

CHAPTER 7

DOUBLE RELAXATION PHENOMENA OF DISUBSTITUTED BENZENES AND ANILINES IN NON-POLAR APROTIC SOLVENTS UNDER HIGH FREQUENCY ELECTRIC FIELD

7.1. Introduction :

The dielectric relaxation phenomena of non-spherical 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 [7.1-7.2]. The dipole moment μ from the relaxation time τ of the polar liquid molecule is of much importance [7.3-7.4] to determine the shape, size, structure and molecular association of a polar molecule. The real ϵ_{ij}' and imaginary ϵ_{ij}'' parts of complex relative permittivity ϵ_{ij}^* , static and infinite frequency relative permittivities ϵ_{oij} 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 τ_2 and τ_1 due to rotation of the whole molecule as well as the flexible part attached to the parent molecule [7.5].

Khameshara and Sisodia [7.6], Gupta *et al* [7.7] and Arrawatia *et al* [7.8] measured the relative permittivities of some disubstituted benzenes and anilines in aprotic non-polar 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 τ based on the single frequency concentration variation method of Gopalakrishna [7.9] and the dipole moment μ by Higasi's method [7.10]. 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 $CaCl_2$. ϵ_{oij} 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 %. ϵ_{ij}' and ϵ_{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* [7.11]. The possible existence of τ_1 and τ_2 of the compounds was, however, detected from the relative permittivity measurements [7.12] under 9.945 GHz electric field at $35^\circ C$.

Nowadays, the usual practice [7.13] is to study the dielectric relaxation phenomena in terms of dielectric orientation susceptibilities χ_{ij} 's. χ_{ij} 's are linked with the orientation polarisation of a polar molecule. So it is better to work with χ_{ij} 's rather than ϵ_{ij} 's or conductivity σ_{ij} 's as the latter are involved with all the polarisation processes and the transport of bound molecular charges respectively [7.14]. The real $\chi_{ij}' (= \epsilon_{ij}' - \epsilon_{\infty ij})$ and imaginary $\chi_{ij}'' (= \epsilon_{ij}'')$ parts of the complex dielectric orientation 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 7.1 are used to obtain their

Table 7.1: The real χ_{ij}' and imaginary χ_{ij}'' , parts of the complex dielectric orientation susceptibility χ_{ij}^* and static dielectric susceptibility χ_{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_1	χ_{ij}'	χ_{ij}''	χ_{oij}	Weight fraction w_j	χ_{ij}'	χ_{ij}''	χ_{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				

conformational structures in terms of molecular and intra-molecular dipole moments μ_2 and μ_1 involved with the estimated τ_2 and τ_1 . The disubstituted benzenes and anilines are thought to absorb electric energy much more strongly in nearly 10 GHz electric field to yield considerable values of τ_1 and τ_2 . The eleven polar-nonpolar liquid mixtures under investigation are found to show the double relaxation phenomena. The most of the polar molecules are isomers of aniline and benzene. Some of the polar solutes are dissolved in C_6H_6 while a few in CCl_4 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 [7.15]. A strong conclusion of double relaxation

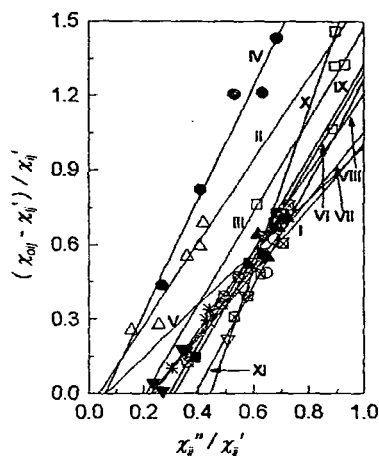


Figure 7.1: Linear variation of $(\chi_{oi} - \chi_{j}') / \chi_{ij}'$ with χ_{ij}'' / χ_{ij}' for different w_j 's at $35^\circ C$ under 9.945 GHz electric field.

- 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 (-⊠-)

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 χ_{oi} ($\pm 1\%$) involved with ϵ_{oi} and $\epsilon_{\infty ij}$ is available. The use of n_{Dij}^2 for $\epsilon_{\infty ij}$ often introduces [7.6-7.8] an additional error in the calculation since $\epsilon_{\infty ij}$ is approximately equal to 1 to 1.5 times of n_{Dij}^2 .

Bergmann *et al* [7.16] however devised a graphical method to obtain τ_1 and τ_2 for a pure polar liquid. The respective weighted contributions c_1 and c_2 towards dielectric relaxations were estimated in terms of τ_1 and τ_2 . Bhattacharyya *et al* [7.17] subsequently attempted to simplify the procedure of Bergmann *et al* [7.16] to get the same for a pure polar molecule with ϵ' , ϵ'' , ϵ_0 and ϵ_∞ measured at two different frequencies in GHz range. The graphical analysis advanced by Higasi *et al* [7.18] on polar-nonpolar liquid mixture was also a crude one.

Thus the object of the present paper is to detect τ_1 and τ_2 and hence to measure μ_1 and μ_2 using χ_{ij} 's based on the single frequency measurement technique [7.12, 7.19]. The aspect of molecular orientation polarisation is, however, achieved by introducing χ_{ij} 's because $\epsilon_{\infty ij}$ which includes fast polarisation, frequently appears as a subtracted term in Bergmann equations. Thus to

Table 7.2: The relaxation times τ_2 and τ_1 from the slope and intercept of straight line Eq.(7.3), correlation coefficients r 's and % of error in regression technique, measured τ_j from the slope of χ_{ij}'' vs χ_{ij}' of Eq.(7.15) and the ratio of the individual slopes of χ_{ij}'' vs w_j and χ_{ij}' vs w_j at $w_j \rightarrow 0$ of Eq.(7.16), reported τ , symmetric and characteristic relaxation times τ_s and τ_{cs} for different disubstituted benzenes and anilines at 35°C under 9.945 GHz electric field.

System with sl.no..	Slope & intercept of Eq.(7.3)		'r'	% of error	Estimated τ_2 and τ_1 in psec		Measured τ_j in psec from Eqs (7.15) & (7.16)		Rept. τ in psec	τ_s in psec	τ_{cs} in psec
(I) o-chloro nitro benzene in C ₆ H ₆	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 ₄	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 ₆ H ₆	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 ₄	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 ₆ H ₆	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 ₆ H ₆	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 ₆ H ₆	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 ₆ H ₆	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 ₆ H ₆	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 ₆ H ₆	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 ₆ H ₆	2.075	0.811	0.97	1.78	24.85	8.36	14.34	14.35	16.6	5.60	4.52

avoid the clumsiness of algebra and to exclude the fast polarisation process Bergmann equations [7.16] are simplified by the established symbols of χ_{ij}' , χ_{ij}'' and χ_{oij} of Table 7.1 in SI units:

$$\frac{\chi_{ij}'}{\chi_{oij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \dots (7.1)$$

$$\frac{\chi_{ij}''}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots (7.2)$$

assuming two broad Debye type dispersions for which the sum of c_1 and c_2 is unity. The Eqs.(7.1) and (7.2) are now solved to get:

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad \dots (7.3)$$

The variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{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

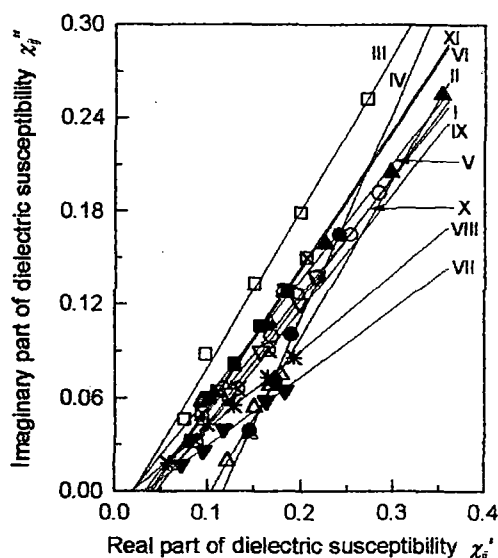


Figure 7.2: Linear variation of χ''_{ij} with χ'_{ij} for different w_j 's.

I. o-chloronitrobenzene in C_6H_6 ($-\bigcirc-$); 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 ($-\boxtimes-$)

correlation coefficients r 's and the % of errors were worked out to place them in Table 7.2 only to see how far the variables of Eq.(7.3) are collinear to each other.

The relaxation times τ 's due to Debye model are measured from the slope of χ''_{ij} vs χ'_{ij} curves of Fig.7.2 and the ratio of the individual slopes of χ''_{ij} vs w_j and χ'_{ij} vs w_j curves at $w_j \rightarrow 0$ of Figs.7.3 and 7.4 respectively. τ 's from both the methods are entered in the 8 and 9 columns of Table 7.2 only to see how far they agree with τ_1 and τ_2 due to double relaxation method of Eq.(7.3).

with intercept $-\omega^2 \tau_1 \tau_2$ and slope $\omega(\tau_1 + \tau_2)$, as shown in Fig.7.1. The intercept and slope of Eq.(7.3) are obtained by linear regression analysis made with the measured χ_{ij} 's of solutes in CCl_4 and C_6H_6 to get τ_2 and τ_1 as found in the 6 and 7 columns of Table 7.2. The variables of Eq.(7.3) are extracted from Table 7.1 where all the data are collected together system wise up to three decimals in close agreement with the expected [7.12] τ_2 and τ_1 of Table 7.2. Both τ_2 and τ_1 were found to deviate significantly when the data of Table 7.1 were taken up to two decimal places with the claimed accuracy of measurement. The

The theoretical c_1 and c_2 towards dielectric dispersions for τ_1 and τ_2 of different disubstituted benzenes and anilines in C_6H_6 and CCl_4 were calculated from Fröhlich's [7.20] theoretical formulations of χ_{ij}''/χ_{oij} and χ_{ij}'''/χ_{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 χ_{ij}''/χ_{oij} and χ_{ij}'''/χ_{oij} with w_j 's of Figs.7.5 and 7.6 in order to place them in Table 7.3 for comparison. The plots of χ_{ij}''/χ_{oij} and χ_{ij}'''/χ_{oij} against w_j of the polar liquids in Figs.7.5 and 7.6 are the least squares fitted curves with the experimental points placed upon them. With the values of the intercepts presented in Table 7.3 from Figs.7.5 and 7.6 and the graphical plot of $(1/\phi)\log(\cos\phi)$ against ϕ in degrees given elsewhere [7.4], the symmetric and asymmetric distribution parameters γ and δ related to symmetric and characteristic relaxation times τ_s and τ_{cs} of the molecules were determined. They are seen in Table 7.3. The object of such determinations of γ , δ , τ_s and τ_{cs} is to conclude the molecular nonrigidity and distribution of relaxation behaviour as well.

The dipole moments μ_2 and μ_1 were then measured in terms of dimensionless parameters b 's involved with measured τ 's of Table 7.2 and coefficients β_1 's and β_2 's presented in Table 7.4 of the variations of $hf \chi_{ij}'$ and total hf conductivity σ_{ij} with w_j 's of Figs.7.4 and 7.7 respectively. The measured μ 's are found in Table 7.4 in order to compare with theoretical dipole moment μ_{theo} 's derived from available bond angles and bond moments of the substituent polar groups attached to the parent molecules as sketched in Fig.7.8. The structural aspect of some interesting polar molecules in Fig.7.8 exhibits the prominent mesomeric, inductive and electromeric effects of the substituted polar groups. All these effects are taken into account by the ratio μ_{expt}/μ_{theo} in agreement with the measured μ 's [7.6-7.8] of Table 7.4.

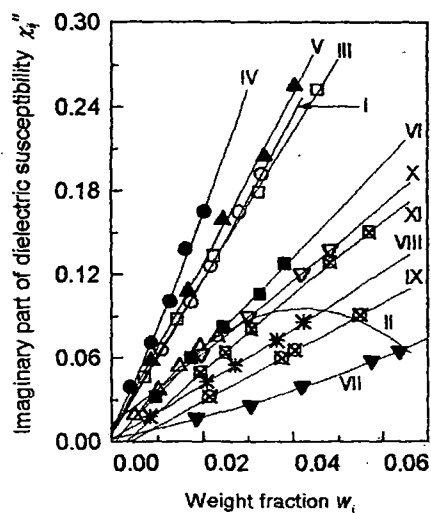


Figure 7.3: Variation of χ_{ij}'' against w_j of solutes

- 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 (-▽-); XI. 5-chloro 2-methyl aniline in C_6H_6 (-⊠-)

Table 7.3: Fröhlich's parameter A , theoretical and experimental values of χ_{ij}'/χ_{oij} & χ_{ij}''/χ_{oij} of Fröhlich equations (7.6) and (7.7) and from fitting Eqs. of Figs.7.5 and 7.6 at $w_j \rightarrow 0$ respectively, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion due to τ_1 and τ_2 , symmetric and asymmetric distribution parameters γ and δ 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 χ_{ij}'/χ_{oij} & χ_{ij}''/χ_{oij} from Eqs (7.6) & (7.7)		Theoretical values of c_1 and c_2		Expt. values of χ_{ij}'/χ_{oij} & χ_{ij}''/χ_{oij} at $w_j \rightarrow 0$ of Figs. (7.5) & (7.6)		Expt. values of c_1 & c_2		Estimated values of γ and δ			
(I) o-chloronitro benzene in C ₆ H 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 ₆ H 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 ₆ H 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 ₆ H 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 ₆ H 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 ₆ H 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 me thyl aniline in C ₆ H 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 ₆ H 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-me thyl aniline in C ₆ H ₆	1.089	0.547	0.475	0.462	0.627	0.907	0.312	1.354	-0.536	-0.03	0.0210		

7.2. Formulations of c_1 and c_2 for τ_1 and τ_2 :

The Eqs.(7.1) and (7.2) are now solved to get c_1 and c_2 where

$$c_1 = \frac{(\chi_{ij}'\alpha_2 - \chi_{ij}'')(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad \dots (7.4)$$

$$c_2 = \frac{(\chi_{ij}'' - \chi_{ij}'\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad \dots (7.5)$$

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 τ with two discrete values of τ_1 and τ_2 could, therefore, be expected. Thus from Fröhlich's equations [7.20] based on distribution of τ between the two extreme values of τ_1 and τ_2 one gets:

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \quad \dots (7.6)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \left[\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1) \right] \quad \dots (7.7)$$

where the Fröhlich parameter A is given by $A = \ln(\tau_2/\tau_1)$. The theoretical values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} of Eqs.(7.6) and (7.7) were used to get theoretical c_1 and c_2 from Eqs.(7.4) and (7.5) in order to compare them with the experimental values of c_1 and c_2 from the graphical plots of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $w_j \rightarrow 0$ as seen in Figs.7.5 and 7.6 respectively. Both the theoretical and experimental c_1 and c_2 are presented in Table 7.3 for comparison.

7.3. Distribution Parameters γ and δ Related to Symmetric and Characteristic Relaxation Times τ_s and τ_{cs} :

The molecules are expected to show either symmetrical circular arc or a skewed arc in addition to other models [7.21] when the values of χ''_{ij}/χ_{oij} are plotted against χ'_{ij}/χ_{oij} at $w_j \rightarrow 0$ for various frequencies of the electric field to yield:

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad \dots (7.8)$$

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad \dots (7.9)$$

Here, γ and δ are the symmetric and asymmetric distribution parameters related to symmetric and characteristic relaxation times τ_s and τ_{cs} respectively. Separating the real and imaginary parts of Eq.(7.8) one gets:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}/\chi_{oij}}{\chi''_{ij}/\chi_{oij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad \dots (7.10)$$

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\left(\frac{\chi'_{ij}/\chi_{oij}}{\chi''_{ij}/\chi_{oij}} \cos \frac{\gamma\pi}{2} - \sin \frac{\gamma\pi}{2} \right)} \right]^{1-\gamma} \quad \dots (7.11)$$

where χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} are obtained from intercepts of each variable with w_j 's of Figs.7.5 and 7.6 in the limit $w_j=0$. Again δ and τ_{cs} can be had from Eq.(7.9) as:

$$\tan(\phi\delta) = \frac{\left(\chi''_{ij}/\chi_{oij} \right)_{w_j \rightarrow 0}}{\left(\chi'_{ij}/\chi_{oij} \right)_{w_j \rightarrow 0}} \quad \dots (7.12)$$

$$\tau_{cs} = \frac{1}{\omega} \tan \phi \quad \dots (7.13)$$

Since ϕ can not be evaluated directly, a theoretical curve of $(1/\phi)\log(\cos\phi)$ with ϕ in degrees was drawn as shown elsewhere [7.4] from which

$$\frac{1}{\phi} \log(\cos \phi) = \frac{\log \left[\left(\chi'_{ij}/\chi_{oij} \right) / \cos(\phi\delta) \right]}{\phi\delta} \quad \dots (7.14)$$

was found out. The known values of $(1/\phi)\log(\cos\phi)$ was then used to obtain ϕ . With known ϕ and δ , τ_{cs} were obtained from Eqs.(7.12) and (7.13) for each molecule. The estimated γ and δ are presented in columns 11 and 12 of Table 7.3. τ_s and τ_{cs} are entered in columns 11 and 12 of Table 7.2 to conclude symmetric relaxation behaviour for disubstituted anilines and asymmetric relaxation behaviour for disubstituted benzenes respectively.

7.4. Theoretical Formulation for Dipole Moments μ_2 and μ_1 :

The Debye equation [7.22] for a polar-nonpolar liquid mixture under hf electric field in terms of χ_{ij} 's is written as:

$$\frac{d\chi''_{ij}}{d\chi'_{ij}} = \omega\tau \quad \dots (7.15)$$

$$\frac{\left(d\chi''_{ij}/dw_j \right)_{w_j \rightarrow 0}}{\left(d\chi'_{ij}/dw_j \right)_{w_j \rightarrow 0}} = \omega\tau \quad \dots (7.16)$$

τ 's of the polar liquids could, however, be estimated from Eqs.(7.15) and (7.16) as seen in 8 and 9 columns of Table 7.2. Again the imaginary part χ''_{ij} of the complex hf susceptibility χ_{ij} as a function of w_j of a solute can be written as [7.23-7.24]:

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

Table 7.4: Slope β_1 of χ_{ij}' vs w_j and β_2 of σ_{ij} vs w_j curves, measured dipole moments μ_j from susceptibility measurement technique and hf conductivity method from Eqs.(7.19) and (7.26) respectively, reported dipole moment, theoretical dipole moment μ_{theo} from available bond angles and bond moments expressed in Coulomb.metre (C.m) and the values of μ_{expt}/μ_{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 μ_j ($\times 10^{-30}$) in Coulomb.metre							$\frac{\mu_{expt}}{\mu_{theo}}$	
	β_1	β_2	From Eq (7.19)		From Eq (7.26)		μ_j^a	μ_j^b	μ_j^r		μ_{theo}
			μ_2	μ_1	μ_2	μ_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-methylaniline 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

μ_j^a = dipole moment by using τ from the direct slope of Eq (7.15)

μ_j^b = dipole moment by using τ from the ratio of individual slopes of Eq (7.16)

μ_j^r = reported dipole moment

μ_{theo} = theoretical dipole moment from the available bond angles and bond moments.

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

$$\left(\frac{d\chi_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_o k_B T M_j} \frac{\omega\tau}{(1+\omega^2\tau^2)} (\varepsilon_i + 2)^2 \quad \dots (7.17)$$

where the density of the solution ρ_{ij} becomes ρ_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, ε_i =relative permittivity of solvent and ε_o =permittivity of free space = 8.854×10^{-12} Farad. metre⁻¹. All are expressed in SI units.

Comparing Eqs.(7.16) and (7.17) one gets:

$$\left(\frac{d\chi_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_o k_B T M_j} \frac{1}{(1+\omega^2\tau^2)} (\varepsilon_i + 2)^2 = \beta_1 \quad \dots (7.18)$$

where β_1 is the slope of χ_{ij}' vs w_j curves of Fig.7.4 at $w_j \rightarrow 0$. Here no approximation in determination of μ_j is made like the conductivity measurement technique [7.4] given below.

After simplification, the *hf* dipole moment μ_j is given by:

$$\mu_j = \left(\frac{27\varepsilon_o k_B T M_j \beta_1}{N\rho_i (\varepsilon_i + 2)^2 b} \right)^{\frac{1}{2}} \quad \dots (7.19)$$

here dimensionless parameter b is given by :

$$b = 1/(1+\omega^2\tau^2) \quad \dots (7.20)$$

7.5. Dipole Moments μ_2 and μ_1 from *hf* Conductivity :

The complex *hf* conductivity σ_{ij}^* of polar-nonpolar liquid mixture in a GHz electric field is given by [7.25]:

$$\sigma_{ij}^* = \sigma_{ij}' + j\sigma_{ij}'' \quad \dots (7.21)$$

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

$$\sigma_{ij} = \omega\varepsilon_o \left(\varepsilon_{ij}'^2 + \varepsilon_{ij}''^2 \right)^{\frac{1}{2}} \quad \dots (7.22)$$

Although $\varepsilon_{ij}' \gg \varepsilon_{ij}''$, but in the high frequency region, $\varepsilon_{ij}' \cong \varepsilon_{ij}''$. ε_{ij}'' is responsible for absorption of electric energy and offers resistance to polarisation. Hence σ_{ij}'' is related to σ_{ij}' by the relation [7.25]:

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

$$\sigma_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau} \sigma'_{ij} \quad \dots (7.23)$$

Here the approximation $\sigma_{ij} \cong \sigma_{ij}'$ is made. Differentiation of Eq.(7.23) with respect to w_j at $w_j \rightarrow 0$ yields:

$$\left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega\tau \left(\frac{d\sigma_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega\tau\beta_2 \quad \dots (7.24)$$

where β_2 is the slope of σ_{ij} vs w_j curves of Fig.7.7 at infinite dilution $w_j \rightarrow 0$ and placed in Table 7.4.

The real part of *hf* conductivity σ_{ij}' at *TK* [7.23] is given by:

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

$$\left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27k_B TM_j} \frac{\omega^2\tau}{1 + \omega^2\tau^2} (\epsilon_i + 2)^2 \quad \dots (7.25)$$

Comparing Eqs.(7.24) and (7.25) one gets the dipole moment μ_j from:

$$\mu_j = \left(\frac{27k_B TM_j \beta_2}{N\rho_{ij} (\epsilon_i + 2)^2 \omega b} \right)^{\frac{1}{2}} \quad \dots (7.26)$$

All the measured dipole moments μ_j 's from the susceptibility measurement technique of Eq.(7.19) and *hf* conductivity method of Eq.(7.26) are entered in the 4,5 and 6,7 columns of Table 7.4 respectively.

7.6. Results and Discussions :

The double relaxation times τ_1 and τ_2 for the polar liquid molecules in different solvents are found out from the slope and intercept of Eq.(7.3) as shown in Fig.7.1 in terms of the orientation susceptibility parameters χ_{ij} 's of Table 7.1. The χ_{ij} 's are, however, derived from the relative permittivities ϵ_{ij} 's [7.6-7.8] for different weight fractions w_j 's of the polar liquids. The variables of Eq.(7.3) i.e $(\chi_{oij} - \chi_{ij})/\chi_{ij}'$ and χ_{ij}''/χ_{ij}' are plotted against each other for different w_j 's of solutes under 9.945 GHz electric field at 35°C to get linear equation by regression analysis. From Fig.7.1 it revealed that the fitting is good for some cases, but poor in other cases. It appears that the linear fit for II (-△-), III (-□-) and IV (-●-) in Figs.7.1 and 7.2 often passes through two among five data, others being off from the fit. Nevertheless, the regression analysis was made on the basis of Eq. (7.3). However, the accuracy of Fig.7.1 is tested by the correlation coefficients r 's, which were

found to be close to unity indicating the variables are almost collinear. The % of errors in terms of r 's in getting the intercepts and slopes were worked out to find the accuracies of τ_1 and τ_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 χ_{oij} involved with ϵ_{oij} and

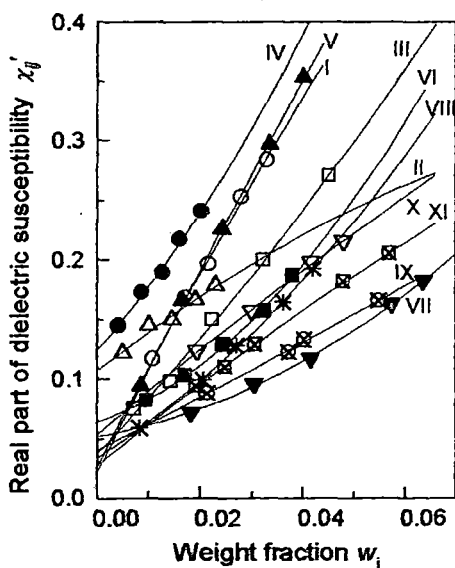


Figure 7.4 : Variation of χ'_{ij} against w_j of solutes

I. o-chloronitrobenzene in C_6H_6 (-O-); II. 4-chloro 3-nitrobenzotrifluoride in CCl_4 (- Δ -); 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 (-* -); IX. 3-chloro 4-methyl aniline in C_6H_6 (- \odot -); X. 4-chloro 2-methyl aniline in C_6H_6 (- ∇ -) and XI. 5-chloro 2-methyl aniline in C_6H_6 (- \boxtimes -)

$\epsilon_{\infty ij}$ is necessary. The refractive index n_{Dij} measured by Abbe's refractrometer often yields $\epsilon_{\infty ij} = n_{Dij}^2$, although Cole Cole [7.26] and Cole Davidson [7.27] 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 χ''_{ij} , χ'_{ij} and χ_{oij} are of 5% and 1% respectively derived from measured [7.6-7.8] relative permittivities ϵ_{ij}'' , ϵ_{ij}' , ϵ_{oij} and $\epsilon_{\infty ij}$. The estimated τ_2 and τ_1 are placed in Table 7.2 in order to compare them with those of Murthy *et al* [7.28] of Eq.(7.15)

and by the ratio of the individual slopes of the variations of χ''_{ij} and χ'_{ij} with w_j 's in the limit $w_j \rightarrow 0$ of Eq.(7.16). The latter method seems to be better to calculate τ since it eliminates polar-polar interaction almost completely. The linear plot of χ''_{ij} against χ'_{ij} of Fig.7.2 for different w_j 's of solute has intercepts although it was expected from Eq.(7.15) that they should pass through the origin. Nevertheless, τ 's are found to be in close agreement with those calculated from the ratio of the individual slopes of the variations of χ''_{ij} and χ'_{ij} with w_j at $w_j \rightarrow 0$ of Eq.(7.16) as shown in Figs.7.3 and 7.4. The experimental points as shown in Figs.7.3 and 7.4 with the fit are tabulated to back up the results of Eq.(7.16) due to Debye model. χ''_{ij} increases monotonically with w_j 's and has a tendency to meet the origin for all the curves. This type of behaviour indicates that χ''_{ij} tends to pass through the origin at $w_j \rightarrow 0$ under 9.945 GHz electric field.

It is evident from Table 7.2 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 τ_1 's and τ_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.(7.8) and (7.9) for such non rigid polar molecules yield τ_s and τ_{cs} from

Eqs.(7.11) and (7.13) to place them in the last two columns of Table 7.2. It reveals that the symmetric and asymmetric relaxation processes are more probable since τ_s and τ_{cs} are almost in agreement with the reported τ 's in a solution. The characteristic relaxation times τ_{cs} are sometimes very high through asymmetric distribution parameter δ and often could not be determined for most of the molecules. The disubstituted benzenes showed τ_2 's in agreement with the reported τ 's and τ_{cs} except *o*-nitrobenzotrifluoride in C_6H_6 which agrees with τ_s only. But

4-chloro 3-nitrobenzotrifluoride in CCl_4 and *m*-nitrobenzotrifluoride in C_6H_6 yield τ_2 in close agreement with reported τ '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 τ_1 's in excellent agreement with the calculated τ_s 's. For the rest disubstituted anilines τ_1 's agree well with the calculated τ_s 's, but the agreement is not better with the measured τ 's from Eqs.(7.15) and (7.16). 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.

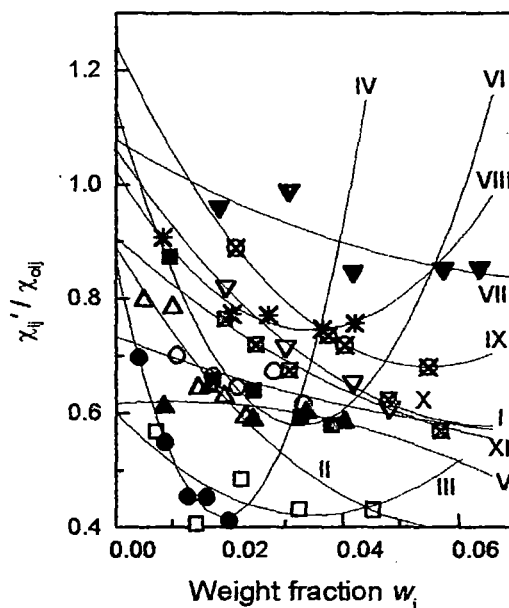


Figure 7.5 : Plot of χ''/χ'_{col} with w_1 of solutes

- 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 (-⊠-)

The relative weighted contributions c_1 and c_2 towards dielectric dispersions due to τ_1 and τ_2 are estimated and placed in Table 7.3 by using Fröhlich's Eqs.(7.6) and (7.7). They are compared with the experimental c_1 and c_2 from the fitted curves of χ_{ij}''/χ_{oij} and χ_{ij}''''/χ_{oij} against w_j in the limit $w_j \rightarrow 0$ of Figs.7.5 and 7.6. The nonlinear fit with only five points for III ($-\square-$) and IV ($-\bullet-$) of Fig.7.5 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 software. All the curves of Figs.7.5 and 7.6 vary usually [7.12] except the convex curve V for *o*-nitrobenzotrifluoride in C_6H_6 . The variations of χ_{ij}''/χ_{oij} with w_j are, however, concave and convex in nature for all systems as observed elsewhere [7.12]. The left hand sides of

Eqs.(7.1) and (7.2) vary with w_j 's in concave and convex manner according to Figs.7.5 and 7.6 are now fixed for τ_1 and τ_2 once estimated from intercept and slope of Eq.(7.3) to yield experimental c_1 and c_2 values from Eqs.(7.4) and (7.5) at $w_j \rightarrow 0$. This study is supposed to yield the accurate values of c_1 and c_2 unlike the earlier one [7.12] based on the graphical extrapolated values of $(\epsilon_{ij}' - \epsilon_{oij})/(\epsilon_{oij} - \epsilon_{oij})$ and $\epsilon_{ij}''/(\epsilon_{oij} - \epsilon_{oij})$ at $w_j \rightarrow 0$ drawn on the basis of scientific judgment. Although, the nature of variations remains unaltered, it is evident from Table 7.3 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 7.3. The experimental values show that $c_1 + c_2 \cong 1$ for almost all the non-spherical polar liquid molecules. But

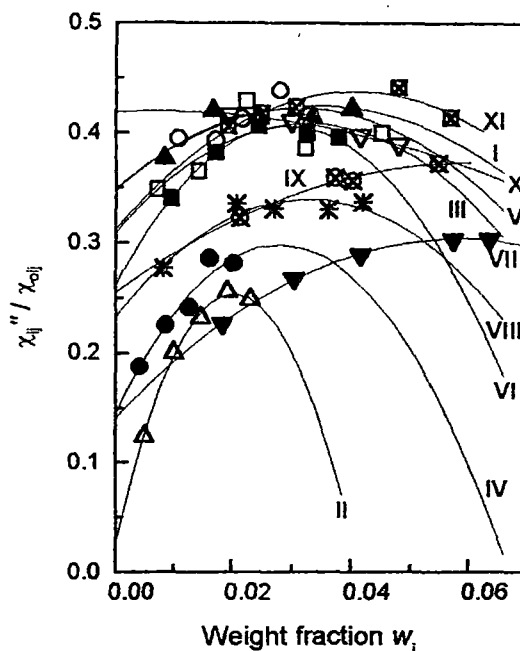


Figure 7.6 : Plot of χ_{ij}''/χ_{oij} with w_j of solutes

- 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 ($-\oplus-$); X. 4-chloro 2-methyl aniline in C_6H_6 ($-\nabla-$) and XI. 5-chloro 2-methyl aniline in C_6H_6 ($-\boxtimes-$)

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 7.3. 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-nitrobenzotrifluoride in CCl_4 ($-\Delta-$), (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.(7.3) 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.(7.3). 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.

Dipole moments μ_2 and μ_1 due to rotation of the whole molecule as well as the flexible parts were, however, measured from Eq.(7.19) using dimensionless parameters b 's involved with τ 's by both the methods and slope β_1 's of χ_{ij}' vs w_j curves of Fig.7.4. The measured values of μ_2 and μ_1 are presented in Table 7.4. The variations of all the χ_{ij}' 's of polar-nonpolar liquid mixtures are found to be parabolic with w_j 's of polar compounds as evident from Fig.7.4. 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 CCl_4 ($-\Delta-$), 4-chloro 3-nitrotoluene in CCl_4 ($-\bullet-$). This behaviour probably reflects the solvent effects on the polar compounds under investigation. The interaction of solute on solvent CCl_4 may occur due to slightly positive charge δ^+ on C atom of CCl_4 and negative charge δ^- on Cl atom of the substituted group in the benzene ring as seen in Fig.7.8. All the systems are of similar nature having monotonic increase of χ_{ij}' with w_j . The dipole moments μ_2 and μ_1 are also derived from the conductivity measurement technique of Eq.(7.26) using the slope β_2 's of σ_{ij} vs w_j curves of Fig.7.7 and are placed in Table 7.4 for comparison. The total hf conductivity σ_{ij} of all the polar-nonpolar liquid mixtures increase monotonically with w_j and cut the ordinate axis within the range

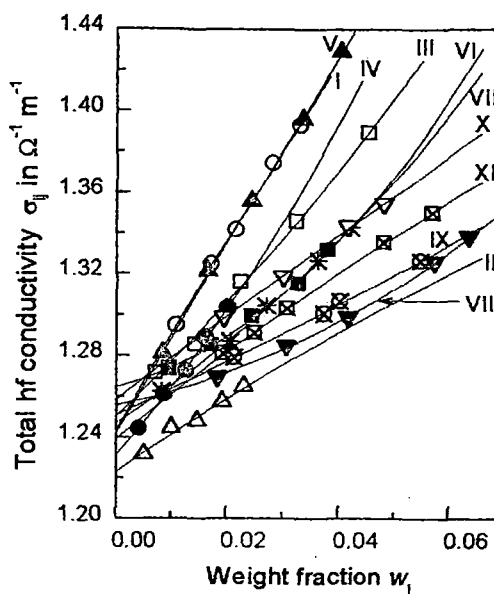


Figure 7.7 : Variation of σ_{ij} against w_j of solutes

I. o-chloronitrobenzene in C_6H_6 ($-\text{O}-$); II. 4-chloro 3-nitrobenzotrifluoride in CCl_4 ($-\Delta-$); 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 ($-\oplus-$); X. 4-chloro 2-methyl aniline in C_6H_6 ($-\nabla-$) and XI. 5-chloro 2-methyl aniline in C_6H_6 ($-\boxtimes-$)

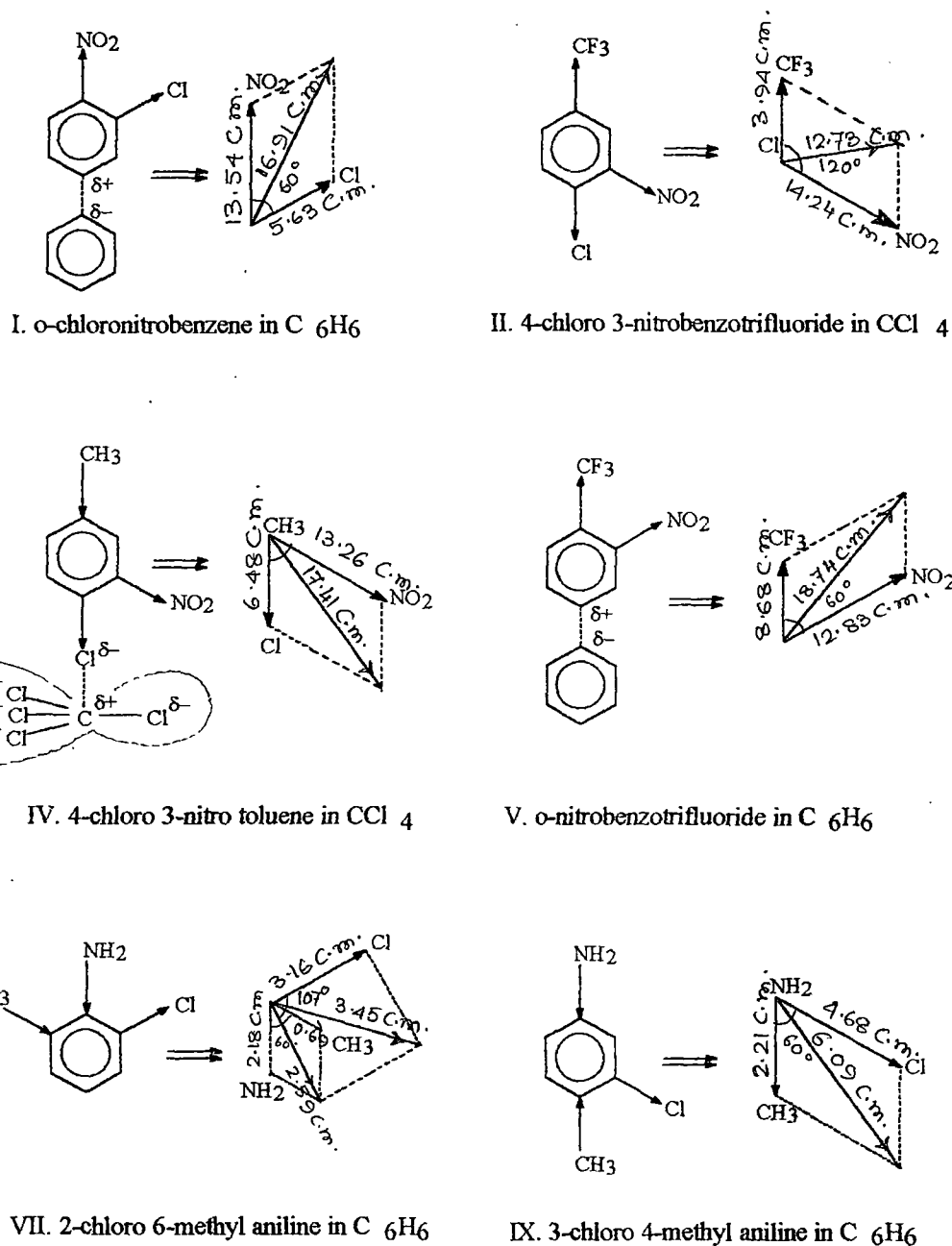


Figure 7.8: Conformational structures of solutes from bond angles and bond moments in multiple 10^{-30} Coulomb. metre (C.m)

$1.2233 \leq \sigma_{ij} \leq 1.2646$ at $w_j=0$ as seen in Fig.7.7. The slight disagreement of μ_1 and μ_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 μ_2 's for disubstituted benzenes and μ_1 's for disubstituted anilines are found to agree with the reported μ 's placed in Table 7.4. This indicates that the flexible parts of the disubstituted benzenes are more rigid in comparison to disubstituted anilines.

The *hf* dipole moment μ_j 's are calculated by using τ from both the methods of direct slope of Eq.(7.15) and the ratio of the individual slopes of Eq.(7.16) in order to place them in Table 7.4. μ_j 's by using τ from the ratio of the individual slopes are in close agreement with the reported values suggesting the fact that the latter method to get τ 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.7.8. 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 μ_{theo} 's depending on the electron affinity of C-atom of the benzene ring. The molecules have C \rightarrow CF₃, C \leftarrow NH₂ ($\angle 142^\circ$), C \rightarrow NO₂, C \rightarrow Cl C \leftarrow CH₃ polar groups of bond moments 9.53×10^{-30} , 4.93×10^{-30} , 14.10×10^{-30} , 5.63×10^{-30} , 1.23×10^{-30} Coulomb.metre (C.m) respectively [7.12,7.19] aligned in different angles in a plane to yield μ_{theo} . Out of these, only -NO₂ and -NH₂ 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 χ_{ij}''/χ_{oij} vs w_j and χ_{ij}''/χ_{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.7.8 in view of rearrangement of charge density in them. All the disubstituted anilines include -Cl, -NH₂ and -CH₃ polar groups of which -Cl and -CH₃ 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 μ values for a polar molecule in two aprotic non-polar solvents may arise due to weak polarity of CCl₄ as shown in Fig.7.8. The difference between μ_{theo} 's and experimental μ_j 's establishes the non consideration of inductive and mesomeric effects. All these effects may be taken into account by the factor μ_{exp}/μ_{theo} to yield the exact μ_1 and μ_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.7.8 were already shown elsewhere [7.12,7.19].

7.7. Conclusions :

The study of relaxation phenomena of disubstituted benzenes and anilines in C₆H₆ and CCl₄ by the modern established symbols of dielectric orientation susceptibilities χ_{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.(7.3) by the regression analysis on the measured data of χ_{ij} 's of different w_j 's are used to get τ_2 and τ_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 orientation polarisation of the molecules. The significant Eqs.(7.15) and (7.16) to obtain τ_j 's and hence μ_j 's from Eq.(7.19) 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 τ_j 's from Eq.(7.16) with the use of the ratio of the individual slopes of χ_{ij}'' vs w_j and χ_{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 τ_j 's and μ_j 's respectively. τ_j 's and μ_j 's are usually claimed to be accurate within 10% and 5% respectively. But the correlation coefficient r and % of errors of Eq.(7.3) demand τ 's and μ '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 ϵ'' for absorption against frequency ω showed the peak. This invited the attention to get the double relaxation times τ_2 and τ_1 from Eq.(7.3). The corresponding sum of the experimental and theoretical values of weighted contributions c_1 and c_2 towards dielectric dispersions due to estimated τ_2 and τ_1 differ significantly to indicate more than two Debye type relaxations in such molecules because of their complexity. The τ 's for disubstituted benzenes as seen in Table 7.2 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. μ_2 and μ_1 due to τ_2 and τ_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 μ_2 for the first six systems and of μ_1 for the rest five systems of Table 7.4 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 μ '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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