

## *Chapter 3*

### **DOUBLE RELAXATION PHENOMENA OF DISUBSTITUTED BENZENES AND ANILINES IN NONPOLAR APROTIC SOLVENTS UNDER HIGH FREQUENCY ELECTRIC FIELD**

### 3.1. Introduction :

The dielectric relaxation phenomena of nonspherical and rigid polar liquid molecule in different nonpolar solvents at a given temperature, under a high frequency (hf) electric field attracted the attention of a large number of workers [3.1-3.2]. The dipole moment  $\mu$  from the relaxation time  $\tau$  of the polar liquid molecule is of much importance [3.3-3.4] to determine the shape, size, structure and molecular association of a polar molecule. The real  $\epsilon_{ij}'$  and imaginary  $\epsilon_{ij}''$  parts of complex relative permittivity  $\epsilon_{ij}^*$ , static and infinite frequency relative permittivities  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  of a polar liquid molecule (j) in a non-polar solvent (i) at a fixed experimental temperature under a single frequency electric field of GHz range are used to obtain the double relaxation times  $\tau_2$  and  $\tau_1$  due to rotation of the whole molecule as well as the flexible part attached to the parent molecule [3.5].

Khameshara and Sisodia [3.6], Gupta et al [3.7] and Arrawatia et al [3.8] measured the relative permittivities of some disubstituted benzenes and anilines in aprotic nonpolar solvents  $C_6H_6$  and  $CCl_4$  under 9.945 GHz electric field at  $35^\circ C$  to predict the conformation of the molecules in terms of the relaxation time  $\tau$ , based on the single frequency concentration variation method of Gopalakrishna [3.9] and the dipole moment  $\mu$  by Higasi's method [3.10]. The compounds are very interesting for the different functional groups like  $-NH_2$ ,  $-CH_3$ ,  $-NO_2$ ,  $-Cl$  etc. attached to the parent molecules. The samples were of purest quality and supplied by M/s Fluka and M/s E Merck respectively. The solvents  $C_6H_6$  and  $CCl_4$  of M/s BDH were used after double distillation and suitably dried over NaCl and  $CaCl_2$ .  $\epsilon_{0ij}$  at  $35^\circ C$  was measured by heterodyne beat method at 300 KHz.  $\epsilon_{\infty ij} = n_{Dij}^2$ , where the refractive index  $n_{Dij}$  was measured by an Abbe's refractometer. The weight fraction  $w_j$  of the respective solute, which is defined by the weight of the solute per unit weight of the solution was taken up to four decimal place as the accuracy in the measurement was 0.0012 %.  $\epsilon_{ij}'$  and  $\epsilon_{ij}''$  within 1% and 5% accuracies were carried out by using the voltage standing wave ratio in slotted line and short-circuiting plunger, based on the method of Heston et al [3.11]. The possible existence of  $\tau_1$  and  $\tau_2$  of the compounds was, however, detected from the relative permittivity measurements [3.12] under 9.945 GHz electric field at  $35^\circ C$ .

Table 3.1: The real  $\chi_{ij}'$  and imaginary  $\chi_{ij}''$ , parts of the complex dielectric orientational susceptibility  $\chi_{ij}^*$  and static dielectric susceptibility  $\chi_{oij}$  which is real for various weight fraction  $w_j$  of different disubstituted benzenes and anilines in  $C_6H_6$  and  $CCl_4$  at 35 °C under 9.945 GHz electric field.

Weight fraction $w_j$	$\chi_{ij}'$	$\chi_{ij}''$	$\chi_{oij}$	Weight fraction $w_j$	$\chi_{ij}'$	$\chi_{ij}''$	$\chi_{oij}$
(I) o-chloronitrobenzene in $C_6H_6$				(II) 4-chloro 3-nitro benzotrifluoride in $CCl_4$			
0.0109	0.117	0.066	0.167	0.0050	0.122	0.019	0.155
0.0173	0.169	0.100	0.254	0.0101	0.145	0.037	0.185
0.0217	0.197	0.126	0.305	0.0147	0.150	0.054	0.233
0.0280	0.253	0.165	0.376	0.0193	0.167	0.068	0.266
0.0330	0.284	0.192	0.461	0.0231	0.179	0.075	0.302
(III) 4-chloro 3-nitro toluene in $C_6H_6$				(IV) 4-chloro 3-nitro toluene in $CCl_4$			
0.0072	0.075	0.046	0.132	0.0041	0.145	0.039	0.208
0.0144	0.098	0.088	0.241	0.0087	0.173	0.071	0.315
0.0224	0.150	0.133	0.310	0.0128	0.190	0.101	0.419
0.0323	0.200	0.179	0.464	0.0162	0.218	0.138	0.482
0.0453	0.271	0.252	0.630	0.0203	0.241	0.165	0.586
(V) o-nitrobenzotrifluoride in $C_6H_6$				(VI) m-nitrobenzotrifluoride in $C_6H_6$			
0.0085	0.094	0.058	0.154	0.0096	0.082	0.032	0.094
0.0167	0.166	0.108	0.257	0.0173	0.103	0.060	0.157
0.0244	0.226	0.159	0.384	0.0245	0.129	0.082	0.202
0.0335	0.297	0.205	0.495	0.0326	0.157	0.106	0.265
0.0402	0.353	0.255	0.604	0.0380	0.187	0.128	0.323
(VII) 2-chloro 6-methyl aniline in $C_6H_6$				(VIII) 3-chloro 2-methyl aniline in $C_6H_6$			
0.0184	0.072	0.017	0.075	0.0083	0.059	0.018	0.065
0.0305	0.096	0.026	0.097	0.0207	0.099	0.043	0.128
0.0417	0.117	0.040	0.138	0.0270	0.128	0.055	0.166
0.0573	0.163	0.058	0.191	0.0363	0.165	0.073	0.221
0.0636	0.183	0.065	0.214	0.0421	0.193	0.086	0.255
(IX) 3-chloro 4-methyl aniline in $C_6H_6$				(X) 4-chloro 2-methyl aniline in $C_6H_6$			
0.0214	0.088	0.032	0.099	0.0196	0.124	0.063	0.151
0.0374	0.123	0.060	0.167	0.0300	0.157	0.090	0.219
0.0403	0.133	0.066	0.185	0.0417	0.199	0.121	0.304
0.0548	0.166	0.091	0.244	0.0481	0.216	0.138	0.354
(XI) 5-chloro 2-methyl aniline in $C_6H_6$							
0.0194	0.094	0.050	0.123				
0.0249	0.110	0.064	0.153				
0.0307	0.129	0.081	0.191				
0.0480	0.182	0.129	0.292				
0.0569	0.206	0.150	0.362				

Nowadays, the usual practice [3.13] is to study the dielectric relaxation phenomena in terms of dielectric orientational susceptibilities  $\chi_{ij}$ 's.  $\chi_{ij}$ 's are linked with the orientational polarisation of a polar molecule. So it is better to work with  $\chi_{ij}$ 's rather than  $\epsilon_{ij}$ 's or conductivity  $\sigma_{ij}$ 's as the later are involved with all the polarisation processes and the transport of bound molecular charges, respectively [3.14]. The real  $\chi_{ij}'(=\epsilon_{ij}'-\epsilon_{\infty ij})$  and

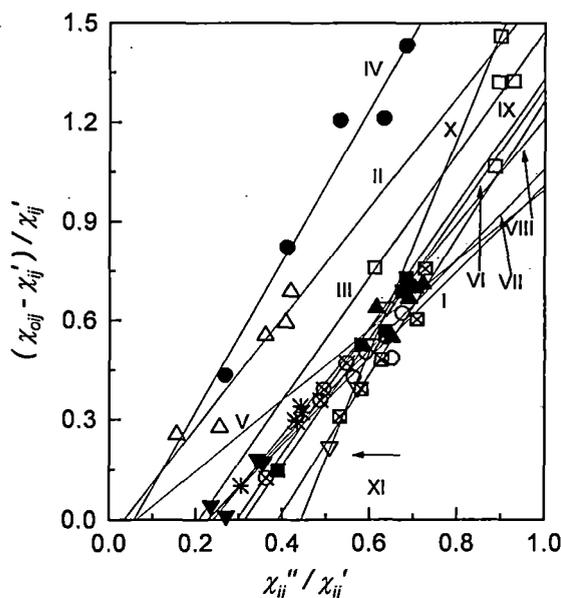


Figure 3.1: Linear variation of  $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$  with  $\chi_{ij}''/\chi_{ij}'$  for different  $w_j$ 's at 35°C under 9.945 GHz electric field.

- I. o-chloronitrobenzene in  $C_6H_6$  (—○—); II. 4-chloro 3-nitrobenzotrifluoride in  $CCl_4$  (—△—); III. 4-chloro 3-nitrotoluene in  $C_6H_6$  (—□—); IV. 4-chloro 3-nitrotoluene in  $CCl_4$  (—●—); V. o-nitrobenzotrifluoride in  $C_6H_6$  (—▲—); VI. m-nitrobenzotrifluoride in  $C_6H_6$  (—■—); VII. 2-chloro 6-methyl aniline in  $C_6H_6$  (—▼—); VIII. 3-chloro 2-methyl aniline in  $C_6H_6$  (—\*—); IX. 3-chloro 4-methyl aniline in  $C_6H_6$  (—⊗—); X. 4-chloro 2-methyl aniline in  $C_6H_6$  (—▽—) and XI. 5-chloro 2-methyl aniline in  $C_6H_6$  (—⊠—)

imaginary  $\chi_{ij}''(=\epsilon_{ij}'')$  parts of the complex dielectric orientational susceptibility  $\chi_{ij}^*(=\epsilon_{ij}^*-\epsilon_{\infty ij})$  and the low frequency susceptibility  $\chi_{oij}(=\epsilon_{oij}-\epsilon_{\infty ij})$  which is real of the disubstituted benzenes and anilines in  $C_6H_6$  and  $CCl_4$  of Table 3.1 are used to obtain their conformational structures in terms of molecular and intra-molecular dipole moments  $\mu_2$  and  $\mu_1$  involved with the estimated  $\tau_2$  and  $\tau_1$ . Disubstituted benzenes and anilines are thought to absorb electric energy

Table 3.2: The relaxation times  $\tau_2$  and  $\tau_1$  from the slope and intercept of straight line Eq.(3.3), correlation coefficients  $r$ 's and % of error in regression technique, measured  $\tau_j$  from the slope of  $\chi_{ij}''$  vs  $\chi_{ij}'$  of Eq.(3.15) and the ratio of the individual slopes of  $\chi_{ij}''$  vs  $w_j$  and  $\chi_{ij}'$  vs  $w_j$  at  $w_j \rightarrow 0$  of Eq.(3.16), reported  $\tau$ , symmetric and characteristic relaxation times  $\tau_s$  and  $\tau_{cs}$  for different disubstituted benzenes and anilines at 35°C under 9.945 GHz electric field.

System with sl.no..	Slope & intercept of Eq.(3.3)		'r'	% of error	Estimated $\tau_2$ and $\tau_1$ in psec		Measured $\tau_j$ in psec from Eqs (3.15) & (3.16)		Rept. $\tau$ in psec	$\tau_s$ in psec	$\tau_{cs}$ in psec
(I) o-chloro nitro benzene in C <sub>6</sub> H <sub>6</sub>	1.310	0.301	0.82	9.88	16.21	4.76	12.08	10.13	13.5	7.87	17.08
(II) 4-chloro 3-nitrobenzotrifluoride in CCl <sub>4</sub>	1.666	0.059	0.95	2.94	26.08	0.58	16.43	22.66	21.1	0.00	--
(III) 4-chloro 3-nitro toluene in C <sub>6</sub> H <sub>6</sub>	1.865	0.389	0.88	6.80	26.02	3.83	16.13	19.89	20.9	10.76	39.65
(IV) 4-chloro 3-nitro toluene in CCl <sub>4</sub>	2.283	0.134	0.98	1.19	35.57	0.96	21.47	22.61	35.0	1.47	38.84
(V) o- nitrobenzo trifluoride in C <sub>6</sub> H <sub>6</sub>	1.063	0.067	0.70	15.38	15.93	1.08	12.09	11.08	13.7	10.89	28.83
(VI) m-nitrobenzotri fluoride in C <sub>6</sub> H <sub>6</sub>	1.898	0.597	0.99	0.60	24.01	6.37	14.33	36.57	19.7	6.20	--
(VII) 2-chloro 6-methyl aniline in C <sub>6</sub> H <sub>6</sub>	1.371	0.313	0.93	4.08	17.31	4.63	7.05	14.55	7.8	4.08	--
(VIII) 3-chloro 2-methyl aniline in C <sub>6</sub> H <sub>6</sub>	1.596	0.386	0.99	0.60	20.79	4.76	7.98	11.49	9.9	4.57	--
(IX) 3-chloro 4- methyl aniline in C <sub>6</sub> H <sub>6</sub>	1.891	0.561	0.99	0.67	24.37	5.90	12.07	13.65	13.6	7.28	--
(X) 4-chloro 2-methyl aniline in C <sub>6</sub> H <sub>6</sub>	3.217	1.428	0.99	0.67	42.97	8.51	12.80	11.04	18.5	7.59	--
(XI) 5-chloro 2-methyl aniline in C <sub>6</sub> H <sub>6</sub>	2.075	0.811	0.97	1.78	24.85	8.36	14.34	14.35	16.6	5.60	4.52

much more strongly in nearly 10 GHz electric field to yield considerable values of  $\tau_1$  and  $\tau_2$ . The 11 polar-nonpolar liquid mixtures under investigation are found to show the double relaxation phenomena. Most of the polar molecules are isomers of aniline and benzene. Some of the polar solutes are dissolved in C<sub>6</sub>H<sub>6</sub> while a few in CCl<sub>4</sub> to observe the solvent

effect too. Moreover, a few of the polar molecules are para-compounds in which a peculiar feature of relaxation phenomena is expected [3.15]. A strong conclusion of double relaxation phenomena of polar molecule in a non-polar solvent based on the single frequency measurement of relaxation parameters can be made only if, the accurate value of  $\chi_{oij}$  ( $\pm 1\%$ ) involved with  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  is available. The use of  $n_{Dij}^2$  for  $\epsilon_{\infty ij}$  often introduces [3.6-3.8] an additional error in the calculation, since  $\epsilon_{\infty ij}$  is approximately equal to 1-1.5 times of  $n_{Dij}^2$ .

Bergmann et al [3.16], however, devised a graphical method to obtain  $\tau_1$  and  $\tau_2$  for a pure polar liquid. The respective weighted contributions  $c_1$  and  $c_2$  towards dielectric relaxations were estimated in terms of  $\tau_1$  and  $\tau_2$ . Bhattacharyya et al [3.17] subsequently attempted to simplify the procedure of Bergmann et al [3.16] to get the same for a pure polar molecule with  $\epsilon'$ ,  $\epsilon''$ ,  $\epsilon_0$  and  $\epsilon_\infty$ , measured at two different frequencies in GHz range. The graphical analysis advanced by Higasi et al [3.18] on polar-nonpolar liquid mixture was also a crude one.

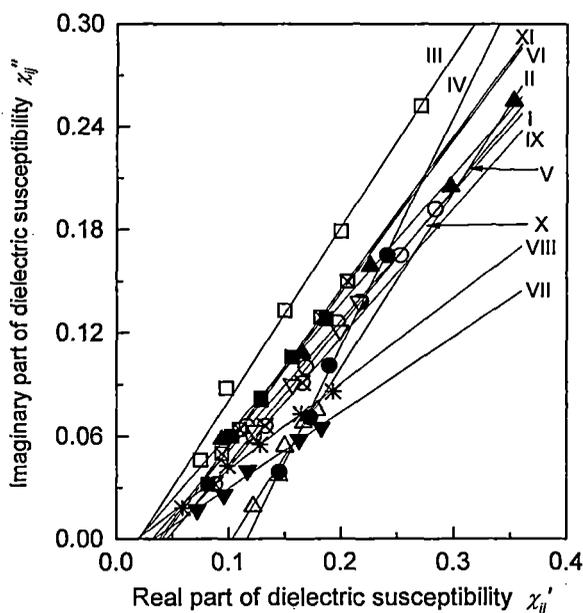


Figure 3.2: Linear variation of  $\chi_{ij}''$  with  $\chi_{ij}'$  for different  $w_j$ 's.

I. o-chloronitrobenzene in  $C_6H_6$  ( $-\circ-$ ); II. 4-chloro 3-nitrobenzotrifluoride in  $CCl_4$  ( $-\triangle-$ ); III. 4-chloro 3-nitrotoluene in  $C_6H_6$  ( $-\square-$ ); IV. 4-chloro 3-nitrotoluene in  $CCl_4$  ( $-\bullet-$ ); V. o-nitrobenzotrifluoride in  $C_6H_6$  ( $-\blacktriangle-$ ); VI. m-nitrobenzotrifluoride in  $C_6H_6$  ( $-\blacksquare-$ ); VII. 2-chloro 6-methyl aniline in  $C_6H_6$  ( $-\blacktriangledown-$ ); VIII. 3-chloro 2-methyl aniline in  $C_6H_6$  ( $-\ast-$ ); IX. 3-chloro 4-methyl aniline in  $C_6H_6$  ( $-\otimes-$ ); X. 4-chloro 2-methyl aniline in  $C_6H_6$  ( $-\nabla-$ ) and XI. 5-chloro 2-methyl aniline in  $C_6H_6$  ( $-\boxtimes-$ )

Thus, the object of the present paper is to detect  $\tau_1$  and  $\tau_2$  and hence, to measure  $\mu_1$  and  $\mu_2$  using  $\chi_{ij}$ 's based on the single frequency measurement technique [3.12, 3.19]. The aspect of molecular orientation polarisation is, however, achieved by introducing  $\chi_{ij}$  because  $\epsilon_{\infty ij}$  which includes fast polarisation, frequently appears as a subtracted term in Bergmann equations. Thus, to avoid the clumsiness of algebra and to exclude the fast polarisation process Bergmann equations [3.16] are simplified by the established symbols of  $\chi'_{ij}$ ,  $\chi''_{ij}$  and  $\chi_{oij}$  of Table 3.1 in SI units:

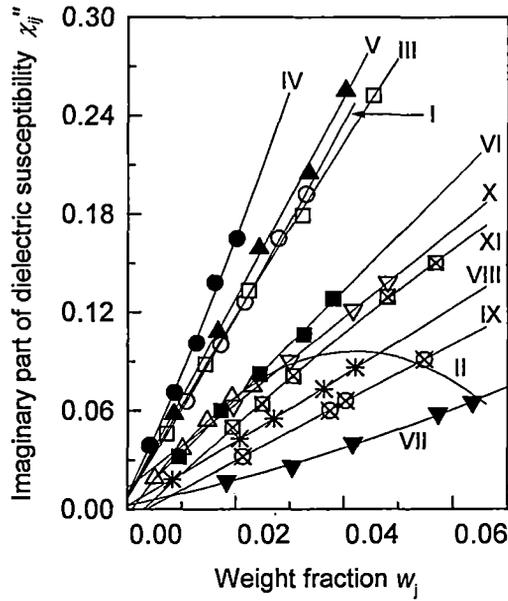


Figure 3.3: Variation of  $\chi''_{ij}$  against  $w_j$  of solutes

I. o-chloronitrobenzene in  $C_6H_6$  ( $-\circ-$ ) II. 4-chloro 3-nitrobenzotrifluoride in  $CCl_4$  ( $-\triangle-$ ); III. 4-chloro 3-nitrotoluene in  $C_6H_6$  ( $-\square-$ ); IV. 4-chloro 3-nitrotoluene in  $CCl_4$  ( $-\bullet-$ ); V. o-nitrobenzotrifluoride in  $C_6H_6$  ( $-\blacktriangle-$ ); VI. m-nitrobenzotrifluoride in  $C_6H_6$  ( $-\blacksquare-$ ); VII. 2-chloro 6-methyl aniline in  $C_6H_6$  ( $-\blacktriangledown-$ ); VIII. 3-chloro 2-methyl aniline in  $C_6H_6$  ( $-\ast-$ ); IX. 3-chloro 4-methyl aniline in  $C_6H_6$  ( $-\otimes-$ ); X. 4-chloro 2-methyl aniline in  $C_6H_6$  ( $-\nabla-$ ) and XI. 5-chloro 2-methyl aniline in  $C_6H_6$  ( $-\boxtimes-$ )

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \dots (3.1)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots (3.2)$$

assuming two broad Debye type dispersions for which the sum of  $c_1$  and  $c_2$  is unity. The Eqs.(3.1) and (3.2) are now solved to get:

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad \dots (3.3)$$

The variables  $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$  and  $\chi''_{ij}/\chi'_{ij}$  are plotted against each other for different  $w_j$ 's of the polar liquid under a single angular frequency  $\omega (=2\pi f)$  of the electric field to get a straight line with intercept  $-\omega^2 \tau_1 \tau_2$  and slope  $\omega(\tau_1 + \tau_2)$ , as shown in Fig.3.1. The intercept and slope of Eq.(3.3) are obtained by linear regression analysis made with the measured  $\chi_{ij}$ 's of solutes in  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$  to get  $\tau_2$  and  $\tau_1$  as found in the 6<sup>th</sup> and 7<sup>th</sup> columns of Table 3.2. The variables of Eq.(3.3) are extracted from Table 3.1, where all the data are collected together, system-wise, up to three decimals in close agreement with the expected [3.12]  $\tau_2$  and  $\tau_1$  of Table 3.2. Both  $\tau_2$  and  $\tau_1$  were found to deviate significantly, when the data of Table 3.1 were taken up to two decimal places with the claimed accuracy of measurement. The correlation coefficients  $r$ 's and the % of errors were worked out to place them in Table 3.2 only to see how far the variables of Eq.(3.3) are collinear to each other.

The relaxation times  $\tau$ 's due to Debye model are measured from the slope of  $\chi_{ij}''$  vs  $\chi_{ij}'$  curves of Fig.3.2 and the ratio of the individual slopes of  $\chi_{ij}''$  vs  $w_j$  and  $\chi_{ij}'$  vs  $w_j$  curves at  $w_j \rightarrow 0$  of Figs.3.3 and 3.4, respectively.  $\tau$ 's from both the methods are entered in the 8<sup>th</sup> and 9<sup>th</sup> columns of Table 3.2 only to see how far they agree with  $\tau_1$  and  $\tau_2$  due to double relaxation method of Eq.(3.3).

The theoretical values of  $c_1$  and  $c_2$  towards dielectric dispersions for  $\tau_1$  and  $\tau_2$  of different disubstituted benzenes and anilines in  $\text{C}_6\text{H}_6$  and  $\text{CCl}_4$  were calculated from Fröhlich's [3.20] theoretical formulations of  $\chi_{ij}'/\chi_{oij}$  and  $\chi_{ij}''/\chi_{oij}$ . The experimental  $c_1$  and  $c_2$ , on the other hand, were found out from  $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$  and  $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$  by graphical variations of  $\chi_{ij}'/\chi_{oij}$  and  $\chi_{ij}''/\chi_{oij}$  with  $w_j$ 's of Figs.3.5 and 3.6, in order to place them in Table 3.3 for comparison. The plots of  $\chi_{ij}'/\chi_{oij}$  and  $\chi_{ij}''/\chi_{oij}$  against  $w_j$  of the polar liquids in Figs.3.5 and 3.6 are the least squares fitted curves with the experimental points placed upon them. With the values of the intercepts presented in Table 3.3 from Figs.3.5 and 3.6 and the

graphical plot of  $(1/\phi)\log(\cos\phi)$  against  $\phi$  in degrees given elsewhere [3.4], the symmetric and asymmetric distribution parameters  $\gamma$  and  $\delta$  related to symmetric and characteristic relaxation times  $\tau_s$  and  $\tau_{cs}$  of the molecules were determined. They are seen in Table 3.3. The object of such determinations of  $\gamma$ ,  $\delta$ ,  $\tau_s$  and  $\tau_{cs}$  is to conclude the molecular nonrigidity and distribution of relaxation behaviour as well.

Table 3.3: Fröhlich's parameter  $A$ , theoretical and experimental values of  $\chi_{ij}'/\chi_{oij}$  &  $\chi_{ij}''/\chi_{oij}$  of Fröhlich equations (3.6) and (3.7) and from fitting Eqs. of Figs.3.5 and 3.6 at  $w_j \rightarrow 0$  respectively, theoretical and experimental relative contributions  $c_1$  and  $c_2$  towards dielectric dispersion due to  $\tau_1$  and  $\tau_2$ , symmetric and asymmetric distribution parameters  $\gamma$  and  $\delta$  for polar-nonpolar liquid mixtures of disubstituted benzenes and anilines at 35°C under 9.945 GHz electric field.

System with sl.no	$A$	Theoretical values of $\chi_{ij}'/\chi_{oij}$ & $\chi_{ij}''/\chi_{oij}$ from Eqs (3.6) & (3.7)		Theoretical values of $c_1$ and $c_2$		Expt. values of $\chi_{ij}'/\chi_{oij}$ & $\chi_{ij}''/\chi_{oij}$ at $w_j \rightarrow 0$ of Figs. (3.5) & (3.6)		Expt. values of $c_1$ & $c_2$		Estimated values of $\gamma$ and $\delta$			
(I) o-chloronitro benzene in $C_6H_6$	1.225	0.746	0.410	0.526	0.533	0.733	0.349	0.599	0.371	0.13	0.0095		
(II) 4-chloro 3-nitrobenzotrifluoride in $CCl_4$	3.806	0.830	0.259	0.687	0.525	0.890	0.027	0.894	-0.012	0.82	---		
(III) 4-chloro 3nitro toluene in $C_6H_6$	1.916	0.677	0.409	0.527	0.649	0.600	0.309	0.508	0.435	0.28	0.0070		
(IV) 4-chloro 3-nitro toluene in $CCl_4$	3.612	0.754	0.301	0.638	0.703	0.863	0.144	0.823	0.253	0.38	0.0024		
(V) o-nitrobenzotrifluoride in $C_6H_6$	2.691	0.873	0.266	0.653	0.444	0.616	0.347	0.288	0.655	0.21	0.0084		
(VI) m-nitrobenzotrifluoride in $C_6H_6$	1.327	0.611	0.455	0.485	0.625	1.134	0.261	1.514	-0.561	-0.45	---		
(VII) 2-chloro 6-methyl aniline in $C_6H_6$	1.319	0.737	0.412	0.527	0.544	1.078	0.141	1.402	-0.468	-0.40	---		
(VIII) 3-chloro 2-methyl aniline in $C_6H_6$	1.474	0.693	0.424	0.518	0.585	1.023	0.232	1.192	-0.194	-0.20	---		
(IX) 3-chloro 4- methyl aniline in $C_6H_6$	1.418	0.622	0.449	0.490	0.632	1.244	0.254	1.614	-0.588	-0.62	---		
(X) 4-chloro 2-methyl aniline in $C_6H_6$	1.619	0.427	0.448	0.416	0.842	1.062	0.419	1.449	-0.556	-0.33	---		
(XI) 5-chloro 2-methyl aniline in $C_6H_6$	1.089	0.547	0.475	0.462	0.627	0.907	0.312	1.354	-0.536	-0.03	0.0210		

The dipole moments  $\mu_2$  and  $\mu_1$  were then measured in terms of dimensionless parameters  $b$ 's involved with measured  $\tau$ 's of Table 3.2 and coefficients  $\beta_1$ 's and  $\beta_2$ 's presented in Table 3.4 of the variations of hf  $\chi_{ij}'$  and total hf conductivity  $\sigma_{ij}$  with  $w_j$ 's of Figs.3.4 and 3.7, respectively. The measured  $\mu$ 's are found in Table 3.4 in order to compare with theoretical dipole moment  $\mu_{\text{theo}}$ 's derived from available bond angles and bond moments of the substituent polar groups attached to the parent molecules as sketched in Fig.3.8. The structural aspect of some interesting polar molecules in Fig.3.8 exhibits the prominent mesomeric, inductive and electromeric effects of the substituted polar groups. All these effects are taken into account by the ratio  $\mu_{\text{expt}}/\mu_{\text{theo}}$ , in agreement with the measured  $\mu$ 's [3.6-3.8] of Table 3.4.

### 3.2. Formulations of $c_1$ and $c_2$ for $\tau_1$ and $\tau_2$ :

The Eqs.(3.1) and (3.2) are now solved to get  $c_1$  and  $c_2$  where

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad \dots (3.4)$$

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad \dots (3.5)$$

where  $\alpha_1 = \omega\tau_1$  and  $\alpha_2 = \omega\tau_2$  provided  $\alpha_2 > \alpha_1$ . The molecules under consideration are of complex type and only a few data are available under single frequency measurement in the low concentration region. A continuous distribution of  $\tau$  with two discrete values of  $\tau_1$  and  $\tau_2$  could, therefore, be expected. Thus, from Fröhlich's Eq. [3.20] based on distribution of  $\tau$  between the two extreme values of  $\tau_1$  and  $\tau_2$ , one gets:

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left( \frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \quad \dots (3.6)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \left[ \tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1) \right] \quad \dots (3.7)$$

where the Fröhlich parameter A is given by  $A = \ln(\tau_2/\tau_1)$ . The theoretical values of  $\chi_{ij}'/\chi_{oij}$  and  $\chi_{ij}''/\chi_{oij}$  of Eqs.(3.6) and (3.7) were used to get theoretical  $c_1$  and  $c_2$  from Eqs.(3.4) and (3.5) in order to compare them with the experimental values of  $c_1$  and  $c_2$  from the graphical plots of  $\chi_{ij}'/\chi_{oij}$  and  $\chi_{ij}''/\chi_{oij}$  at  $w_j \rightarrow 0$  as seen in Figs.3.5 and 3.6 respectively. Both the theoretical and experimental  $c_1$  and  $c_2$  are presented in Table 3.3 for comparison.

### 3.3. Distribution parameters $\gamma$ and $\delta$ related to symmetric and characteristic relaxation times $\tau_s$ and $\tau_{cs}$ :

The molecules are expected to show either symmetrical circular arc or a skewed arc in addition to other models [3.21] when the values of  $\chi_{ij}''/\chi_{oij}$  are plotted against  $\chi_{ij}'/\chi_{oij}$  at  $w_j \rightarrow 0$  for various frequencies of the electric field to yield:

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad \dots (3.8)$$

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad \dots (3.9)$$

Here,  $\gamma$  and  $\delta$  are the symmetric and asymmetric distribution parameters related to symmetric and characteristic relaxation times  $\tau_s$  and  $\tau_{cs}$ , respectively. Separating the real and imaginary parts of Eq.(3.8) one gets:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[ \left( 1 - \frac{\chi_{ij}'}{\chi_{oij}} \right) \frac{\chi_{ij}'/\chi_{oij}}{\chi_{ij}''/\chi_{oij}} - \frac{\chi_{ij}''}{\chi_{oij}} \right] \quad \dots (3.10)$$

$$\tau_s = \frac{1}{\omega} \left[ 1 / \left( \frac{\chi_{ij}'/\chi_{oij}}{\chi_{ij}''/\chi_{oij}} \cos \frac{\gamma\pi}{2} - \sin \frac{\gamma\pi}{2} \right) \right]^{\frac{1}{1-\gamma}} \quad \dots (3.11)$$

where  $\chi_{ij}'/\chi_{oij}$  and  $\chi_{ij}''/\chi_{oij}$  are obtained from intercepts of each variable with  $w_j$ 's of Figs.3.5 and 3.6 in the limit  $w_j=0$ . Again  $\delta$  and  $\tau_{cs}$  can be had from Eq.(3.9) as:

$$\tan(\phi\delta) = \frac{(\chi''_{ij}/\chi_{oij})_{w_j \rightarrow 0}}{(\chi'_{ij}/\chi_{oij})_{w_j \rightarrow 0}} \quad \dots (3.12)$$

$$\tau_{cs} = \frac{1}{\omega} \tan \phi \quad \dots (3.13)$$

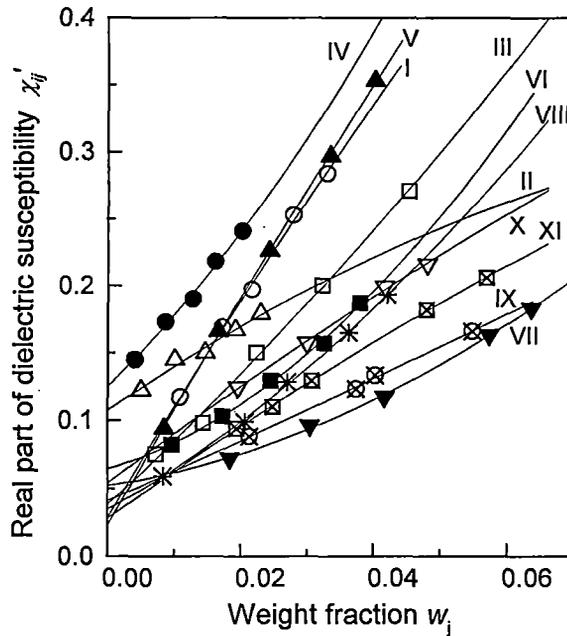


Figure 3.4 : Variation of  $\chi'_{ij}$  against  $w_j$  of solutes

- I. o-chloronitrobenzene in  $C_6H_6$  (-○-); II. 4-chloro 3-nitrobenzotrifluoride in  $CCl_4$  (-△-); III. 4-chloro 3-nitrotoluene in  $C_6H_6$  (-□-); IV. 4-chloro 3-nitrotoluene in  $CCl_4$  (-●-); V. o-nitrobenzotrifluoride in  $C_6H_6$  (-▲-); VI. m-nitrobenzotrifluoride in  $C_6H_6$  (-■-); VII. 2-chloro 6-methyl aniline in  $C_6H_6$  (-▼-); VIII. 3-chloro 2-methyl aniline in  $C_6H_6$  (-\*-); IX. 3-chloro 4-methyl aniline in  $C_6H_6$  (-⊗-); X. 4-chloro 2-methyl aniline in  $C_6H_6$  (-▽-) and XI. 5-chloro 2-methyl aniline in  $C_6H_6$  (-⊠-)

Since,  $\phi$  can not be evaluated directly, a theoretical curve of  $(1/\phi)\log(\cos\phi)$  with  $\phi$  in degrees was drawn as shown elsewhere [3.4], from which:

$\frac{1}{\phi} \log(\cos\phi) = \frac{\log[(\chi'_{ij}/\chi_{oij})/\cos(\phi\delta)]}{\phi\delta}$	$\dots (3.14)$
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Table 3.4: Slope  $\beta_1$  of  $\chi_{ij}'$  vs  $w_j$  and  $\beta_2$  of  $\sigma_{ij}$  vs  $w_j$  curves, measured dipole moments  $\mu_j$  from susceptibility measurement technique and  $hf$  conductivity method from Eqs.(3.19) and (3.26) respectively, reported dipole moment, theoretical dipole moment  $\mu_{theo}$  from available bond angles and bond moments expressed in Coulomb.metre (C.m) and the values of  $\mu_{expt}/\mu_{theo}$  for different disubstituted benzenes and anilines at 35 °C under 9.945 GHz electric field.

System with sl.no. & mol.wt.	Slope of $\chi_{ij}'-w_j$ & $\sigma_{ij}-w_j$ curves		Dipole moments $\mu_j$ ( $\times 10^{-30}$ ) in Coulomb.metre								$\mu_{expt}/\mu_{theo}$
	$\beta_1$	$\beta_2$	From Eq (3.19)		From Eq (3.26)		$\mu_j^a$	$\mu_j^b$	$\mu_j^r$	$\mu_{theo}$	
			$\mu_2$	$\mu_1$	$\mu_2$	$\mu_1$					
(I) o-chloronitro benzene in $C_6H_6$ $M_j=0.1575$ Kg	8.326	4.706	16.93	12.41	17.11	12.54	14.90	14.07	14.50	17.60	0.96
(II) 4-chloro3-nitrobenzotrifluoride in $CCl_4$ $M_j=0.2255$ Kg	3.358	1.875	13.02	6.81	13.08	6.84	9.76	11.80	10.57	12.60	1.03
(III) 4-chloro 3-nitro toluene in $C_6H_6$ $M_j=0.1715$ Kg	4.490	2.570	17.39	9.37	17.69	9.53	12.94	14.54	14.97	18.60	0.93
(IV) 4-chloro 3-nitro toluene in $CCl_4$ $M_j=0.1715$ Kg	4.854	3.001	17.40	7.15	18.39	7.56	11.95	12.36	15.60	18.50	0.94
(V) o-nitrobenzotrifluoride in $C_6H_6$ $M_j=0.1910$ Kg	8.598	4.662	18.78	13.34	18.59	13.20	16.68	16.18	16.54	20.60	0.91
(VI) m-nitrobenzotrifluoride in $C_6H_6$ $M_j=0.1910$ Kg	1.426	0.702	9.77	5.83	9.22	5.50	7.27	13.52	12.24	12.47	0.78
(VII) 2-chloro 6-methyl aniline in $C_6H_6$ $M_j=0.1415$ Kg	0.728	0.560	4.91	3.47	5.79	4.09	3.64	4.50	7.73	6.16	0.56
(VIII) 3-chloro 2-methyl aniline in $C_6H_6$ $M_j=0.1415$ Kg	2.674	1.693	10.47	6.66	11.20	7.13	7.14	7.86	10.07	8.27	0.81
(IX) 3-chloro4-methyl aniline in $C_6H_6$ $M_j=0.1415$ Kg	2.128	1.269	10.38	6.07	10.78	6.30	7.14	7.49	8.70	7.33	0.83
(X) 4-chloro2-methyl aniline in $C_6H_6$ $M_j=0.1415$ Kg	3.650	2.063	21.38	8.45	21.61	8.54	9.56	9.07	10.94	10.20	0.83
(XI) 5-chloro2-methyl aniline in $C_6H_6$ $M_j=0.1415$ Kg	3.481	2.196	13.46	8.22	14.37	8.78	9.79	9.79	0.34	9.44	0.87

$\mu_j^a$  = dipole moment by using  $\tau$  from the direct slope of Eq (3.15)

$\mu_j^b$  = dipole moment by using  $\tau$  from the ratio of individual slopes of Eq (3.16)

$\mu_j^r$  = reported dipole moment

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

was found out. The known values of  $(1/\phi)\log(\cos\phi)$  was then used to obtain  $\phi$ . With known  $\phi$  and  $\delta$ ,  $\tau_{cs}$  were obtained from Eqs.(3.12) and (3.13) for each molecule. The estimated  $\gamma$  and  $\delta$  are presented in columns 11 and 12 of Table 3.3. Values of  $\tau_s$  and  $\tau_{cs}$  are entered in columns 11 and 12 of Table 3.2 to conclude symmetric relaxation behaviour for disubstituted anilines and asymmetric relaxation behaviour for disubstituted benzenes, respectively.

#### 3.4. Theoretical formulation for dipole moments $\mu_2$ and $\mu_1$ :

The Debye equation [3.22] for a polar-nonpolar liquid mixture under hf electric field in terms of  $\chi_{ij}$ 's is written as:

$$\frac{d\chi_{ij}''}{d\chi_{ij}'} = \omega\tau \quad \dots (3.15)$$

$$\frac{(d\chi_{ij}''/dw_j)_{w_j \rightarrow 0}}{(d\chi_{ij}'/dw_j)_{w_j \rightarrow 0}} = \omega\tau \quad \dots (3.16)$$

$\tau$ 's of the polar liquids could, however, be estimated from Eqs.(3.15) and (3.16) as seen in 8<sup>th</sup> and 9<sup>th</sup> columns of Table 3.2. Again the imaginary part  $\chi_{ij}''$  of the complex hf susceptibility  $\chi_{ij}^*$  as a function of  $w_j$  of a solute can be written as [3.23-3.24]:

$$\chi_{ij}'' = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 k_B T M_j} \frac{\omega\tau}{1 + \omega^2\tau^2} (\varepsilon_{ij} + 2)^2 w_j$$

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

$$\left( \frac{d\chi_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_0 k_B T M_j} \frac{\omega\tau}{(1 + \omega^2\tau^2)} (\varepsilon_i + 2)^2 \quad \dots (3.17)$$

where the density of the solution  $\rho_{ij}$  becomes  $\rho_i$ =density of solvent,  $(\varepsilon_{ij}+2)^2$  becomes  $(\varepsilon_i+2)^2$  at  $w_j \rightarrow 0$ ,  $k_B$ =Boltzmann constant,  $N$ =Avogadro's number,  $\varepsilon_i$ =relative permittivity of solvent

and  $\epsilon_0$ =permittivity of free space =  $8.854 \times 10^{-12}$  Farad. metre<sup>-1</sup>. All are expressed in SI units.

Comparing Eqs.(3.16) and (3.17) one gets:

$$\left( \frac{d\chi'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{27\epsilon_0 k_B T M_j} \frac{1}{(1 + \omega^2 \tau^2)} (\epsilon_i + 2)^2 = \beta_1 \quad \dots (3.18)$$

where  $\beta_1$  is the slope of  $\chi'_{ij}$  vs  $w_j$  curves of Fig.3.4 at  $w_j \rightarrow 0$ . Here, no approximation in determination of  $\mu_j$  is made, like the conductivity measurement technique [3.4] given below.

After simplification, the hf dipole moment  $\mu_j$  is given by:

$$\mu_j = \left( \frac{27\epsilon_0 k_B T M_j \beta_1}{N\rho_i (\epsilon_i + 2)^2 b} \right)^{\frac{1}{2}} \quad \dots (3.19)$$

where dimensionless parameter b is given by :

$$b = 1/(1 + \omega^2 \tau^2) \quad \dots (3.20)$$

### 3.5. Dipole moments $\mu_2$ and $\mu_1$ from hf conductivity :

The complex hf conductivity  $\sigma_{ij}^*$  of polar-nonpolar liquid mixture in a GHz electric field is given by [3.25]:

$$\sigma_{ij}^* = \sigma'_{ij} + j\sigma''_{ij} \quad \dots (3.21)$$

where  $\sigma'_{ij}$ (= $\omega\epsilon_0\epsilon_{ij}''$ ) and  $\sigma''_{ij}$ (= $\omega\epsilon_0\epsilon_{ij}'$ ) are the real and imaginary parts of the complex conductivity  $\sigma_{ij}^*$  in  $\Omega^{-1} .m^{-1}$ . The magnitude of the total hf conductivity is:

$$\sigma_{ij} = \omega\epsilon_0 (\epsilon_{ij}''^2 + \epsilon_{ij}'^2)^{\frac{1}{2}} \quad \dots (3.22)$$

Although  $\epsilon_{ij}' \gg \epsilon_{ij}''$ , but in the high frequency region,  $\epsilon_{ij}' \cong \epsilon_{ij}''$ .  $\epsilon_{ij}''$  is responsible for absorption of electric energy and offers resistance to polarisation. Hence  $\sigma_{ij}''$  is related to  $\sigma_{ij}'$  by the relation [3.25]:

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

$$\sigma_{ij}' = \sigma_{\infty ij} + \frac{1}{\omega\tau} \sigma_{ij}'' \quad \dots (3.23)$$

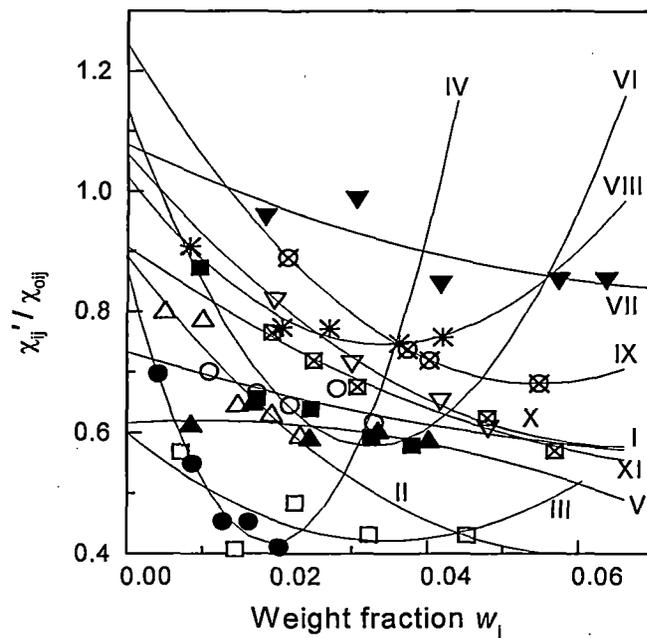


Figure 3.5 : Plot of  $\chi_{ij}''/\chi_{\infty ij}$  with  $w_j$  of solutes

- I. o-chloronitrobenzene in  $C_6H_6$  (—○—); II. 4-chloro 3-nitrobenzo-trifluoride in  $CCl_4$  (—△—); III. 4-chloro 3-nitrotoluene in  $C_6H_6$  (—□—); IV. 4-chloro 3-nitrotoluene in  $CCl_4$  (—●—); V. o-nitrobenzotrifluoride in  $C_6H_6$  (—▲—); VI. m-nitrobenzotrifluoride in  $C_6H_6$  (—■—); VII. 2-chloro 6-methyl aniline in  $C_6H_6$  (—▼—); VIII. 3-chloro 2-methyl aniline in  $C_6H_6$  (—\*—); IX. 3-chloro 4-methyl aniline in  $C_6H_6$  (—⊗—); X. 4-chloro 2-methyl aniline in  $C_6H_6$  (—▽—) and XI. 5-chloro 2-methyl aniline in  $C_6H_6$  (—⊠—)

Here, the approximation  $\sigma_{ij}'' \cong \sigma_{ij}'$  is made. Differentiation of Eq.(3.23) with respect to  $w_j$  at  $w_j \rightarrow 0$  yields:

$$\left(\frac{d\sigma'_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \omega\tau \left(\frac{d\sigma_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \omega\tau\beta_2 \quad \dots (3.24)$$

where  $\beta_2$  is the slope of  $\sigma_{ij}$  vs  $w_j$  curves of Fig.3.7 at infinite dilution  $w_j \rightarrow 0$  and placed in Table 3.4.

The real part of hf conductivity  $\sigma'_{ij}$  at T K [3.23] is given by:

$$\sigma'_{ij} = \frac{N\rho_{ij}\mu_j^2}{27k_B TM_j} \frac{\omega^2\tau}{1+\omega^2\tau^2} (\epsilon_{ij} + 2)^2 w_j$$

$$\left(\frac{d\sigma'_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27k_B TM_j} \frac{\omega^2\tau}{1+\omega^2\tau^2} (\epsilon_i + 2)^2 \quad \dots (3.25)$$

Comparing Eqs.(3.24) and (3.25) one gets the dipole moment  $\mu_j$  from:

$$\mu_j = \left(\frac{27k_B TM_j \beta_2}{N\rho_{ij} (\epsilon_i + 2)^2 \omega b}\right)^{\frac{1}{2}} \quad \dots (3.26)$$

All the measured dipole moments  $\mu_j$ 's from the susceptibility measurement technique of Eq.(3.19) and hf conductivity method of Eq.(3.26) are entered in the 4<sup>th</sup> -7<sup>th</sup> columns of Table 3.4 respectively.

### 3.6. Results and discussions :

The double relaxation times  $\tau_1$  and  $\tau_2$  for the polar liquid molecules in different solvents are found out from the slope and intercept of Eq.(3.3), as shown in Fig.3.1, in terms of the orientational susceptibility parameters  $\chi_{ij}$ 's of Table 3.1. The  $\chi_{ij}$ 's are, however, derived from the relative permittivities  $\epsilon_{ij}$ 's [3.6-3.8] for different weight fractions  $w_j$ 's of the polar liquids. The variables of Eq.(3.3) i.e  $(\chi_{oij}-\chi_{ij}')/\chi_{ij}'$  and  $\chi_{ij}''/\chi_{ij}'$  are plotted against each other for different  $w_j$ 's of solutes under 9.945 GHz electric field at 35<sup>o</sup>C to get linear equation by regression analysis. From Fig.3.1, it revealed that, the fitting is good for some cases, but poor in other cases. It appears that the linear fit for II (- $\Delta$ -), III (- $\square$ -) and IV (- $\bullet$ -) in Figs.3.1 and 3.2 often passes through two among five data points, others being off

from the fit. Nevertheless, the regression analysis was made on the basis of Eq. (3.3). However, the accuracy of Fig.3.1 is tested by the correlation coefficients  $r$ 's, which were found to be close to unity, indicating the variables are almost collinear.

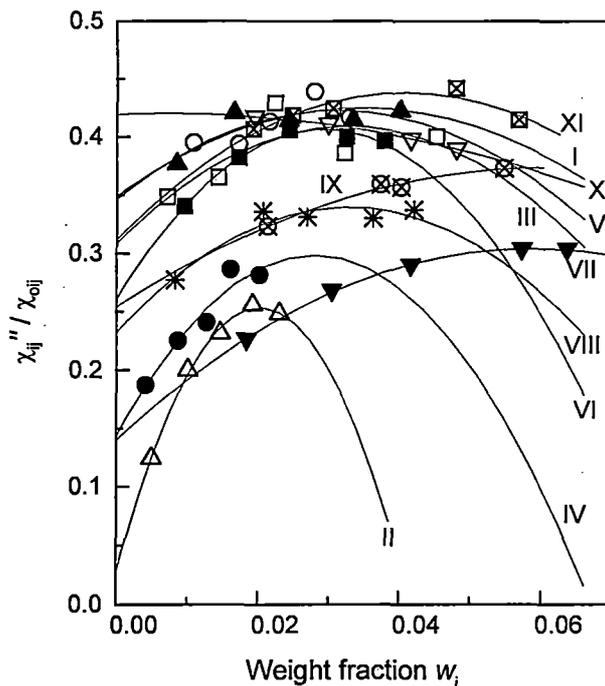


Figure 3.6 : Plot of  $\chi''_{ij}/\chi''_{oij}$  with  $w_j$  of solutes

I. o-chloronitrobenzene in  $C_6H_6$  (-○-); II. 4-chloro 3-nitrobenzo-trifluoride in  $CCl_4$  (-△-) III. 4-chloro 3-nitrotoluene in  $C_6H_6$  (-□-) IV. 4-chloro 3-nitrotoluene in  $CCl_4$  (-●-) V. o-nitro-benzotrifluoride in  $C_6H_6$  (-▲-) VI. m-nitrobenzotrifluoride in  $C_6H_6$  (-■-) VII. 2-chloro 6-methyl aniline in  $C_6H_6$  (-▼-) VIII. 3-chloro 2-methyl aniline in  $C_6H_6$  (-\*-) IX. 3-chloro 4-methyl aniline in  $C_6H_6$  (-⊗-) X. 4-chloro 2-methyl aniline in  $C_6H_6$  (-▽-) and XI. 5-chloro 2-methyl aniline in  $C_6H_6$  (-⊠-)

The % of errors in terms of  $r$ 's in getting the intercepts and slopes were worked out to find the accuracies of  $\tau_1$  and  $\tau_2$  respectively. In order to locate the double relaxation phenomena of the polar liquid molecules in non-polar aprotic solvents under investigation, accurate measurement of  $\chi_{oij}$  involved with  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  is necessary. The refractive index  $n_{Dij}$  measured by Abbe's refractometer often yields  $\epsilon_{\infty i} = n_{Dij}^2$ , although Cole Cole [3.26] and Cole

Davidson [3.27] plots usually give  $\epsilon_{\infty ij} \cong 1.0$  to 1.5 times of  $n_{Dij}^2$ . This often introduces an additional error in the calculations. Nevertheless, the accuracies of  $\chi_{ij}''$ ,  $\chi_{ij}'$  and  $\chi_{oij}$  are of 5% and 1%, respectively derived from measured [3.6-3.8] relative permittivities  $\epsilon_{ij}''$ ,  $\epsilon_{ij}'$ ,  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$ . The estimated  $\tau_2$  and  $\tau_1$  are placed in Table 3.2, in order to compare them with those of Murthy et al [3.28] of Eq.(3.15) and by the ratio of the individual slopes of the variations of  $\chi_{ij}''$  and  $\chi_{ij}'$  with  $w_j$ 's in the limit  $w_j \rightarrow 0$  of Eq.(3.16). The latter method seems to be better to calculate  $\tau$ , since it eliminates polar-polar interaction almost completely. The linear plot of  $\chi_{ij}''$  against  $\chi_{ij}'$  of Fig.3.2 for different  $w_j$ 's of solute has intercepts although it was expected from Eq.(3.15) that, they should pass through the origin. Nevertheless,  $\tau$ 's are found to be in close agreement with those calculated from the ratio of the individual slopes of the variations of  $\chi_{ij}''$  and  $\chi_{ij}'$  with  $w_j$  at  $w_j \rightarrow 0$  of Eq.(3.16) as shown in Figs.3.3 and 3.4. The experimental points as shown in Figs.3.3 and 3.4 with the fit are presented (Table 3.2) to back up the results of Eq.(3.16) due to Debye model. Values of  $\chi_{ij}''$  increase monotonically with  $w_j$ 's and have a tendency to meet the origin for all the curves. This type of behaviour indicates that  $\chi_{ij}''$  tends to pass through the origin at  $w_j \rightarrow 0$  under 9.945 GHz electric field.

It is evident from Table 3.2 that, all the disubstituted benzenes exhibit the whole molecular rotation while the disubstituted anilines show the rotation of the flexible parts under 10 GHz electric field when  $\tau_1$ 's and  $\tau_2$ 's are compared with the reported data. This indicates the flexible parts are more rigid in the disubstituted benzenes rather than the disubstituted anilines. The assumptions of symmetric and asymmetric relaxation behaviours from Eqs.(3.8) and (3.9) for such non rigid polar molecules yield  $\tau_s$  and  $\tau_{cs}$  from Eqs.(3.11) and (3.13) to place them in the last two columns of Table 3.2. It reveals that the symmetric and asymmetric relaxation processes are more probable since  $\tau_s$  and  $\tau_{cs}$  are almost in agreement with the reported  $\tau$ 's in a solution. The characteristic relaxation times  $\tau_{cs}$  are sometimes very high through asymmetric distribution parameter  $\delta$  and often could not be determined for most of the molecules.

The disubstituted benzenes showed  $\tau_2$ 's in agreement with the reported  $\tau$ 's and  $\tau_{cs}$  except o-nitrobenzotrifluoride in  $C_6H_6$ , which agrees with  $\tau_s$  only. But, 4-chloro 3-nitrobenzotrifluoride in  $CCl_4$  and m-nitrobenzotrifluoride in  $C_6H_6$  yield  $\tau_2$  in close

agreement with reported  $\tau$ 's although they showed  $\tau_s \cong \tau_1$ . Only 2-chloro 6-methyl aniline and 3-chloro 2-methyl aniline in  $C_6H_6$  showed  $\tau_1$ 's in excellent agreement with the calculated  $\tau_s$ 's. For the rest disubstituted anilines  $\tau_1$ 's agree well with the calculated  $\tau_s$ 's, but the agreement is not better with the measured  $\tau$ 's from Eqs.(3.15) and (3.16). It thus reveals that, a part of the disubstituted anilines is rotating, obeying symmetric relaxation behaviour, while most of the disubstituted benzenes showed asymmetric relaxation process for their whole molecular rotations.

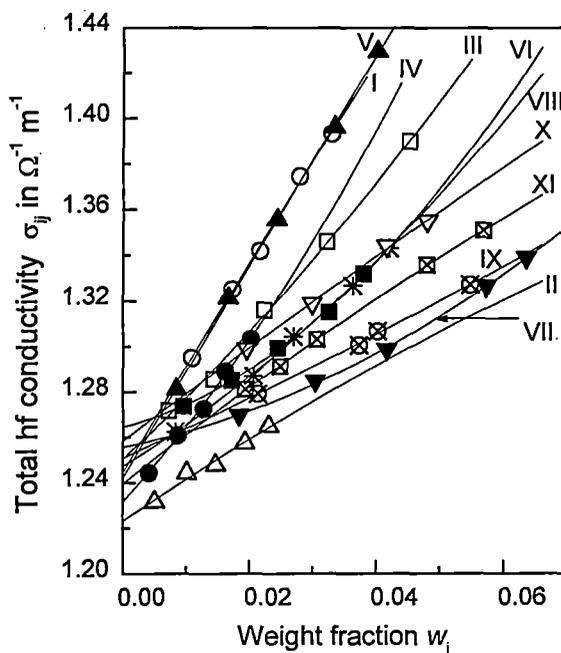


Figure 3.7 : Variation of  $\sigma_{ij}$  against  $w_j$  of solutes

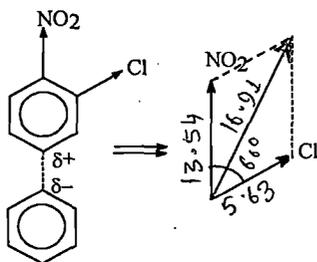
- I. o-chloronitrobenzene in  $C_6H_6$  (-○-); II. 4-chloro 3-nitrobenzo-trifluoride in  $CCl_4$  (-△-); III. 4-chloro 3-nitrotoluene in  $C_6H_6$  (-□-); IV. 4-chloro 3-nitrotoluene in  $CCl_4$  (-●-); V. o-nitro-benzotrifluoride in  $C_6H_6$  (-▲-); VI. m-nitrobenzotrifluoride in  $C_6H_6$  (-■-); VII. 2-chloro 6-methyl aniline in  $C_6H_6$  (-▼-); VIII. 3-chloro 2-methyl aniline in  $C_6H_6$  (-\*-); IX. 3-chloro 4-methyl aniline in  $C_6H_6$  (-⊗-); X. 4-chloro 2-methyl aniline in  $C_6H_6$  (-▽-) and XI. 5-chloro 2-methyl aniline in  $C_6H_6$  (-⊠-)

The relative weighted contributions  $c_1$  and  $c_2$  towards dielectric dispersions due to  $\tau_1$  and  $\tau_2$  are estimated and placed in Table 3.3, by using Fröhlich's Eqs.(3.6) and (3.7). They are compared with the experimental  $c_1$  and  $c_2$  from the fitted curves of  $\chi_{ij}'/\chi_{oij}$  and  $\chi_{ij}''/\chi_{oij}$

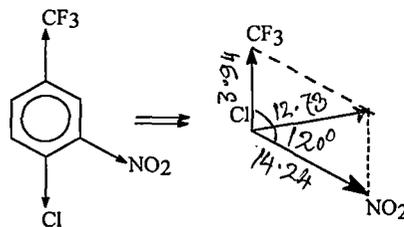
against  $w_j$  in the limit  $w_j \rightarrow 0$  of Figs.3.5 and 3.6. The nonlinear fit with only five points for III ( $-\square-$ ) and IV ( $-\bullet-$ ) of Fig.3.5 appeared to be non-convincing and misleading, but three accurate experimental points are enough for such fit. However, the fit is done with a PC and appropriate software. All the curves of Figs.3.5 and 3.6 vary usually [3.12] except the convex curve V for o-nitrobenzotrifluoride in  $C_6H_6$ . The variations of  $\chi_{ij}'/\chi_{oij}$  with  $w_j$  are, however, concave and convex in nature for all systems as observed elsewhere [3.12]. The left hand sides of Eqs.(3.1) and (3.2) vary with  $w_j$ 's in concave and convex manner according to Figs.3.5 and 3.6 are now fixed for  $\tau_1$  and  $\tau_2$  once estimated from intercept and slope of Eq.(3.3) to yield experimental  $c_1$  and  $c_2$  values from Eqs.(3.4) and (3.5) at  $w_j \rightarrow 0$ .

This study is supposed to yield the accurate values of  $c_1$  and  $c_2$  unlike the earlier one [3.12] based on the graphical extrapolated values of  $(\epsilon_{ij}' - \epsilon_{\infty ij})/(\epsilon_{oij} - \epsilon_{\infty ij})$  and  $\epsilon_{ij}''/(\epsilon_{oij} - \epsilon_{\infty ij})$  at  $w_j \rightarrow 0$  drawn on the basis of scientific judgment. Although, the nature of variations remains unaltered, it is evident from Table 3.3 that,  $c_2$ 's are often negative for 4-chloro 3-nitrobenzotrifluoride in  $CCl_4$ , m-nitrobenzotrifluoride in  $C_6H_6$  and for all the disubstituted anilines unlike other systems. This perhaps signifies that the rotation of the flexible parts of the polar molecules are not in accord with the whole molecular rotation due to inherent inertia of the substituted parts of the molecules under hf electric field. The theoretical values of  $c_1+c_2$  are found to be greater than the sum of the experimental ones as listed in Table 3.3.

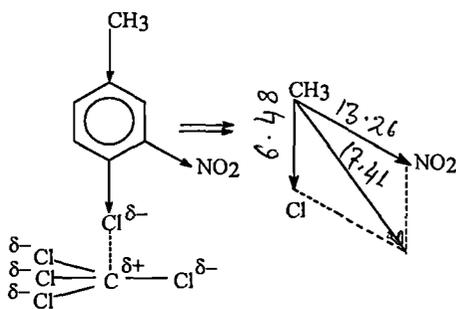
The experimental values show that  $c_1+c_2 \cong 1$  for almost all the non-spherical polar liquid molecules. But (II) 4-chloro 3-nitrobenzo-trifluoride in  $CCl_4$  ( $-\triangle-$ ), (X) 4-chloro 2-methyl aniline ( $-\nabla-$ ) and (XI) 5-chloro 2-methyl aniline ( $-\boxtimes-$ ) in  $C_6H_6$  show considerably lower values of  $c_1+c_2$ . This may indicate the reliability of Eq.(3.3) so far derived for such molecules, although they show high correlation coefficients  $r$ 's and the corresponding very low % of errors to get the intercept and slope of Eq.(3.3). The largest theoretical  $c_1+c_2$  value for (IV) 4-chloro 3-nitro toluene in  $CCl_4$  ( $-\bullet-$ ) is 1.34, showing a deviation of nearly 34%, unlike the other systems. The possible existence of more than two broad Debye type dispersions may be taken into account for such molecules of varying complexities as reported in Tables and Figures.



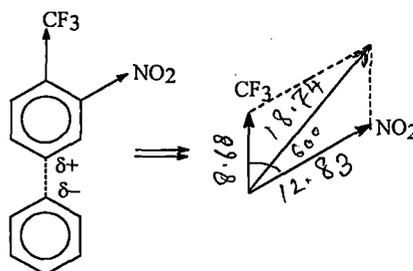
I. o-chloronitrobenzene in  $C_6H_6$



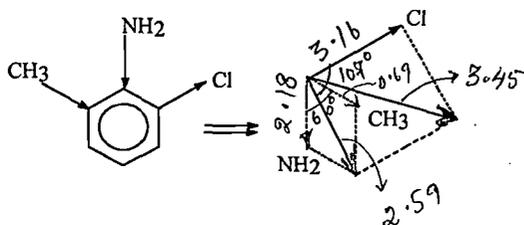
II. 4-chloro 3-nitrobenzotrifluoride in  $CCl_4$



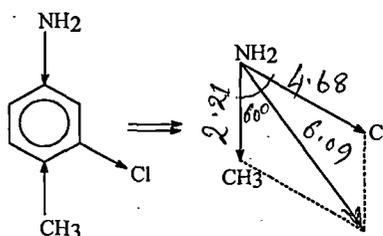
IV. 4-chloro 3-nitro toluene in  $CCl_4$



V. o-nitrobenzotrifluoride in  $C_6H_6$



VII. 2-chloro 6-methyl aniline in  $C_6H_6$



IX. 3-chloro 4-methyl aniline in  $C_6H_6$

Figure 3.8: Conformational structures of solutes from bond angles and bond moments multiplied by  $10^{-30}$  Coulomb. metre (C.m)

Dipole moments  $\mu_2$  and  $\mu_1$  due to rotation of the whole molecule as well as the flexible parts were, however, measured from Eq.(3.19) using dimensionless parameters  $b$ 's involved with  $\tau$ 's by both the methods and slope  $\beta_1$ 's of  $\chi_{ij}'$  vs  $w_j$  curves of Fig.3.4. The

measured values of  $\mu_2$  and  $\mu_1$  are presented in Table 3.4. The variations of all the  $\chi_{ij}'$ 's of polar-nonpolar liquid mixtures are found to be parabolic with  $w_j$ 's of polar compounds as evident from Fig.3.4. They are found to cut the ordinate axis at  $w_j=0$  within  $0.0238 \leq \chi_{ij}' \leq 0.0645$  except 4-chloro 3-nitrobenzotrifluoride in  $\text{CCl}_4$  ( $-\Delta-$ ), 4-chloro 3-nitrotoluene in  $\text{CCl}_4$  ( $-\bullet-$ ). This behaviour probably reflects the solvent effects on the polar compounds under investigation. The interaction of solute on solvent  $\text{CCl}_4$  may occur due to slightly positive charge  $\delta^+$  on C atom of  $\text{CCl}_4$  and negative charge  $\delta^-$  on Cl atom of the substituted group in the benzene ring, as seen in Fig.3.8. All the systems are of similar nature having monotonic increase of  $\chi_{ij}'$  with  $w_j$ .

The dipole moments  $\mu_2$  and  $\mu_1$  are also derived from the conductivity measurement technique of Eq.(3.26) using the slope  $\beta_2$ 's of  $\sigma_{ij}$  vs  $w_j$  curves of Fig.3.7 and are placed in Table 3.4 for comparison. The total hf conductivity  $\sigma_{ij}$  of all the polar-nonpolar liquid mixtures increase monotonically with  $w_j$  and cut the ordinate axis within the range  $1.2233 \leq \sigma_{ij} \leq 1.2646$  at  $w_j=0$  as seen in Fig.3.7. The slight disagreement of  $\mu_1$  and  $\mu_2$  derived from both the methods is due to the fact that the hf conductivity includes the fast polarisation probably for the bound molecular charge associated with the molecule. All  $\mu_2$ 's for disubstituted benzenes and  $\mu_1$ 's for disubstituted anilines are found to agree with the reported  $\mu$ 's placed in Table 3.4. This indicates that, the flexible parts of the disubstituted benzenes are more rigid in comparison to disubstituted anilines.

The hf dipole moment  $\mu_j$ 's are calculated by using  $\tau$  from both the methods of direct slope of Eq.(3.15) and the ratio of the individual slopes of Eq.(3.16) in order to place them in Table 3.4.  $\mu_j$ 's by using  $\tau$  from the ratio of the individual slopes are in close agreement with the reported values suggesting the fact that the latter method to get  $\tau$  is more realistic. In such case one polar molecule is surrounded by a large number of non-polar solvent molecules and remains in a quasi-isolated state.

A special attention is, therefore, paid to obtain the conformational structures of some of the complex molecules as shown schematically in Fig.3.8. The inductive, electromeric and resonance effects combined with mesomeric effect of the substituted polar groups play the key role to yield the theoretical dipole moment  $\mu_{\text{theo}}$ 's depending on the electron affinity

of C-atom of the benzene ring. The molecules have  $C \rightarrow CF_3$ ,  $C \leftarrow NH_2$  ( $\angle 142^\circ$ ),  $C \rightarrow NO_2$ ,  $C \rightarrow Cl$   $C \leftarrow CH_3$  polar groups of bond moments  $9.53 \times 10^{-30}$ ,  $4.93 \times 10^{-30}$ ,  $14.10 \times 10^{-30}$ ,  $5.63 \times 10^{-30}$ ,  $1.23 \times 10^{-30}$  Coulomb.metre (C.m) respectively [3.12,3.19] aligned in different angles in a plane to yield  $\mu_{theo}$ . Out of these, only  $-NO_2$  and  $-NH_2$  groups are in the habit to show resonance effect ( $-R$  or  $+R$ ) in the molecules either by pulling or pushing electrons towards C-atom of the benzene ring. This resonance effect is more stronger than inductive effects ( $+I$  or  $-I$ ) to exhibit the peculiar behaviours as seen in the  $\chi_{ij}'/\chi_{oij}$  vs  $w_j$  and  $\chi_{ij}''/\chi_{oij}$  vs  $w_j$  curves for the disubstituted benzenes II, IV, V, VI including all the disubstituted anilines.

The structure of these polar molecules is of special interest as sketched in Fig.3.8 in view of rearrangement of charge density in them. All the disubstituted anilines include  $-Cl$ ,  $-NH_2$  and  $-CH_3$  polar groups, of which  $-Cl$  and  $-CH_3$  have very weak inductive effects ( $+I$  or  $-I$ ). They are easily influenced by the GHz electric field to show the rotation of their flexible parts. Further, the observed difference in  $\mu$  values for a polar molecule in two aprotic non-polar solvents may arise due to weak polarity of  $CCl_4$  as shown in Fig.3.8. The difference between  $\mu_{theo}$ 's and experimental  $\mu_j$ 's establishes the non consideration of inductive and mesomeric effects. All these effects may be taken into account by the factor  $\mu_{expt}/\mu_{theo}$  to yield the exact  $\mu_1$  and  $\mu_2$  values of the molecules. All the polar molecules have  $sp^2$  hybridized carbon atoms of benzene ring and the substituted parts are associated with  $sp^3$  orbital. The interaction of orbitals may lead to gain knowledge on accumulation of charge on the substituted groups in addition to various effects present in them. The conformational structures of other molecules except six of Fig.3.8 were already shown elsewhere [3.12,3.19].

### 3.7. Conclusions :

The study of relaxation phenomena of disubstituted benzenes and anilines in  $C_6H_6$  and  $CCl_4$  by the modern established symbols of dielectric orientation susceptibilities  $\chi_{ij}$ 's measured under a single frequency electric field is very encouraging. It seems to be more topical, significant and useful contribution to predict the conformational structures and various molecular associations of the molecules at any given temperature. The intercept and

slope of the derived linear Eq.(3.3) by the regression analysis on the measured data of  $\chi_{ij}$ 's of different  $w_j$ 's are used to get  $\tau_2$  and  $\tau_1$ . The methodology so far developed in SI units is superior because of the unified, coherent and rationalised nature of the established symbols of dielectric terminologies and parameters, which are directly linked with orientational polarisation of the molecules. The significant Eqs.(3.15) and (3.16) to obtain  $\tau_j$ 's and hence  $\mu_j$ 's from Eq.(3.19) help the future workers to shed more light on the relaxation phenomena of the complicated non-spherical polar liquids and liquid crystals. The prescribed method to obtain  $\tau_j$ 's from Eq.(3.16) with the use of the ratio of the individual slopes of  $\chi_{ij}''$  vs  $w_j$  and  $\chi_{ij}'$  vs  $w_j$  curves at  $w_j \rightarrow 0$  is a significant improvement over the existing ones, as it eliminates polar-polar interaction almost completely in  $\tau_j$ 's and  $\mu_j$ 's respectively.

$\tau_j$ 's and  $\mu_j$ 's are usually claimed to be accurate within 10% and 5% respectively. But, the correlation coefficient  $r$  and % of errors of Eq.(3.3) demand that,  $\tau$ 's and  $\mu$ 's are more than accurate. The non-spherical disubstituted benzene and aniline molecules absorb electric energy much more strongly, nearly 10 GHz electric field, at which the  $\epsilon''$  for absorption against frequency  $\omega$  showed a peak. This invited the attention to get the double relaxation times  $\tau_2$  and  $\tau_1$  from Eq.(3.3). The corresponding sum of the experimental and theoretical values of weighted contributions  $c_1$  and  $c_2$  towards dielectric dispersions due to estimated  $\tau_2$  and  $\tau_1$  differ significantly to indicate more than two Debye type relaxations in such molecules because of their complexity. The  $\tau$ 's for disubstituted benzenes as seen in Table 3.2 show the whole molecular rotation, while the flexible parts of the disubstituted anilines rotate under 10 GHz electric field.

Disubstituted anilines exhibit the symmetric relaxation behaviour while the asymmetric relaxation behaviour occurs in disubstituted benzenes in  $C_6H_6$  except 4-chloro 3-nitrobenzotrifluoride in  $CCl_4$  and m-nitro benzotrifluoride in  $C_6H_6$  respectively.  $\mu_2$  and  $\mu_1$  due to  $\tau_2$  and  $\tau_1$  are expected to be smaller when they are measured from the susceptibility measurement technique rather than the hf conductivity method, where the approximation of  $\sigma_{ij} \cong \sigma_{ij}''$  is usually made. The difference of  $\mu_2$  for the first six systems and of  $\mu_1$  for the rest five systems of Table 3.4 between conductivity and susceptibility measurement may arise either by elongation or reduction of the bond moments of the substituted polar groups by the factor  $\mu_{\text{expt}}/\mu_{\text{theo}}$  in agreement with the measured  $\mu$ 's to take into account of the inductive,

mesomeric and electromeric effects of the polar groups in the molecules. Thus, the correlation between the conformational structures with the observed results enhances the scientific content to add a new horizon of understanding to the existing knowledge of dielectric relaxation phenomena.

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