ε_{ij}', ε_{ij}'' of some polysubstituted benzenes in C_6H_6 at 30^0, 35^0, 40^0 and 45^0C under nearly 10 GHz electric field. The purpose of the study was to see the variation of τ's and μ's with temperature and concentration based on Goplakrishna's method [4.1].

Although, the molecules appear to be of outdated interest, two polar molecules have identical molecular weights in comparison to the third one, which is slightly higher. One molecule is a para-compound showing zero dipole moment at lower and higher temperatures. The substituted polar groups are attached with the parent benzene ring with different angles. We are, therefore tempted to use the measured relative permittivities [4.6] to get τ_j and μ_j of these liquids by *hf* conductivity measurement method [4.7]. The methodology is, however, involved with the transfer of dipolar charge of a polar molecule in a given solvent [4.8]. The present method of study in SI unit is superior because of its unified, coherent and rationalised nature. The dependency of τ_j's and μ_j's on t in ^{0}C is of much significance to get an idea of molecular environment and to shed more light on the structural conformations [4.9].

The measured dimensionless dielectric constants like real k_{ij}' and imaginary k_{ij}'' parts of complex dielectric constant k_{ij}^* at 30^0, 35^0, 40^0 and 45^0C are placed in Table 4.1. The real σ_{ij}' and imaginary σ_{ij}'' parts of the *hf* complex conductivity σ_{ij}^* in $\Omega^{-1}m^{-1}$ are, however, related to k_{ij}'' and k_{ij}' respectively. τ_j's are calculated from the linear slope of σ_{ij}'' against σ_{ij}' curves [4.10] for different w_j's of solute at a given temperature. The variation of σ_{ij}'' against σ_{ij}' is not strictly linear for different w_j's. (Fig.4.1). The ratio of the individual slopes of variations of σ_{ij}'' and σ_{ij}' with w_j's in Figs.4.2 and 4.3 in the limit w_j=0 may be used to get τ_j's, in which polar-polar interactions are almost eliminated. All the τ_j's are shown in Table 4.2 and are smaller than the reported τ's [4.6]. We, therefore, recalculated both τ's and μ's based on Gopalakrishna's method [4.1] which are in agreement with those of conductivity measurement. All τ's and μ's are presented in Tables 4.2 and 4.4 respectively for comparison.

Thermodynamic energy parameters: enthalpy of activation ΔH_τ, free energy of activation ΔF_τ and entropy of activation ΔS_τ for dielectric relaxations are also computed from the slope and intercept of $\ln(\tau_j T)$ against $1/T$ of Fig.4.4 with τ_j's measured by both the methods [4.11]. The values are entered in Table 4.3 in order to infer molecular dynamics of polar molecules in benzene. The enthalpy of activation ΔH_η for viscous process was, however, obtain from the linear slope γ of $\ln(\tau_j T)$ against $\ln\eta$ and ΔH_τ of Eq.(4.4). The coefficients of viscosity η of solvent C_6H_6 are $5.65\text{x}10^{-3}$, $5.30\text{x}10^{-3}$, $5.03\text{x}10^{-3}$ and $4.70\text{x}10^{-3}$ poise at 30^0, 35^0, 40^0 and 45^0C respectively.

Table 4.1: The real and imaginary parts of dimensionless dielectric constants of different aromatic polar liquids in benzene for different weight fractions w_j's at various experimental temperatures in ^{0}C.

Weight fraction	k_{ij}'	k_{ij}''	k_{ij}'	k_{ij}''	k_{ij}'	k_{ij}''	k_{ij}'	k_{ij}''
w_j	30^{0}C		35^{0}C		40^{0}C		45^{0}C	
			(I) meta-diisopropylbenzene					
0.012	2.2990	0.0424	2.3062	0.0401	2.3151	0.0393	2.3271	0.0384
0.018	2.3323	0.0570	2.3425	0.0552	2.3541	0.0545	2.3660	0.0523
0.025	2.3614	0.0721	2.3711	0.0692	2.3923	0.0660	2.4105	0.0595
0.032	2.3852	0.1083	2.4084	0.0985	2.4212	0.0854	2.4462	0.0734
0.045	2.4104	0.1251	2.4234	0.1092	2.4451	0.0982	2.4671	0.0832
			(II) para-methylbenzoylchloride					
0.011	2.1603	0.0488	2.1663	0.0440	2.1723	0.0410	2.1783	0.0381
0.018	2.1960	0.0585	2.2018	0.0553	2.2078	0.0523	2.2140	0.0492
0.028	2.2351	0.0690	2.2411	0.0662	2.2470	0.0632	2.2530	0.0603
0.039	2.2754	0.0762	2.2812	0.0731	2.2872	0.0701	2.2931	0.0672
0.050	2.3089	0.0928	2.3147	0.0899	2.3204	0.0872	2.3263	0.0842
			(III) ortho-chloroacetophenone					
0.011	2.1843	0.0351	2.1861	0.0330	2.1901	0.0310	2.1982	0.0294
0.023	2.2198	0.0462	2.2322	0.0442	2.2394	0.0450	2.2456	0.0376
0.032	2.2590	0.0573	2.2698	0.0552	2.2700	0.0491	2.2801	0.0421
0.045	2.2991	0.0692	2.3002	0.0653	2.3204	0.0551	2.3324	0.0579
0.051	2.3323	0.0810	2.3452	0.0791	2.3612	0.0770	2.3711	0.0650

Dipole moments μ_j's (shown in Table 4.4) are estimated from the linear coefficients β's of $hf\ \sigma_{ij}$ against w_j's as displayed in Fig.4.5 in the limit w_j=0. The variation of μ_j's and τ_j's with t in ^{0}C are presented in Fig.4.6. The temperature dependence of the mesomeric and inductive moments of the substituted polar groups attached to the parent molecules [4.12] are taken into account to display the theoretical dipole moments μ_{theo}'s in Fig.4.7.

Table 4.2: The slope of linear relation σ_{ij}''–σ_{ij}' curves of Fig. 4.1, correlation coefficient 'r', % of errors in regression technique, ratio of slopes of σ_{ij}''–w_j and σ_{ij}'–w_j curves at $w_j \to 0$ of Figs.4.2 and 4.3, estimated τ_j from Eq.(4.2) and reported τ in psec.

Systerm with sl. no.	t in ^{0}C	Slope of σ_{ij}''–σ_{ij}' curve of Eq.(4.2)	'r'	% of error of Eq.(4.2)	Ratio of slopes of σ_{ij}''–w_j & σ_{ij}'–w_j at $w_j \to 0$	τ_j^a	τ_j^b	Rept. τ in psec.
(I) m-diisopro-	30	1.217	0.972	1.67	1.809	13.08	8.80	10.92
pylbenzene	35	1.633	0.990	0.60	2.173	9.75	7.33	8.88
in C_6H_6	40	2.183	0.990	0.60	2.916	7.29	5.46	6.54
	45	3.227	0.988	0.72	4.207	4.93	3.79	4.30
(II) p-methyl-	30	3.491	0.988	0.72	5.858	4.56	2.72	3.85
benzoylchloride	35	3.369	0.989	0.66	4.828	4.73	3.30	4.04
in C_6H_6	40	3.342	0.988	0.72	4.931	4.77	3.23	4.05
	45	3.339	0.988	0.72	4.910	4.77	3.24	4.18
(III) o-chloro-	30	3.268	0.999	0.06	3.793	4.87	4.20	4.43
acetophenone	35	3.406	0.998	0.12	5.234	4.68	3.04	4.16
in C_6H_6	40	3.841	0.963	2.19	12.625	4.15	1.26	3.47
	45	4.614	0.987	0.78	17.625	3.45	0.90	3.09

τ_j^a = Estimated relaxation time from Eq.(4.2) with slope of σ_{ij}''–σ_{ij}'.
τ_j^b = Estimated relaxation time from Eq.(4.2) with ratio of slopes of σ_{ij}''–w_j and σ_{ij}'–w_j at $w_j \to 0$.

4.2. Theoretical Formulation :

Under electric field of giga hertz range the *hf* complex conductivity σ_{ij}^* of polar-nonpolar liquid mixture is :

$$\sigma_{ij}^* = \omega\varepsilon_o k_{ij}'' + j\omega\varepsilon_o k_{ij}' \qquad \ldots\ldots(4.1)$$

where $\omega\varepsilon_o k_{ij}'$ ($=\sigma_{ij}''$) and $\omega\varepsilon_o k_{ij}''$ ($=\sigma_{ij}'$) are the imaginary and real parts of σ_{ij}^*. $\omega(=2\pi f)$ is the angular frequency of the applied electric field of frequency f. ε_o= permittivity of free space= $8.854\text{x}10^{-12}$ F.m^{-1} and j is a complex number $=\sqrt{-1}$. The magnitude of total *hf* conductivity is :

$$\sigma_{ij} = \omega\varepsilon_o (k_{ij}''^2 + k_{ij}'^2)^{1/2}$$

σ_{ij}' and σ_{ij}'' of a given weight fraction w_j are, however, related to τ_j by :

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

$$\left(\frac{d\sigma_{ij}''}{d\sigma_{ij}'}\right)_{w_j \to 0} = \frac{\left(d\sigma_{ij}''/dw_j\right)_{w_j \to 0}}{\left(d\sigma_{ij}'/dw_j\right)_{w_j \to 0}} = \frac{1}{\omega\tau_j} \qquad \ldots\ldots(4.2)$$

The variation of σ_{ij}'' against σ_{ij}' for different w_j's is not always linear as shown in Fig.4.1. In such case, one may use the ratio of the individual slopes of variations of σ_{ij}'' and σ_{ij}' against w_j's as seen in Figs.4.2 and 4.3 in the limit w_j=0 to get τ_j.

Table 4.3: Thermodynamic energy parameters: enthalpy of activation ΔH_τ, entropy of activation ΔS_τ and free energy of activation ΔF_τ, value of γ from Eq.(4.4), enthalpy of activation ΔH_η due to viscous process, Debye factor and Kalman factor of the following aromatic polar liquids in benzene at different temperatures.

Systerm with sl. no.	t in ^{0}C	ΔH_τ in K J mole^{-1}	ΔS_τ in J mole^{-1} K^{-1}	ΔF_τ in K J mole^{-1}	Value of γ from Eq.(4.4)	ΔH_η from $\Delta H_\eta=\Delta H_\tau/\gamma$ in K J mole^{-1}	Debye factor $(\tau_j T/\eta)\times10^7$	Kalman Factor $\tau_j T/\eta^\gamma$
(I) m-diisopro-pylbenzene in C_6H_6	30	42.52	106.96	10.11	4.29	9.91	4.72	11.74
	35		106.07	9.85			4.26	13.08
	40		106.17	9.29			3.40	12.39
	45		106.94	8.51			2.56	11.69
(II) p-methyl-benzoylchloride in C_6H_6	30	-10.84	-59.41	7.16	-1.10	9.85	1.46	2.78×10^{-12}
	35		-60.57	7.82			1.92	3.19×10^{-12}
	40		-59.96	7.93			2.01	3.00×10^{-12}
	45		-59.58	8.11			2.19	2.83×10^{-12}
(III) o-chloro-acetophenone in C_6H_6	30	85.60	255.28	8.25	8.73	9.81	2.25	5.36×10^{10}
	35		253.25	7.60			1.77	6.89×10^{10}
	40		255.99	5.48			0.78	4.58×10^{10}
	45		254.36	4.71			0.61	6.02×10^{10}

τ_j's by both the methods of $(d\sigma_{ij}''/d\sigma_{ij}')$ and the ratio of individual slopes of Eq.(4.2) are used to get free energy of activation ΔF_τ of a polar liquid. From Eyring's rate theory [4.11] one gets:

$$\ln(\tau_j T) = \ln(Ae^{-\Delta S_\tau/R}) + \Delta H_\tau / RT \qquad \ldots\ldots (4.3)$$

Since $\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau$

The intercept and slope of $\ln(\tau_j T)$ against $1/T$ as shown in Fig.4.4 are, however, related to ΔS_τ and ΔH_τ of molecules. η of C_6H_6 is related to τ_j at different temperatures by:

$$\tau_j = A\eta^\gamma / T \qquad \ldots\ldots (4.4)$$

Where γ is the slope of the linear relation of $\ln(\tau_j T)$ against $\ln\eta$. Again, σ_{ij}'' may be approximated to σ_{ij} for their identical nature of variations with w_j's as evidenced by Figs.4.2 and 4.5 respectively.

Hence Eq.(4.2) can be written as :

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

$$\left(\frac{d\sigma'_{ij}}{dw_j}\right)_{w_j\to 0} = \beta\omega\tau_j \qquad \text{.....(4.5)}$$

where β is the linear coefficient of variation of σ_{ij}–w_j curves of Fig.4.5 at $w_j\to 0$. All β's are placed in Table 4.4. The real part σ_{ij}' at T K is [4.13]:

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

$$\left(\frac{d\sigma'_{ij}}{dw_j}\right)_{w_j\to 0} = \frac{N\rho_i\mu_j^2}{27k_BTM_j}\left(\frac{\omega^2\tau_j}{1+\omega^2\tau_j^2}\right)\left(k_i+2\right)^2 \qquad \text{.....(4.6)}$$

where N=Avogadro's number, ρ_i=density of solvent, k_i=dimensionless dielectric constant of solvent, M_j=molecular weight of the polar liquid (j) and k_B=Boltzmann constant. All the symbols are in SI units. From Eqs.(4.5) and (4.6) one gets μ_j of a polar molecule in Coulomb metre (C.m):

$$\mu_j = \left(\frac{27k_BTM_j}{N\rho_i(k_i+2)^2}\frac{\beta}{\omega b}\right)^{1/2} \qquad \text{.....(4.7)}$$

The dimensionless parameter b is related to τ_j by :

$$b = \frac{1}{1+\omega^2\tau_j^2} \qquad \text{.....(4.8)}$$

The measured τ_j's of the polar liquids presented in Table 4.2 are compared with the recalculated τ's based on Gopalakrishna's [4.1] method.

$$x = \frac{\varepsilon_{ij}'^2+\varepsilon'_{ij}+\varepsilon''^2_{ij}-2}{(\varepsilon'_{ij}+2)^2+\varepsilon''^2_{ij}} \qquad y = \frac{3\varepsilon''_{ij}}{(\varepsilon'_{ij}+2)^2+\varepsilon''^2_{ij}}$$

$$\tau = \frac{1}{\omega}\frac{dy}{dx} \qquad \text{.....(4.9)}$$

All the μ_j's with b's are finally found in Table 4.4 to compare with recalculated μ's from :

$$\mu = \left[\frac{9k_BTM_j}{4\pi N\rho_i}\left\{1+\left(\frac{dy}{dx}\right)^2\right\}\frac{dx}{dw_j}\right]^{1/2} \qquad \text{.....(4.10)}$$

All the computed μ_j's reported μ's along with μ_{theo}'s of Fig.4.7 are seen in Table 4.4.

4.3. Results and Discussions :

The relaxation times τ_j's of polysubstituted benzenes under 3 cm wavelength electric field, were calculated simultaneously from Eq.(4.2) with the slope of σ_{ij}'' against σ_{ij}' of *hf* conductivity σ_{ij}^* of Fig.4.1 and the ratio of slopes of the variations of σ_{ij}'' and σ_{ij}' with w_j's of Figs.4.2 and 4.3 from data of Table 4.1 at different experimental temperatures. τ_j's (Table 4.2) from slope of linear relation σ_{ij}''–σ_{ij}' curve (Fig.4.1) are slightly larger than the ratio of slopes of Eq.(4.2). The latter method is reliable as the polar-polar interactions are almost eliminated. The variation of σ_{ij}'' with σ_{ij}' is non linear (Fig.4.1) for all the liquids like σ_{ij}'' and σ_{ij}' with w_j's of Figs.4.2 & 4.3 respectively. The slopes of curves in Fig.4.1 are almost same for *p*-methylbenzoylchloride, but for o-chloroacetophenone the curves are of almost constant intercepts and slightly increasing slopes with temperature to yield almost same τ_j for their same polarity [4.14] and identical structures. Meta-diisopropylbenzene indicates the lower intercept and higher slopes as the temperature rises. τ_j's from Eq.(4.2) of σ_{ij}''–σ_{ij}' curves decrease with temperature to obey Debye relaxation mechanism like the variation of σ_{ij}'' and σ_{ij}' with w_j's for the molecules at 30^0, 35^0, 40^0 and 45^0C respectively. Nevertheless, the conductivity method yields microscopic τ_j's [4.15]. The molecule m-diisopropylbenzene has greater τ because of larger size than those of isomeric p-methylbenzoylchloride and o-chloroacetophenone. τ_j's in Table 4.2 for these molecules having the same number of C-atoms do not vary much from Eqs.(4.2) and (4.9) respectively probably for the different positions of the substituted polar groups attached to the parent molecules of Fig.4.7.

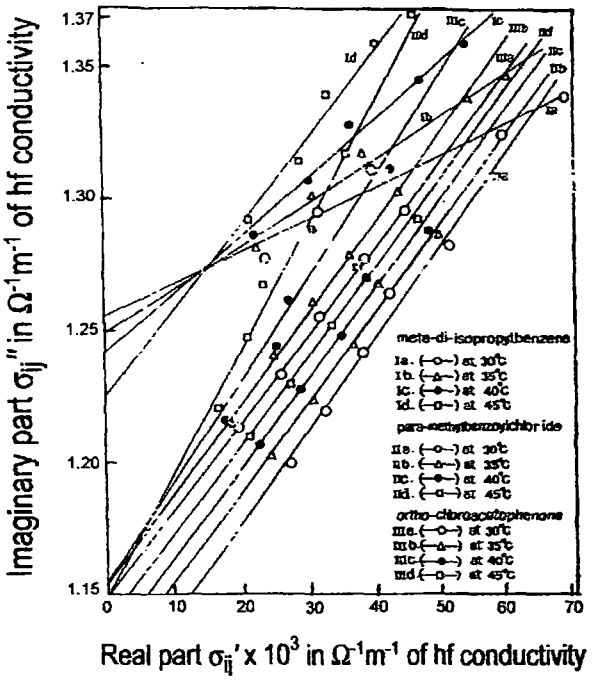

Figure 4.1: Variation of imaginary part σ_{ij}'' in $\Omega^{-1}m^{-1}$ against real part σ_{ij}' in $\Omega^{-1}m^{-1}$ of *hf* conductivity for different weight fractions w_j's of polysubstituted benzenes in benzene under 10 GHz electric field at various experimental temperatures.

For m-diisopropylbenzene both σ_{ij}'' and σ_{ij} in Figs.4.2 and 4.5 start from 1.228 $\Omega^{-1}m^{-1}$ to 1.236 $\Omega^{-1}m^{-1}$ and increase gradually to assume maximum within $0.045 \leq w_j \leq 0.051$ and then decrease as w_j increases. This sort of behaviour arises for the transfer of localised charge species of

such dipoles [4.16] which increases up to a certain w_j and then ceases gradually in the higher concentrations. Similar observation is noted in *p*-methylbenzoylchloride showing maximum at nearly w_j=0.096. All these facts indicate the phase transition of lower conductivity in the higher concentration [4.16] probably due to dimer formations. Ortho-chloroacetophenone showed a regular monotonic increase, as coefficients of quadratic term of w_j in both σ_{ij}'' and σ_{ij} are positive. The variation of σ_{ij}' with w_j's for all polar molecules in Fig.4.3 decreases with t ^{0}C to exhibit the

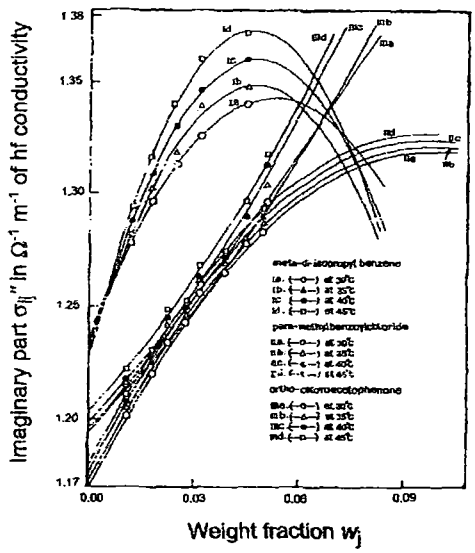

Figure 4.2: Variation of imaginary part σ_{ij}'' in $\Omega^{-1}m^{-1}$ of *hf* conductivity with weight fractions w_j's of polysubstituted benzenes in benzene under 10 GHz electric field.

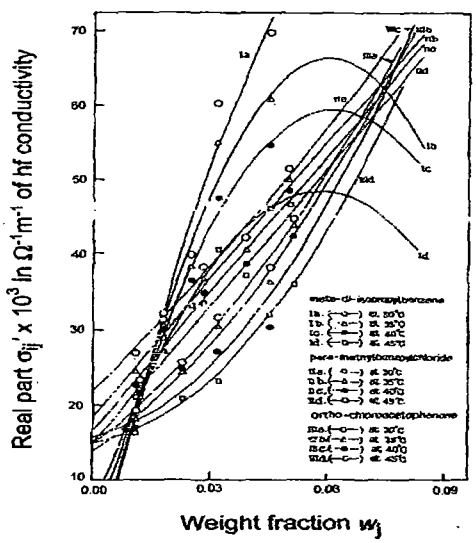

Figure 4.3: Variation of imaginary part σ_{ij}' in $\Omega^{-1}m^{-1}$ of *hf* conductivity with weight fractions w_j's of polysubstituted benzenes in benzene under 10 GHz electric field.

semiconducting nature while σ_{ij}'' and σ_{ij} of Figs.4.2 and 4.5 showed the regular increase. The percentage of errors as well as correlation coefficients r's are made for Eq.(4.2) to get τ_j's. It is interesting to note that τ_j for *m*-diisopropylbenzene and *o*-chloroacetophenone in C_6H_6 obey Debye relaxation mechanism. The energy difference between activated and normal states of the random dipole orientations increases with t ^{0}C to decrease τ_j's. τ_j's for *p*-methylbenzoylchloride initially increases and then become constant with t ^{0}C indicating the non-Debye relaxation for its asymmetry gained by two polar groups in a line. The large difference between τ_j's and reported τ's [4.6] prompted us to recalculate τ's placed in the 9th column of Table 4.2 based on Gopalakrishna's method [4.1]. The recalculated τ's and μ's are now closer to τ_j's of columns 7 and 8 of Table 4.2 and μ_j's of column 9 of Table 4.4 based on the method of conductivity measurement [4.7].

The thermodynamic energy parameters ΔH_τ, ΔS_τ and ΔF_τ (Table 4.3) were calculated from $\ln(\tau_j T)$ against $1/T$ in Fig.4.4 with the measured τ_j's by both the methods. In *p*-

methylbenzoylchloride $-\Delta S_\tau$ indicates the activated states are more stable supported by $-\Delta H_\tau$ also. ΔS_τ for *m*-diisopropylbenzene and *o*-chloroacetophenone indicates the unstability of the activated states. Unlike *p*-methylbenzoylchloride, $\gamma >$ 0.5 for *m*-diisopropylbenzene and *o*-chloroacetophenone indicates that they do not behave as solid phase rotators. Such polar liquids in C_6H_6 favour solute-solvent molecular formation. ΔH_η involved with translational and rotational energy are less than ΔH_τ due to high values of γ for all the systems. They thus need maximum energy to rotate under *hf* electric field. The γ's from the slope of $\ln(\tau_j T)$ against $\ln\eta$ are used to estimate Kalman factor $\tau_j T/\eta^\gamma$ and Debye factor $\tau_j T/\eta$ to place them in Table 4.3. Kalman factors being proportional to the volumes of the rotating units are of different orders, but constant with temperature for a given system. Debye factors, on the other hand, are of the order of 10^{-7} for all systems. This suggests the applicability of Debye-Smyth model of dielectric relaxation mechanism for all the liquids including *p*-methylbenzoylchloride although it is non-Debye in

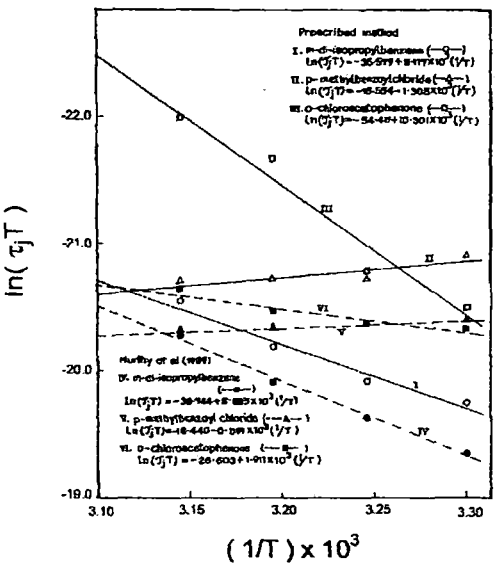

Figure 4.4: The linear plot of $\ln(\tau_j T)$ against 1/T

Table 4.4: The coefficients of *hf* conductivity σ_{ij} of aromatic polar liquid with weight fraction w_j in C_6H_6 at 30^0, 35^0, 40^0 and 45^0C in Fig.4.5, dimensionless parameters *b*'s, computed, reported and theoretical dipole moments in Coulomb metre (C.m).

Systerm with sl. no & mol. wt.	*t* in ^{0}C	Coefficients of σ_{ij}–w_j in $\Omega^{-1}m^{-1}$ of Fig.4.5 $\sigma_{ij}=\alpha+\beta w_j+\xi w_j^2$ α	β	ξ	Dimensionless parameter *b*		Computed $\mu_j\times10^{30}$ in C.m		Rept. $\mu\times10^{30}$ in C.m Eq.(4.10)	$\mu_{theo}\times10^{30}$ in C.m of Fig.4.7
(I) m-diisopro-	30	1.236	4.016	-36.919	0.597	0.766	14.34	12.66	9.07	
pylbenzene	35	1.228	5.110	-53.613	0.727	0.825	14.86	13.95	8.90	3.77
in C_6H_6	40	1.230	5.475	-56.900	0.827	0.895	14.61	14.04	8.84	
M_j=0.162 Kg	45	1.228	6.196	-65.944	0.913	0.946	14.99	14.72	8.90	
(II) p-methyl-	30	1.171	3.059	-15.421	0.924	0.972	9.87	9.63	8.17	
benzoylchloride	35	1.173	3.059	-15.464	0.919	0.959	10.03	9.82	8.27	8.80
in C_6H_6	40	1.177	3.064	-15.617	0.918	0.961	10.18	9.95	8.34	
M_j=0.156 Kg	45	1.180	3.064	-15.685	0.918	0.960	10.31	10.08	8.44	
(III) o-chloro-	30	1.197	1.477	9.038	0.915	0.935	6.90	6.82	8.07	
acetophenone	35	1.195	1.894	3.180	0.921	0.965	7.89	7.71	8.20	7.40
in C_6H_6	40	1.201	1.580	11.513	0.936	0.994	7.23	7.02	8.57	
M_j=0.156 Kg	45	1.204	1.615	11.737	0.955	0.997	7.34	7.19	8.74	

relaxation behaviour. μ_j's of the polar liquids at t ^{0}C are estimated from β's of σ_{ij}–w_j curves of Fig.4.5 and dimensionless parameters b's of Eq.(4.8) involved with the measured τ_j's from the ratio of the individual slopes of Figs.4.2 and 4.3 at $w_j \rightarrow 0$. The σ_{ij} in $\Omega^{-1}m^{-1}$ when plotted with w_j's increases with temperatures showing maximum at a certain w_j for *m*-diisopropylbenzene and *p*-methylbenzoylchloride like σ_{ij}''–w_j curves. This signifies the phase transition from higher to lower conductivity for transfer of charged species of molecules. The slopes and intercepts of σ_{ij}–w_j and σ_{ij}''–w_j curves for *p*-methylbenzoylchloride and *o*-chloroacetophenone are almost the same for their same polarity [4.14] indicating $\sigma_{ij} \approx \sigma_{ij}''$ in Eq.(4.5). The usual variations of μ_j and τ_j [4.17] with t ^{0}C

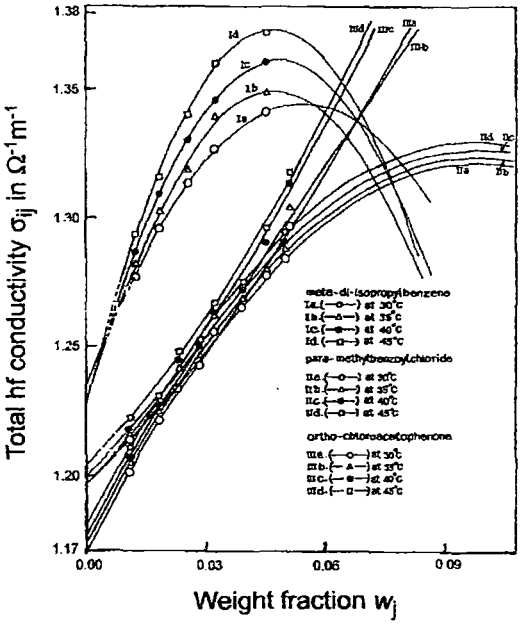

Figure 4.5: Variation of total *hf* conductivity σ_{ij} in $\Omega^{-1}m^{-1}$ with weight fractions w_j's under 10 GHz electric field at various experimental temperatures

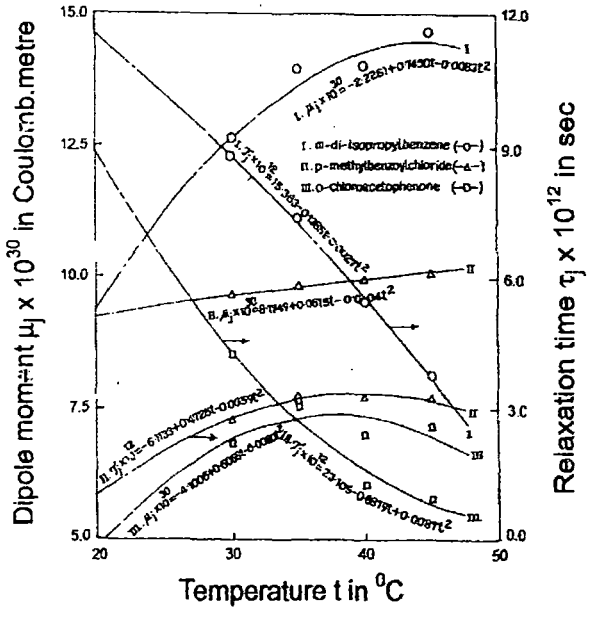

Figure 4.6: Variation of observed dipole moment μ_j and relaxation time τ_j with temperatures t in ^{0}C of different polysubstituted benzenes in benzene under 10 GHz electric field.

are shown graphically in Fig.4.6. τ_j's decrease with temperature for the curves I and III of *m*-diisopropylbenzene and *o*-chloroacetophenone. The μ_j's from Eq.(4.7) increase gradually to maximum 14.49×10^{-30} C.m at 44.88 ^{0}C, 10.54×10^{-30} C.m at 76.88^{0}C and 7.41×10^{-30} C.m at 37.93 ^{0}C respectively signifying the largest asymmetry gained by all the molecules. τ_j's are zero at 54.03 ^{0}C for the curve I and 16.22 ^{0}C, 63.88 ^{0}C for curve II. But for curve III; $\tau_j=0$ at $t=\infty$. The μ_j's are 13.80×10^{-30} C.m for the curve I and 9.07×10^{-30} C.m, 10.47×10^{-30} C.m for curve II. But undefined for curve III respectively. The variation of τ_j and μ_j with t ^{0}C are convex for curve II indicating the non-

Debye relaxation behaviour to reveal solute-solvent molecular association as observed from γ of Table 4.3.

μ_{theo} from the available bond angles and bond moments of the substituted polar groups of molecules of Fig.4.7 is placed in Table 4.4 with the reported μ from Eq.(4.10). The close agreement

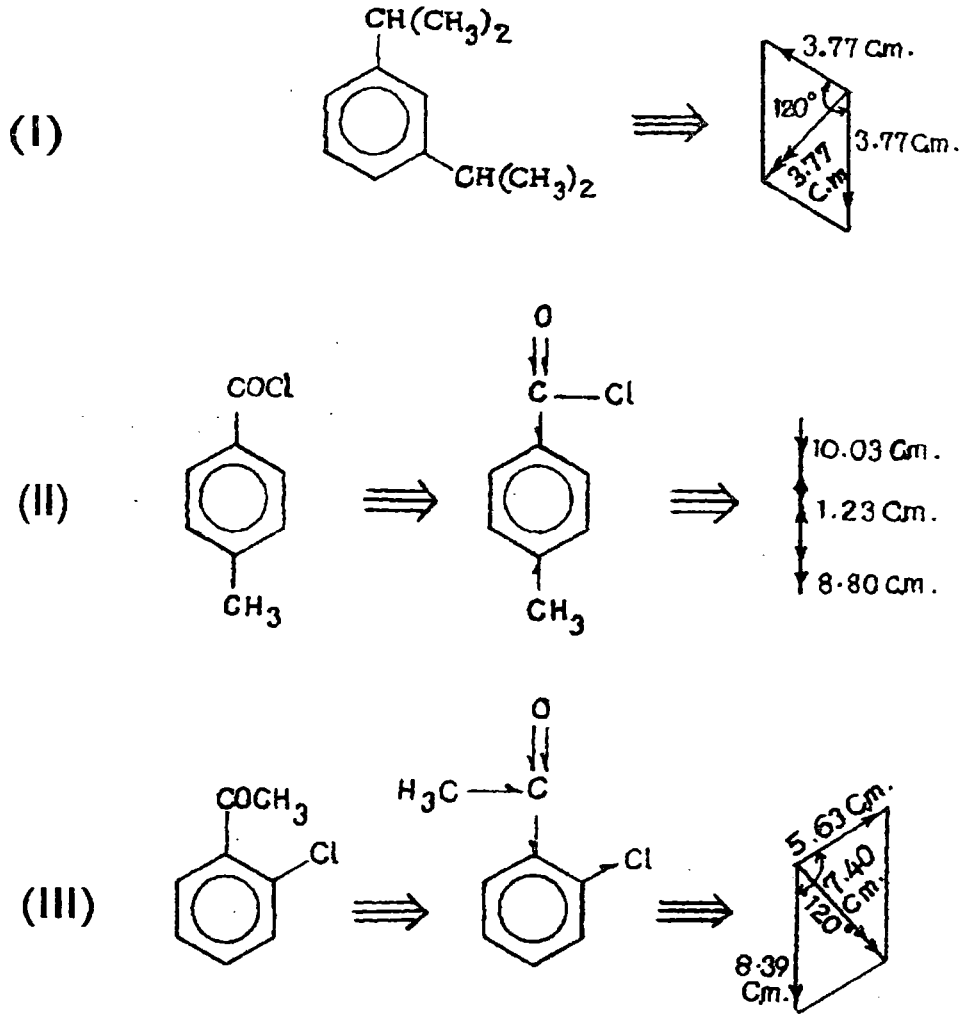

Figure 4.7: Conformational structures of (I) meta-diisopropylbenzene (II) para-methylbenzoylchloride (III) ortho-chloroacetophenone.

of μ_j's of Eq.(4.7) with Eq.(4.10) suggests the basic soundness of the present method. The wide disagreement between μ_j and μ_{theo} of Table 4.4 of the first molecule unlike the latter two suggest bond moments of the substituted polar groups are either stretched by a factor μ_j/μ_{theo} of 3.36, 3.70, 3.72, 3.90; or shortened by 0.09, 1.12, 1.13, 1.50 and 0.92, 1.04, 0.95, 0.97 respectively in order to consider inductive and mesomeric effects in them. The electromeric effect caused by >C=O in second and third molecules may be the reason to make μ_j more closer to μ_{theo} [4.18].

4.4. Conclusion :

The study of dielectric relaxation phenomena of polysubstituted benzenes in benzene under 3 cm wavelength electric field in terms of τ_j's and μ_j's in SI units at various experimental temperatures in ^{0}C by the method of *hf* conductivity measurement is more topical and significant. The use of ratio of the slopes of σ_{ij}''–w_j and σ_{ij}'–w_j curves to obtain τ_j's appears to be reliable as it avoids polar-polar interaction unlike the linear slope of σ_{ij}''–σ_{ij}' curves. The appearance of peak in σ_{ij}–w_j and σ_{ij}''–w_j curves at different t ^{0}C for systems I and II indicates the change of phase of lower conductivity as w_j increases. O-chloroacetophenone, on the other hand, showed the monotonic increase of σ_{ij} and σ_{ij}'' with w_j's at all the temperatures. The temperature dependence the of μ_j's and τ_j's although they are measured in the limit of w_j=0 supports this behaviour. τ_j is zero for *m*-diisopropylbenzene at 54.03 ^{0}C while *p*-methylbenzoylchloride at 16.22 ^{0}C and 63.88 ^{0}C respectively indicating orderness at those temperatures. *o*-chloroacetophenone showed τ_j's decreasing with temperature and becomes zero at $t=\infty$. The correspsonding μ's are $\mu_s=13.80\text{x}10^{-30}$ C.m for *m*-diisopropylbenzene and $\mu_s=9.07\text{x}10^{-30}$ C.m and $\mu_s=10.47\text{x}10^{-30}$ C.m for *p*-methylbenzoylchloride respectively as static μ_s. Both τ_j's and μ_j's in tables and figures are within 10% and 5% accuracies. The increase or decrease of μ_j's with temperature t in ^{0}C is explained by asymmetric or symmetric configurations of the molecules. The energy parameters from $\ln(\tau_j T)$ against $1/T$ with τ_j's from the ratio of individual slopes of σ_{ij}''–w_j and σ_{ij}'–w_j curves at various temperatures indicate the stability of random dipole orientations in the activated states. The deviation of μ_{theo} from the bond angles and bond moments of polar groups of molecules from measured μ_j in terms of τ_j can be explained by inductive, mesomeric and electromeric effect. The correlation between the conformational structures with the observed results enhances the scientific contents and adds a new horizon of understanding to the existing knowledge of dielectric relaxation.

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