

CHAPTER 8

**DIELECTRIC RELAXATION PHENOMENA OF
RIGID POLAR LIQUID MOLECULES UNDER
GIGA HERTZ ELECTRIC FIELD**

8.1. Introduction :

Dielectric relaxation studies of polar liquids in non-polar solvents are of much importance as they provide interesting information of solute-solvent or solute-solute molecular association [8.1-8.2] under high frequency (*hf*) electric field. The associational aspects of polar liquids can, however be inferred from the measured relaxation time τ by Cole-Cole [8.3], Cole-Davidson [8.4] plot or by single frequency concentration variation method [8.5] and dipole moment μ from the measured *hf* conductivity σ_{ij} and estimated τ [8.6].

Srivastava and Srivastava [8.7] measured the real ϵ_{ij}' and imaginary ϵ_{ij}'' parts of complex relative permittivity ϵ_{ij}^* of chloral and ethyltrichloroacetate in benzene, *n*-heptane and *n*-hexane in 4.2, 9.8 and 24.6 GHz electric field by Smyth's method [8.8] at 30°C. The polar solutes (j) chloral (CCl₃CHO) and ethyltrichloroacetate (CCl₃COOCH₂CH₃) were of puram grade of M/s BDH, England, *n*-hexane and *n*-heptane from M/s E Merck Darmstadt, Germany. Both solutes and solvents were doubly distilled before making solutions of varying concentrations called the weight fractions w_j of solutes that are defined as the weight of the solute per unit weight of the solution up to four decimal places as shown in Table 8.1 in each solvent. The static relative permittivity ϵ_{oij} at 100 KHz and refractive index n_{Dij} of the solutions were measured. The purpose of this study was to observe the solute-solvent or solute-solute molecular interactions. They, however, inferred that these molecules might possess two or more relaxation processes towards dielectric dispersions.

Nowadays, the usual practice is to study the dielectric relaxation processes in terms of *hf* dielectric orientation susceptibility χ_{ij}^* rather than ϵ_{ij}^* or *hf* conductivity σ_{ij}^* [8.9-8.10]. ϵ_{ij}^* includes within it all the polarisation processes while σ_{ij}^* is more linked to transport of bound molecular charges. It is, therefore, better to work with susceptibilities χ_{ij} 's as they are concerned with orientation polarisation. The dielectric susceptibilities real $\chi_{ij}' (= \epsilon_{ij}' - \epsilon_{\infty ij})$ and imaginary $\chi_{ij}'' (= \epsilon_{ij}'')$ parts of complex dielectric susceptibility $\chi_{ij}^* (= \epsilon_{ij}^* - \epsilon_{\infty ij})$ and the low frequency dielectric susceptibility $\chi_{oij} (= \epsilon_{oij} - \epsilon_{\infty ij})$ which is real were derived from measured relative permittivities [8.7]. The experimental results thus collected together are placed in Table 8.1. One could not make a strong conclusion of double relaxation phenomena of polar molecule in a nonpolar solvent based on the single frequency measurement of relaxation parameters provided the accurate value of χ_{oij} involved with ϵ_{oij} and $\epsilon_{\infty ij}$ is not available. The use of n_{Dij}^2 for $\epsilon_{\infty ij}$ [8.7] often introduces the additional error in the calculation. Nevertheless, the data of Table 8.1 are accurate up to 5% for χ_{ij}'' and 2% for χ_{ij}' and χ_{oij} respectively.

The non-spherical as well as nonrigid polar liquid molecules often possess two or more τ in GHz electric field for the rotation of different flexible polar groups attached to the parent molecule

Table 8.1: Concentration variation of the real χ_{ij}' and imaginary χ_{ij}'' parts of dimensionless complex dielectric orientation susceptibility χ_{ij}^* and the static dielectric orientation susceptibility χ_{oij} which is real derived from the measured relative permittivities ϵ_{ij}' , ϵ_{ij}'' , ϵ_{oij} and $\epsilon_{\infty ij}$ of chloral and ethyltrichloroacetate in different non-polar solvents at 30 °C

Frequency in GHz	Weight	$\chi_{ij}' = \epsilon_{ij}' - \epsilon_{\infty ij}$	$\chi_{ij}'' = \epsilon_{ij}''$	$\chi_{oij} = \epsilon_{oij} - \epsilon_{\infty ij}$	Weight	$\chi_{ij}' = \epsilon_{ij}' - \epsilon_{\infty ij}$	$\chi_{ij}'' = \epsilon_{ij}''$	$\chi_{oij} = \epsilon_{oij} - \epsilon_{\infty ij}$
	fraction w_j				fraction w_j			
	I Chloral in benzene				II Chloral in <i>n</i> -heptane			
(a) 4.2	0.0255	0.0750	0.005	0.0790	0.1349	0.1853	0.022	0.2052
	0.0977	0.2107	0.031	0.2117	0.2008	0.2996	0.029	0.3238
	0.1813	0.3984	0.080	0.4004	0.2706	0.4128	0.045	0.4531
	0.2511	0.5653	0.088	0.5703	0.3366	0.5356	0.060	0.5787
(b) 9.8	0.0899	0.1803	0.041	0.2024	0.0807	0.0891	0.029	0.1271
	0.1711	0.3377	0.057	0.3719	0.1416	0.1646	0.036	0.2146
	0.1903	0.3695	0.072	0.4153	0.2003	0.2599	0.050	0.3099
	0.2510	0.5149	0.083	0.5608	0.2683	0.3828	0.055	0.4528
	0.3476	0.7333	0.099	0.8183	0.3324	0.5262	0.080	0.5722
(c) 24.6	0.0152	0.0632	0.047	0.0664	0.0795	0.0795	0.024	0.1079
	0.0899	0.1603	0.066	0.2024	0.1349	0.1753	0.038	0.2052
	0.1711	0.3177	0.104	0.3719	0.2008	0.2696	0.054	0.3238
	0.1903	0.3895	0.146	0.4153	0.2706	0.3928	0.068	0.4531
	0.3476	0.7333	0.208	0.8183	0.3366	0.5256	0.091	0.5787
	III Ethyltrichloroacetate in benzene				IV Ethyltrichloroacetate in <i>n</i> -hexane			
(a) 4.2	0.0211	0.1031	0.043	0.1292	0.0595	0.1430	0.052	0.1700
	0.0521	0.2061	0.095	0.2513	0.0649	0.1525	0.066	0.1839
	0.0755	0.2885	0.154	0.3457	0.1137	0.2673	0.108	0.3154
	0.1202	0.4432	0.224	0.5312	0.1722	0.3908	0.185	0.4887
	0.1734	0.5891	0.310	0.7610				
	0.2388	0.7969	0.454	1.0569				
(b) 9.8	0.0207	0.0835	0.023	0.1315	0.0210	0.0369	0.021	0.0755
	0.0498	0.1456	0.046	0.2406	0.0595	0.1030	0.041	0.1700
	0.0802	0.2083	0.079	0.3643	0.0649	0.1125	0.066	0.1839
	0.1193	0.2934	0.115	0.5264	0.1137	0.1973	0.093	0.3154
	0.1764	0.4199	0.194	0.7759	0.1722	0.3408	0.126	0.4887
	0.2444	0.6074	0.226	1.0824	0.2360	0.4333	0.190	0.6970
(c) 24.6	0.0211	0.0331	0.010	0.1292	0.0639	0.0522	0.073	0.1842
	0.0521	0.0761	0.025	0.2513	0.0845	0.1008	0.098	0.2298
	0.0755	0.1385	0.059	0.3457	0.1193	0.1167	0.137	0.3297
	0.1202	0.2132	0.086	0.5312	0.1683	0.1512	0.185	0.4782
	0.1734	0.2391	0.105	0.7610				

and the whole molecule itself [8.11]. Bergmann *et al* [8.12], 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 also estimated in terms of τ_1 and τ_2 . A graphical method [8.13] was, soon employed from Fröhlich's distribution function [8.14] to get τ_2 and τ_1 of a pure polar solute. The

methods indicate that a single frequency measurement is not sufficient to have correct τ_1 and τ_2 . Bhattacharya *et al* [8.15] subsequently attempted to get τ_1 , τ_2 and c_1 , c_2 for a polar molecule with ϵ' , ϵ'' , ϵ_0 and ϵ_∞ measured at two different frequencies in GHz region. The graphical analysis made by Higasi *et al* [8.16] on polar-nonpolar liquid mixture was, also a crude approximation.

Saha *et al* [8.6] and Sit *et al* [8.17] recently put forward an analytical method based on single frequency measurement of relative permittivities ϵ_{ij}' , ϵ_{ij}'' , ϵ_{oij} and $\epsilon_{\infty ij}$ of polar-nonpolar liquid mixtures of different w_j 's at a given temperature to get τ_1 , τ_2 and c_1 , c_2 respectively. Earlier investigation had been made on different chain-like polar molecules like alcohols in nonpolar solvents [8.18-8.19] to see the double relaxation phenomena at

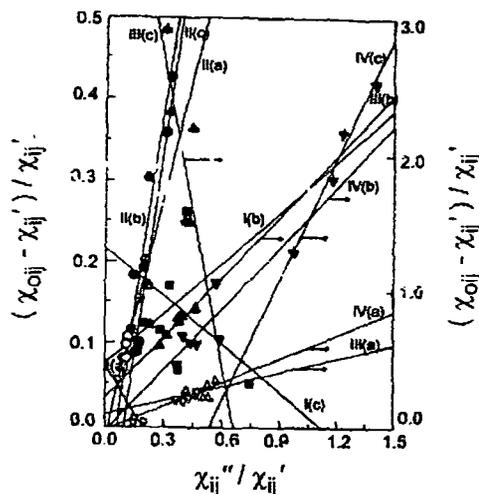


Figure 8.1: Linear variation of $(\chi_{oij} - \chi_{ij}') / \chi_{ij}'$ against χ_{ij}'' / χ_{ij}' for different w_j 's at 30°C.

I(a), I(b) and I(c) for chloral in benzene ($-\square-$, $-\blacksquare-$, $-\boxplus-$); II(a), II(b) and II(c) for chloral in *n*-heptane ($-\circ-$, $-\bullet-$, $-\oplus-$); III(a), III(b) and III(c) for ethyltrichloroacetate in benzene ($-\triangle-$, $-\blacktriangle-$, $-\blacktriangledown-$) and IV(a), IV(b) and IV(c) for ethyltrichloroacetate in *n*-hexane ($-\nabla-$, $-\blacktriangledown-$, $-\blacktriangledown-$) at 4.2, 9.8 and 24.6 GHz electric fields respectively

three different electric field frequencies in terms of relative permittivities. However, no such study is made on the aforesaid rigid aliphatic polar liquid molecules in different solvents under various electric field frequencies from measured χ_{ij} 's of Table 8.1. Chloral is widely used in medicine as drug to induce sleep and relieve pain and in the manufacture of D.D.T. as insecticides. Ethyltrichloroacetate, on the other hand, is used for artificial fragrance of fruits and flowers.

Thus the object of the present paper is to detect the existence of double relaxation times τ_1 , and τ_2 due to rotation of the flexible part and the whole molecules themselves using χ_{ij} 's based on the single frequency measurement technique [8.6-8.17]. The aspect of molecular orientation polarisation is, however, accomplished by introducing χ_{ij} 's because $\epsilon_{\infty ij}$ which includes fast polarisation frequently appears as a subtracted term in Bergmann's equations. Thus in order to avoid the clumsiness of algebra and exclude the fast polarisation Bergmann equations [8.12] in terms of established symbols of χ_{ij}' , χ_{ij}'' and χ_{oij} can be written as:

$$\frac{\chi'_{ij}}{\chi_{oij}} = c_1 \frac{1}{1 + \omega^2 \tau_1^2} + c_2 \frac{1}{1 + \omega^2 \tau_2^2} \quad \dots (8.1)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots (8.2)$$

assuming two separate broad dispersions for which the sum of c_1 and c_2 is unity. Eqs.(8.1) and (8.2) are solved to get

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad \dots (8.3)$$

When the variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ are plotted against χ''_{ij}/χ'_{ij} for different ω_j 's of solute under a given angular frequency $\omega (=2\pi f)$ of the electric field, a straight line results with the intercept- $\omega^2 \tau_1 \tau_2$ and slope $\omega(\tau_1 + \tau_2)$, as displayed in Fig.8.1. The intercept and slope of Eq.(8.3) are obtained by linear regression analysis made on the measured susceptibilities for different ω_j 's of chloral in *n*-heptane and ethyltrichloroacetate in *n*-hexane of Table 8.1 to get τ_1 and τ_2 as found in columns 7 and 8 of Table 8.2 extracted from the data of Table 8.1 based on minimum chi-squares value.

Table 8.2: The estimated relaxation time τ_2 and τ_1 from the slope and the intercept of straight line Eq.(8.3) with correlation coefficients (r) and minimum chi-squares values together with measured τ from the slope of $\chi''_{ij} - \chi'_{ij}$ of Eq.(8.16) and τ_2 's from single broad dispersion from Eq.(8.4) for rigid aliphatic polar molecules at 30°C under different frequencies of electric fields.

System with sl. no. & mol. wt. M_j	Frequency f in GHz	Slope and intercept of Eq.(8.3)		Corrl. coeff. r	Minimum chi-squares value of Eq.(8.3)	Estimated τ_2 and τ_1 in p-sec		τ^a	τ^b	τ^c
(I) Chloral in benzene $M_j=0.1475$ Kg	(a) 4.2	-0.3872	-0.0732	-0.91	-0.010	5.27	-	7.53	-	4.77
	(b) 9.8	0.2101	-0.0733	0.49	0.006	6.42	-	1.88	1.78*	10.12
	(c) 24.6	-0.1936	-0.2161	-0.41	0.180	2.45	-	1.72	-	2.01
(II) Chloral in <i>n</i> -heptane $M_j=0.1475$ Kg	(a) 4.2	0.9995	0.0175	0.69	0.003	37.16	0.67	4.09	-	-
	(b) 9.8	1.6592	0.1040	0.93	0.053	25.89	1.06	1.78	0.46*	-
	(c) 24.6	1.7431	0.1748	0.96	0.020	10.60	0.69	0.90	-	-
(III) Ethyltrichloroacetate in benzene $M_j=0.1915$ Kg	(a) 4.2	0.3546	-0.0698	0.37	0.047	18.78	-	23.00	-	18.71
	(b) 9.8	1.5115	-0.1800	0.97	0.005	26.36	-	7.28	6.50***	32.53
	(c) 24.6	-7.4034	-4.8872	-0.76	0.337	3.95	-	3.18	-	35.35
(IV) Ethyltrichloroacetate in <i>n</i> -hexane $M_j=0.1915$ Kg	(a) 4.2	0.5843	0.0382	0.86	0.004	19.30	2.86	18.66	-	-
	(b) 9.8	1.5181	0.0548	0.66	0.153	24.05	0.60	6.28	5.70***	-
	(c) 24.6	2.9886	1.6134	0.99	0.010	14.76	4.58	7.09	-	-

τ^a = Measured τ in p-sec from Eq.(8.16)

τ^b = Reported τ in p-sec

τ^c = τ_2 in p-sec from single broad dispersion of Eq.(8.4)

Assuming a single Debye-like broad dispersion for a polar molecule in a given solvent, Eq.(9.3) is reduced to [9.17] with $\tau_1=0$,

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega\tau_2 \frac{\chi''_{ij}}{\chi'_{ij}} \quad \dots (8.4)$$

in order to get τ_2 for the two polar liquids in benzene as seen in the 11th column of Table 8.2. Both the correlation coefficients r 's and the minimum chi-squares values are entered in the 5th and 6th columns of Table 8.2.

The theoretical c_1 and c_2 towards dielectric dispersions for chloral and ethyltrichloroacetate in n -heptane and n -hexane were calculated from Fröhlich's [8.14] theoretical equations of χ'_{ij}/χ_{oij}

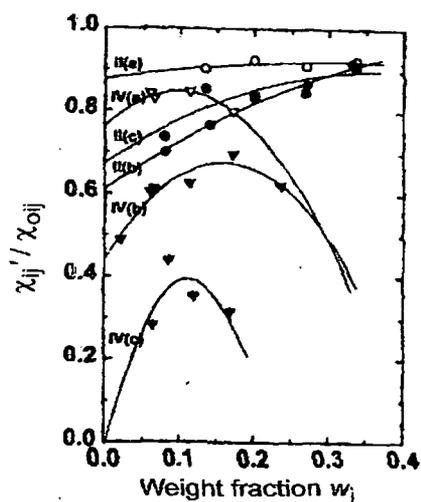


Figure 8.2: Variation of χ''_{ij}/χ_{oij} against w_j 's of chloral and ethyltrichloroacetate at 30°C.

II(a), II(b) and II(c) for chloral in n -heptane ($-\circ-$, $-\bullet-$, $-\oplus-$); and IV(a), IV(b) and IV(c) for ethyltrichloroacetate in n -hexane ($-\nabla-$, $-\blacktriangledown-$, $-\triangle-$) at 4.2, 9.8 and 24.6 GHz electric fields respectively

and χ''_{ij}/χ_{oij} with the estimated τ_2 and τ_1 of Table 8.2. The experimental c_1 and c_2 , on the other hand, were computed from the values χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $w_j \rightarrow 0$ by graphical method of Figs.8.2 and 8.3 in order to place them in Table 8.3 for comparison. The plot of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} against w_j of the respective solutes in Figs.8.2 and 8.3 are the least squares fitted parabolaes with the experimental data placed upon them. They are of convex and concave shapes except ethyltrichloroacetate in n -hexane at 9.8 and 24.6 GHz electric fields.

With the values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} in the limit of $w_j=0$ of Figs.8.2 and 8.3, and the graphical plot of $(1/\phi)\log(\cos\phi)$ against ϕ in degrees of Fig.8.4, 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 and are placed in Table 8.3 to conclude the molecular non-rigidity and symmetric distribution as well.

The dipole moments μ_2 and μ_1 of Table 8.4 from τ_2 and τ_1 of Table 8.2 were then measured in terms of the linear coefficients β 's of the variations of χ_{ij} 's with w_j 's of Fig.8.5. All the familiar parabolic curves χ_{ij} 's with w_j 's are found to increase with frequency (f) of the electric field. The

measured μ 's are compared with theoretical dipole moment μ_{theo} 's derived from available bond angles and bond moments of the substituent polar groups attached to the parent ones as sketched in Fig.8.6. The associational aspect of the polar molecules with solvents in Fig.8.6 exhibits the mesomeric, inductive and electromeric effects. All these effects are taken into account by the ratio of μ_{expt}/μ_{theo} in agreement with the experimental results as seen in Table 8.4. They are finally compared with the reported μ 's and μ_1 's obtained from $\mu_1 = \mu_2(c_1/c_2)^{1/2}$ assuming both the relaxation processes are equally probable.

Table 8.3: Fröhlich parameter A [$=\ln(\tau_2/\tau_1)$], relative contributions c_1 and c_2 towards dielectric dispersion due to τ_1 and τ_2 , theoretical and experimental values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} of Fröhlich's Eqs.(8.7) and (8.8) and from fitting equations of Figs.8.2 and 8.3 at $\omega_j \rightarrow 0$ respectively and symmetric and asymmetric distribution parameters γ and δ related to symmetric and characteristic relaxation times τ_s and τ_{cs} for polar-nonpolar liquid mixtures at 30°C.

System with sl. no.	f in GHz	A	Theoretical values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} from Eq.(8.7) and (8.8)		Theoretical values of c_1 and c_2	Experimental values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} at $\omega_j \rightarrow 0$		Experimental values of c_1 and c_2	Estimated values of γ and δ	τ_s and τ_{cs} in p-sec				
(II)	4.2	4.0137	0.9161	0.1886	0.7373	0.3512	0.880	0.161	0.7287	0.2927	0.29	0.18	4.60	59.71
Chloral in	9.8	3.1956	0.8028	0.2958	0.6463	0.5639	0.615	0.320	0.4334	0.6492	0.25	0.42	10.52	35.51
<i>n</i> -heptane	24.6	2.7319	0.7634	0.3355	0.6043	0.6111	0.675	0.289	0.5395	0.5211	0.28	0.36	3.13	13.49
(IV)														
Ethyltrichl	4.2	1.9093	0.9411	0.2071	0.6310	0.3950	0.765	0.325	0.1494	0.7762	0.14	0.50	16.18	39.29
oroacetate	9.8	3.6910	0.8429	0.2547	0.6891	0.4943	0.445	0.286	0.2583	0.5968	0.33	0.43	20.48	65.69
in	24.6	1.1702	0.3937	0.4629	0.4152	0.7264	-0.015	0.298	-0.3167	1.2155	-0.21	-	18.73	-
<i>n</i> -hexane														

8.2. Theoretical Formulations of c_1 and c_2 for τ_1 and τ_2 :

Eqs.(8.1) and (8.2) are solved for c_1 and c_2 to get

$$c_1 = \frac{(\chi_{ij}'\alpha_2 - \chi_{ij}'')(\alpha_1^2 + 1)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad \dots (8.5)$$

$$c_2 = \frac{(\chi_{ij}'' - \chi_{ij}'\alpha_1)(\alpha_2^2 + 1)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad \dots (8.6)$$

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 [8.12]. Thus from Fröhlich's theory[8.14] based on distribution of τ between the two extreme values of τ_1 and τ_2 one gets

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \quad \dots (8.7)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \left[\tan^{-1}(\omega \tau_2) - \tan^{-1}(\omega \tau_1) \right] \quad \dots (8.8)$$

where $A = \text{Fröhlich parameter} = \ln(\tau_2/\tau_1)$. The theoretical values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} of Eqs.(8.7) and (8.8) were used to get theoretical c_1 and c_2 from Eqs.(8.1) and (8.2) in order to compare them with c_1 and c_2 from the graphical plots of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $\omega_f \rightarrow 0$ as seen in Figs.8.2 and 8.3. Both the theoretical and experimental c_1 and c_2 are placed in Table 8.3.

8.3. Distribution Parameters γ and δ Related to τ_s and τ_{cs} :

All the chemical systems are almost identical for the three frequencies employed. Nevertheless, the existence of double relaxations for chloral in *n*-heptane and ethyltrichloroacetate in *n*-hexane reflects the material property of the chemical systems (Table 8.2) indicating the molecular non-rigidity. In such case, the molecule may either show symmetrical circular arc or a skewed arc [8.20] when the values of χ''_{ij}/χ_{oij} is plotted against χ'_{ij}/χ_{oij} at $\omega_f \rightarrow 0$ for various frequencies of the electric field to yield:

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad \dots (8.9)$$

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad \dots (8.10)$$

Here, γ and δ are the symmetric and asymmetric distribution parameters which are, related to symmetric and characteristic relaxation times τ_s and τ_{cs} respectively. Separating the real and imaginary parts from Eq.(8.9) one has

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}/\chi_{oij}}{\chi''_{ij}/\chi_{oij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad \dots (8.11)$$

$$\tau_s = \frac{1}{\omega} \left[\sqrt{\left(\frac{\chi'_{ij}/\chi_{oij}}{\chi''_{ij}/\chi_{oij}} \cos \frac{\gamma\pi}{2} - \sin \frac{\gamma\pi}{2} \right)} \right]^{1-\gamma} \quad \dots (8.12)$$

where χ_{ij}''/χ_{oij} and χ_{ij}'''/χ_{oij} are obtained from Figs.8.2 and 8.3 at $w_j \rightarrow 0$. Again δ and τ_{cs} can be had from Eq.(8.10)as:

$$\tan(\phi\delta) = \frac{\chi''}{\chi'} \quad \dots (8.13)$$

and

$$\tau_{cs} = \frac{1}{\omega} \tan \phi \quad \dots (8.14)$$

Since ϕ cannot be evaluated directly, a theoretical curve of $(1/\phi)\log(\cos\phi)$ with ϕ in degrees was drawn in Fig.8.4 from which

$$\frac{1}{\phi} \log(\cos \phi) = \frac{\log[(\chi'_{ij}/\chi_{oij})/\cos(\phi\delta)]}{\phi\delta} \quad \dots (8.15)$$

can be found out. The known value of $(1/\phi)\log(\cos\phi)$ was then use to obtain ϕ . With known ϕ and δ , τ_{cs} were found out from Eqs.(8.13) and (8.14). The estimated γ and δ are entered in columns 12 and 13 with τ_s and τ_{cs} in columns 14 and 15 of Table 8.3 to conclude the symmetric relaxation behaviour for such liquids.

8.4. Theoretical Formulation for Dipole Moments μ_2 and μ_1 :

The Debye equation [8.14] for a polar-nonpolar liquid mixture under hf electric field in terms of χ_{ij} 's is written as:

$$\frac{d\chi''_{ij}}{d\chi'_{ij}} = \omega\tau$$

or,

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega\tau \left(\frac{d\chi'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} \quad \dots (8.16)$$

τ 's of the polar liquid could, however, be estimated from Eq.(8.16) in order to place in column 9 of Table 8.2. Again, the imaginary part of dielectric orientation susceptibility χ_{ij}'' as a function of w_j of a solute can be written as [8.21-8.22]

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

Differentiation of the above equation with respect to w_j and at $w_j \rightarrow 0$ yields:

$$\left(\frac{d\chi_{ij}''}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_o k_B T M_j} \left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) (\varepsilon_i+2)^2 \quad \dots (8.17)$$

where the density of the solution ρ_{ij} becomes ρ_i = density of solvent, $(\varepsilon_{ij}+2)^2 \rightarrow (\varepsilon_i+2)^2$ 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} F.m⁻¹. All are expressed in SI units.

Comparing Eqs.(8.16) and (8.17) one gets

$$\omega\tau \left(\frac{d\chi_{ij}'}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_o k_B T M_j} \left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) (\varepsilon_i+2)^2 = \omega\tau\beta \quad \dots (8.18)$$

where β is the slope of $\chi_{ij}'-w_j$ curves of Fig.8.5 at $w_j \rightarrow 0$. Here, no approximation in determination of μ_j is made like the conductivity measurement technique done elsewhere [8.23].

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

$$\mu_j = \left(\frac{27\varepsilon_o k_B T M_j \beta}{N\rho_i (\varepsilon_i+2)^2 b}\right)^{\frac{1}{2}} \quad \dots (8.19)$$

where

$$b = 1/(1+\omega^2\tau^2) \quad \dots (8.20)$$

is the dimensionless parameter involved with measured τ 's of Table 8.2. All the μ 's, b 's and β 's as computed for chloral and ethyltrichloroacetate in different solvents at 30°C are placed in Table 8.4 to compare with μ_{theo} 's from the available bond angles and bond moments in Coulomb-metre (C.m).

8.5. Results and Discussions :

The double or single relaxation phenomena for chloral and ethyltrichloroacetate in benzene, *n*-heptane and *n*-hexane under 24.6, 9.8 and 4.2 GHz electric field frequencies were studied from the slopes and intercepts of linear plots in Fig.8.1 for the variables $(\chi_{oij}-\chi_{ij}')/\chi_{ij}'$ against χ_{ij}''/χ_{ij}' of theoretical formulation of Eq.(8.3) for different w_j 's of solutes at 30°C. The dielectric orientation susceptibilities χ_{ij}' , χ_{ij}'' and χ_{oij} are collected together in Table 8.1 from the measured relative permittivities of ε_{ij}' , ε_{ij}'' , ε_{oij} and $\varepsilon_{\infty ij}$ [8.7]. The linear regression analysis made on Eq.(8.3) with the data of Table 8.1 was, however, done by the use of a PC and software. The correlation coefficients r 's are placed in Table 8.2 in getting the intercepts and slopes of Eq.(8.3) to see how far the data of Table 8.1 are collinear. The errors involved in the linear regression analysis of Eq(8.3) are expressed by chi-squares values which were initially very large in some cases. One therefore, should have become selective to choose a few data for some systems for which chi-squares values were adjusted

Table 8.4: Estimated coefficients of $\chi_{ij}'-w_j$ equations, dimensionless parameters b_2, b_1 [Eq.(8.20)], estimated dipole moments μ_2 and μ_1 from Eq.(8.19) and μ_{theo} from bond angle and bond moment together with μ_1 from $\mu_1=\mu_2(c_1/c_2)^{1/2}$ and reported μ in Coulomb.metre (C.m).

System with sl. no. & mol. wt. M_j	f in GHz	Coefficients of $\chi_{ij}'-w_j$ equation $\chi_{ij}'=\alpha+\beta w_j+\xi w_j^2$			Dimensionless parameter		Estimated $\mu \times 10^{30}$ in C.m	Reported $\mu \times 10^{30}$ in C.m	Estimated $\mu_i \times 10^{30}$ in C.m from $\mu_i = \mu_2(c_1/c_2)^{1/2}$		
		α	β	ξ	b_1	b_2			μ_1	μ_2	
(I) Chloral in benzene $M_j=0.1475$ Kg	4.2	0.0291	1.7212	1.6641	-	0.9810	-	5.21	5.17*	-	-
	9.8	0.0218	1.6402	1.1834	-	0.8648	-	5.42	4.87**	-	10.02
	24.6	0.0333	1.4368	1.6834	-	0.8746	-	5.04	4.73*	-	-
(II) Chloral in <i>n</i> -heptane $M_j=0.1475$ Kg	4.2	-0.0250	1.5050	0.4654	0.9997	0.5098	5.99	8.39	6.13*	12.16	-
	9.8	0.0150	0.7168	2.4649	0.9958	0.2824	4.14	7.78	6.00**	8.33	10.02
	24.6	-0.0223	1.2478	1.1078	0.9888	0.2714	5.48	10.47	5.63*	10.41	-
(III) Ethyltrichloroacetate in benzene $M_j=0.1915$ Kg	4.2	0.0295	3.5204	-1.3400	-	0.8028	-	9.39	9.70*	-	-
	9.8	0.0490	1.7935	1.9676	-	0.2751	-	11.45	6.50**	-	10.50
	24.6	-0.0309	2.7329	-6.6401	-	0.7285	-	8.68	8.13*	-	-
(IV) Ethyltrichloroacetate in <i>n</i> -hexane $M_j=0.1915$ Kg	4.2	2.6215	2.6215	-1.7604	0.9943	0.7940	9.16	10.28	10.30*	12.98	-
	9.8	1.9711	1.9711	-0.2513	0.9986	0.3132	7.95	14.19	8.67**	16.74	10.50
	24.6	2.4108	2.4108	-6.6385	0.6662	0.1612	10.76	21.87	13.27*	16.53	-

to be minimum for the effective utilization of the experimental data [8.7]. The large chi-squares values initially obtained for Eq.(8.3) further indicate the probable uncertainty in the measurements. The minimum chi-squares values so adjusted on the data are presented in column 6 of Table 8.2. The data for chloral in benzene ($-\square-$, $-\boxplus-$) at 4.2 and 24.6 GHz and ethyltrichloroacetate in *n*-hexane ($-\nabla-$) at 9.8 GHz do not appear to lie on the straight line. The display of data set for ethyltrichloroacetate in benzene ($-\Delta-$, $-\blacktriangle-$) at 4.2 and 24.6 GHz and in *n*-hexane ($-\nabla-$) at 4.2 GHz is over a narrow range, which often renders the linear regression of doubtful validity. Perfect linearity between variables of Eq.(8.3) is said to be achieved if $r=-1$ or $+1$ although, the correlation coefficient r 's for the systems ($-\boxplus-$, $-\square-$, $-\nabla-$) are -0.41 , -0.91 and 0.66 respectively. The high value of $r=-0.91$ for chloral in benzene ($-\square-$) at 4.2 GHz indicates that the variables of Eq.(8.3) are almost linearly correlated with each other while comparatively lower values of r 's of -0.41 and 0.66 for chloral in benzene at 24.6 GHz ($-\boxplus-$) and ethyltrichloroacetate in *n*-hexane at 9.8 GHz ($-\nabla-$) may occur for the experimental difficulty of the accurate measurements of the relative permittivities in the 24.6 GHz electric field. The desired variables $(\chi_{oij}-\chi_{ij}')/\chi_{ij}'$ and χ_{ij}''/χ_{ij}' of Eq.(8.3) for ethyltrichloroacetate in benzene ($-\Delta-$) and *n*-hexane ($-\nabla-$) at 4.2 GHz and ethyltrichloroacetate in benzene at 24.6 GHz ($-\blacktriangle-$) are incidentally of narrow range although the relative permittivities

were measured [8.7] for a wide range of concentration as seen in Table 8.1. Nevertheless, the straight lines of the data set for the systems under consideration as displayed in Fig.8.1 are made on the basis of minimum chi-squares values mathematically adjusted between two variables. The high values of r 's as shown in Table 8.2 signify the applicability of linear regression analysis on the data set mentioned above.

Four data set out of six, showed mono while other two double relaxations which are important. Nevertheless, the measurement technique employed and sampling of the polar-nonpolar liquid mixtures for various concentrations called w_j 's were so prepared [8.7-8.8] that χ_{ij}' , χ_{oij} and χ_{ij}'' of Table 8.1 for different w_j 's are of

2% and 5% accuracies. This type of anomaly showed in benzene and n -hexane the associational aspects [8.24] of polar molecules. The estimated values of τ_2 and τ_1 from the intercepts and slopes of Table 8.2 are placed in the 7th and 8th columns of Table 8.2. Double relaxation phenomena are, however, observed for chloral in n -heptane and ethyltrichloroacetate in n -hexane at 4.2 GHz (J -band) 9.8 GHz (X -band) and 24.6 GHz (Q -band) hf electric field. This fact indicates that the phenomena of double or single relaxation are the material property of the chemical system in

addition to the dependency on solvent used. It further reveals that the existence of double relaxation phenomena in aliphatic solvents at all the frequencies is greater than in the aromatic solvent. Both chloral and ethyltrichloroacetate in benzene showed the single relaxation by showing τ_2 only. The existence of fractional +ve charge δ^+ on C-atom and δ^- on O-atom of $>C=O$ group in both the polar liquids produces electromeric effect to form π -complexes with the delocalised π -electron cloud δ^- of benzene ring. This prefers the solute-solvent molecular association and yields single τ_2 in benzene. The τ_2 's were calculated from Eq.(8.4) assuming single broad Debye-like dispersion [8.17]. They are placed in column 11 of Table 8.2. It is interesting to note that τ_1 's for two molecules agree well with the measured τ from Eq.(8.16) involved with measured susceptibility.

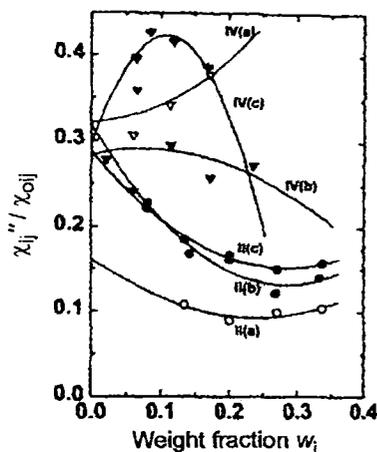


Figure 8 3: Variation of χ_{ij}''/χ_{oij} against w_j 's of chloral and ethyltrichloroacetate at 30°C.

II(a), II(b) and II(c) for chloral in n -heptane ($-O-$, $-●-$, $-⊕-$); and IV(a), IV(b) and IV(c) for ethyltrichloroacetate in n -hexane ($-∇-$, $-▼-$, $-▽-$) at 4.2, 9.8 and 24.6 GHz electric fields respectively

Thus the hf susceptibility measurement always yields the microscopic as well as macroscopic τ as observed for double relaxation phenomena through conductivity measurements [8.18].

Almost all τ_2 's of Table 8.2 are higher at 9.8 GHz, but of low values both at 4.2 and 24.6 GHz electric field in different solvents. Such behaviour occurs probably due to strong absorption of electric energy in the effective dispersive region of 9.8 GHz. The solute-solvent or solute-solute molecular association break up at higher and lower frequencies from nearly 10 GHz electric field. Almost all the τ_1 agree with the reported τ seen in the 10th column Table 8.2 exhibiting the probability of rotation of a part of the molecule under hf electric field [8.9]

The theoretical values of the relative contributions and c_1 and c_2 towards dielectric dispersions due to τ_1 and τ_2 are, however, calculated from Eqs.(8.5) and (8.6) with the theoretical values of χ_{ij}''/χ_{oij} and χ_{ij}''/χ_{oij} of Fröhlich's [8.14] Eqs.(8.7) and (8.8). They are compared with the

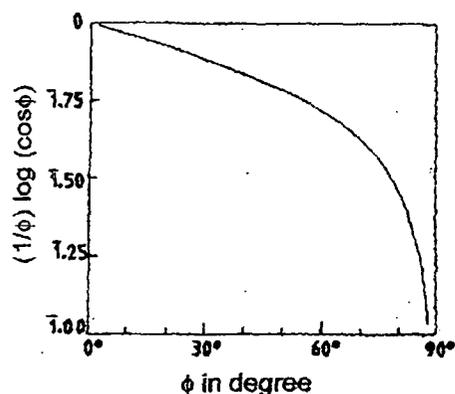


Figure 8.4: Plot of $(1/\phi)\log(\cos\phi)$ against ϕ in degree.

experimental c_1 and c_2 derived from Eqs.(8.5) and (8.6) with the graphically estimated χ_{ij}''/χ_{oij} and χ_{ij}''/χ_{oij} of Figs.8.2 and 8.3 at $w_j \rightarrow 0$. Both the methods yield $c_1 + c_2 \cong 1$ suggesting the applicability of the methods. The variations of χ_{ij}''/χ_{oij} and χ_{ij}''/χ_{oij} with w_j are convex and concave unlike the observation made earlier [8.6, 8.17], except ethyltrichloroacetate in *n*-hexane at 9.8 and 24.6 GHz both of which show the convex variation. Such type of behaviour is explained by the fact that unlike increase of τ

[8.25] it decreases with w_j probably due to solute-solute or solute-solvent molecular associations. All the experimental values of c_1 and c_2 are placed in Table 8.3 for comparison with the theoretical c_1 and c_2 .

In order to test the non-rigid relaxation behaviour of the molecules the symmetric and asymmetric distribution parameters γ and δ were estimated from Eqs.(8.11) and (8.13) for fixed values of χ_{ij}''/χ_{oij} and χ_{ij}''/χ_{oij} at $w_j \rightarrow 0$ from Figs.8.2 and 8.3. γ and δ are, however, related to symmetric and asymmetric relaxation times τ_s and τ_{cs} of Eqs.(8.12) and (8.14). The values of $(1/\phi)\log(\cos\phi)$ against ϕ in degrees as shown in Fig.8.4 is essential to get δ . Knowing ϕ from the curve of Fig.8.4; δ 's were found out. Both γ , δ and τ_s , τ_{cs} are placed in Table 8.3. The values of γ establish the non-rigid and symmetrical distribution of dielectric parameters of the molecules in *n*-hexane and *n*-heptane at all the frequencies unlike δ , as they are found to be very low [8.26].

The dipole moments μ_2 and μ_1 of polar molecules as presented in Table 8.4 were estimated from Eq.(8.19) in terms of dimensionless parameters b 's of Eq.(8.20) and slope β of the familiar $\chi_{ij}'-w_j$ curves of Fig.8.5 as seen Table 8.4. The variation of χ_{ij}' with w_j are almost similar as seen

Fig.8.5 and Table 8.4 like conductivity measurement presented elsewhere [8.23]. Estimated dipole moments are found in agreement with the reported μ 's to signify the applicability of the present method. μ_2 's are found to increase from 24.6 GHz to 4.2 GHz electric field showing the maximum values at 9.8 GHz for both chloral and ethyltrichloroacetate in benzene. This type of behaviour may be due to strong absorption of electric energy at 9.8 GHz and solute-solvent association of polar solute with benzene ring. But μ_2 's for chloral in *n*-heptane and ethyltrichloroacetate in

n-hexane increase gradually from 4.2 GHz. This sort of variation is probably due to rupture of solute-solute and solute-solvent molecular associations in the *hf* electric field and the corresponding increase in the absorption for smaller molecular species [8.27].

The μ_2 and μ_1 for chloral in *n*-heptane and ethyltrichloroacetate in *n*-hexane at 4.2, 9.8 and 24.6 GHz as well as μ_2 of those liquids in benzene (Table 8.4) are, however, compared with μ_{theo} 's due to available bond angles and bond moments 8.0, 5.0, 0.3 and 2.4 multiple of 10^{-30} Coulomb metre (C.m) for the substituent polar groups of $C=O$, $C=Cl$, $C=C$ and $C \rightarrow OCH_3$ (making an angle 57° with bond axis) respectively with the parent molecules of Fig.8.6. μ_{theo} 's are entered in column 12 of Table 8.4. Chloral shows slightly larger μ_{theo} for solute-solute molecular associations [Fig.8.6 (ii)] in the comparatively concentrated solution as expected [8.28]. The solute-solute molecular association arises due to interaction of fractional positive charge δ^+ on C-atom and negative charge δ^- on O-atom of $>C=O$ group of two solute molecules. Only $>C=O$ exhibits electromeric effect. The solvent C_6H_6 on the other hand, is a cyclic compound with three double bonds and six p -electrons on six C-atoms. Hence π - π interaction or resonance effect combined with

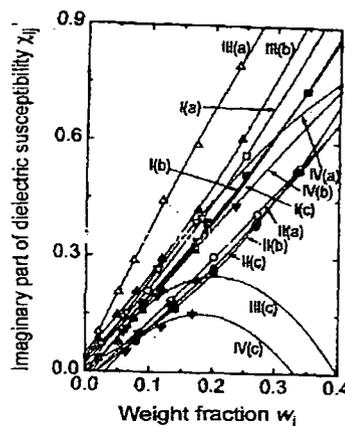


Figure 8.5: Variation of real part of dielectric susceptibility χ_{ij}' with w_j of solutes at 30°C .

I(a), I(b) and I(c) for chloral in benzene ($-\square-$, $-\blacksquare-$, $-\boxplus-$); II(a), II(b) and II(c) for chloral in *n*-heptane ($-\circ-$, $-\bullet-$, $-\oplus-$); III(a), III(b) and III(c) for ethyltrichloroacetate in benzene ($-\triangle-$, $-\blacktriangle-$, $-\blacktriangleleft-$) and IV(a), IV(b) and IV(c) for ethyltrichloroacetate in *n*-hexane ($-\nabla-$, $-\blacktriangledown-$, $-\blacktriangledownleft-$) at 4.2, 9.8 and 24.6 GHz electric fields respectively

inductive effect known as mesomeric effect is expected to play an important role in the measured hf μ_j . Special attention is, therefore, paid to study the solute-solvent molecular association with C_6H_6 . This is explained by the interaction between C-atom of carbonyl group and π -delocalised electron

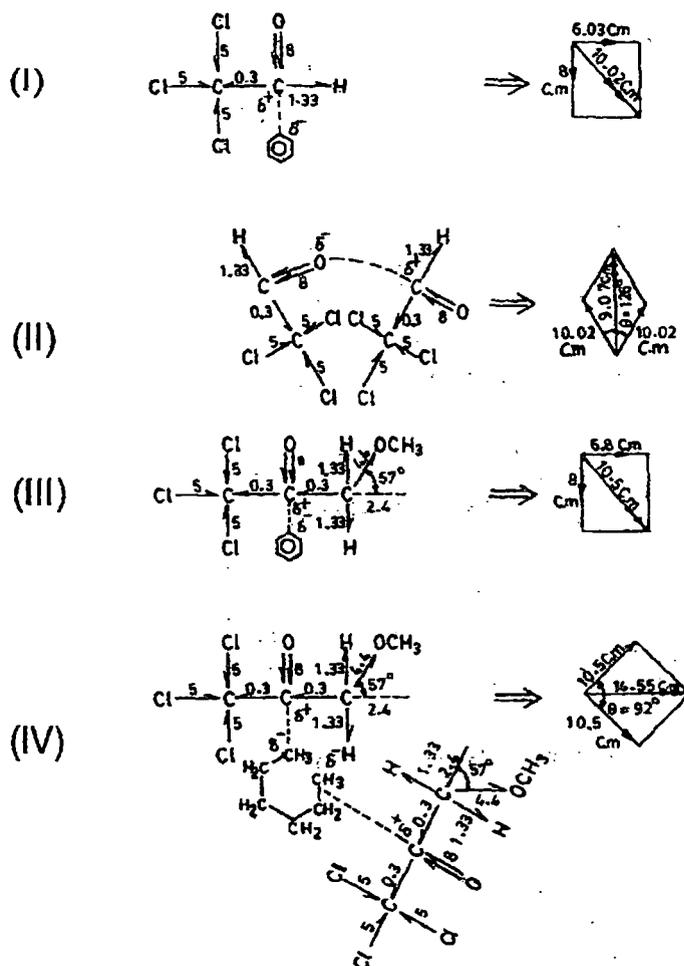


Figure 8.6: Conformational structures of chloral and ethyltrichloroacetate from bond angles and bond moments (expressed in multiple of 10^{-30} Coulomb.metre).

(I) Solute-solvent molecular association of chloral in benzene, (II) Solute-solute molecular association of chloral in *n*-heptane, (III) Solute-solvent molecular association of ethyltrichloroacetate in benzene and (IV) Solute-solute molecular association of ethyltrichloroacetate in *n*-hexane

cloud of benzene ring. Ethyltrichloroacetate, on the other hand, shows μ_{theo} in agreement with the estimated μ_j 's in C_6H_6 . This is due to solute-solvent molecular association as sketched in Fig.8.6(i) and (iii). Larger values of measured μ_j 's are explained by the solute-solute molecular interactions in

solvent *n*-hexane due to interaction between adjacent C and O atoms of $>C=O$ groups of two molecules as shown in Fig.8.6(iv). However, the reduced bond moments by $\mu_{\text{exp}}/\mu_{\text{theo}}$ corroborate μ_{theo} 's in agreement with the experimental μ 's to measure mesomeric, inductive and electromeric effects of the substituent polar groups of the molecules.

8.6. Conclusion :

Theoretical considerations for the effective utilization of the established symbols of dielectric terminologies and parameters in terms of dielectric susceptibilities from dielectric relative permittivities appear to be more topical, significant and useful contribution in the study of dielectric relaxation mechanism as they are directly concerned with orientation polarisation of the polar molecules. The significant formulations so far derived in terms of χ_{ij}' , χ_{ij}'' and χ_{oij} measured under the single frequency measurements of relative permittivities help one to grasp a new physical insight into the molecular interactions. The single frequency measurement of relaxation parameters provide a unique method to get macroscopic and microscopic relaxation times and hence dipole moments of the whole and the flexible part of a molecule. The estimation of τ_1 and τ_2 from the linear Eq.(8.3) is simple and straightforward to get μ from Eq.(8.19) in terms of slope of familiar $\chi_{ij}'-w_j$ curve. The correlation coefficient and chi-squares values signify the minimum error introduced into the desired parameters. The molecules under identical state of environment show interesting phenomena of double or even single relaxation depending upon the solvent used. Aliphatic polar molecules have the greater probability of showing double relaxation in non-polar aliphatic solvents. Various types of molecular associations like solute-solute and solute-solvent association are thus inferred from the usual departure of the graphical plots of χ_{ij}''/χ_{oij} and χ_{ij}'/χ_{oij} with w_j following Bergmann's equations. Non-rigid characteristics of the molecules are ascertained by the symmetric distribution parameter in solvents. The molecular associations are supported by the conformational structures of the molecules in which the mesomeric, inductive and electromeric effects play an important role. The correlation between the conformational structures of the compounds with the observed results enhances the scientific contents and adds a new horizon to understanding the existing knowledge of dielectric relaxation.

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