

CHAPTER 9

**RELAXATION PHENOMENA OF POLAR NON-
POLAR LIQUID MIXTURES UNDER LOW AND
HIGH FREQUENCY ELECTRIC FIELD**

9.1. Introduction :

The dielectric relaxation phenomena of dipolar liquid molecules in non-polar solvents under high frequency electric field is of special importance to study the structure as well as different inter and intra molecular interactions besides solute-solvent and solute-solute molecular associations [9.1-9.2]. Nowadays, it is being thought to be an essential tool to investigate the inductive, mesomeric and electromeric moments of the substituent polar groups present in the polar molecule through the time and frequency domain AC spectroscopy [9.3] or dielectric orientation susceptibility [9.4] or conductivity measurement technique [9.5]. The *hf* conductivity σ_{ij} is concerned with only bound molecular charges while the *hf* susceptibility χ_{ij} contains only orientation polarisation of the dipolar molecule. The dipole moment μ_j and the relaxation time τ_j are, however, easily measured from the conductivity measurements.

Purohit *et al* [9.6-9.7] and Srivastava & Srivastava [9.8] had measured the real ϵ_{ij}' , imaginary ϵ_{ij}'' parts of the complex relative permittivities ϵ_{ij}^* , static or low frequency and infinite frequency relative permittivities ϵ_{oij} and $\epsilon_{\infty ij}$ of some aliphatic molecules (j) chloral [CCl3CHO], ethyltrichloroacetate [CCl3COOCH2CH3], trifluoroethanol [CF3CH2OH], trifluoroacetic acid [CF3COOH] and octanoyl chloride [CH3(CH2)6COCl] in non-polar solvents (i) under 9.8 GHz electric field at 30°C, 25°C and 35°C respectively. The inductive, mesomeric and electromeric moments of the substituent polar groups attached to the parent molecules play the vital role in the formation of solute-solute (dimer) and solute-solvent (monomer) molecular associations. Chloral is widely used in medicine as a drug to induce sleep and relieve pain and in the manufacture of DDT as insecticides. Ethyltrichloroacetate, on the other hand, is used as artificial fragrance of fruits and flowers. Trifluoroethanol and Trifluoroacetic acid in C6H6 have a tendency to form either monomer or dimer formations through hydrogen bonding except octanoyl chloride. The liquids were of puram grade of M/s BDH, England but octanoyl chloride was of puram grade of M/s Fluka, AG.

We, therefore, thought to restudy all these polar molecules from *hf* complex conductivity σ_{ij}^* in terms of the internationally accepted symbols of dielectric terminologies and parameters in SI units to predict their τ and μ . The molecules have often a tendency to exhibit double relaxation times τ_1 and τ_2 due to rotation of their flexible polar groups attached to parent molecules and the whole molecules themselves [9.9] under a single frequency electric field of GHz range at a given temperature. The polar molecules showed double relaxation phenomena in a particular solvent when the measured data are adjusted to chi-squares minimization [9.10]. The most effective dispersive region of almost all the polar molecules lies in the neighbourhood of 10 GHz electric field [9.11]. Moreover, the comparison of *hf* μ_j obtained from *hf* conductivity σ_{ij} measurement with the static μ_s from the measured static parameter X_{ij} seems to be interesting to see how far μ_j involved with τ_j

Table 9.1: Static relative permittivity ϵ_{0ij} , infinite frequency relative permittivity. $\epsilon_{\infty ij}$, real part ϵ_{ij}' and imaginary part ϵ_{ij}'' of complex relative permittivity ϵ_{ij}^* of chloral, ethyltrichloro acetate, at 30°C, trifluoroethanol, trifluoroacetic acid at 25°C and octanoyl chloride at 35°C in different non polar solvents under 9.8 GHz electric field.

System with sl. no & mol. wt	Weight fraction w_j	ϵ_{0ij}	$\epsilon_{\infty ij}$	Weight fraction w_j	ϵ_{ij}'	ϵ_{ij}''
(I) Chloral in benzene $M_j=0.1475$ Kg	0.0255	2.314	2.2350	0.0152	2.26	0.015
	0.0977	2.441	2.2293	0.0899	2.42	0.035
	0.1813	2.622	2.2216	0.1711	2.56	0.057
	0.2511	2.785	2.2147	0.1903	2.60	0.066
	0.3493	3.011	2.2067	0.2510	2.75	0.087
	0.4019	3.189	2.2020	0.3476	2.97	0.116
(II) Chloral in <i>n</i> -heptane $M_j=0.1475$ Kg	0.0224	1.925	1.9154	0.0224	1.93	0.017
	0.0807	2.048	1.9209	0.0807	2.01	0.029
	0.1416	2.140	1.9254	0.1416	2.09	0.036
	0.2003	2.240	1.9301	0.2003	2.19	0.050
	0.2683	2.390	1.9372	0.2683	2.32	0.055
	0.3324	2.516	1.9438	0.3324	2.47	0.080
(III) Ethyltrichloro- acetate in benzene $M_j=0.1915$ Kg	0.0207	2.368	2.2365	0.0207	2.32	0.023
	0.0498	2.475	2.2344	0.0498	2.38	0.046
	0.0802	2.596	2.2317	0.0802	2.44	0.079
	0.1193	2.753	2.2266	0.1193	2.52	0.115
	0.1764	2.996	2.2201	0.1764	2.64	0.194
	0.2444	3.295	2.2126	0.2444	2.82	0.226
(IV) Ethyltrichloro- acetate in <i>n</i> -hexane $M_j=0.1915$ Kg	0.0266	1.980	1.8837	0.0210	1.92	0.021
	0.0639	2.072	1.8878	0.0595	1.99	0.041
	0.0845	2.119	1.8892	0.0649	2.00	0.066
	0.1193	2.223	1.8933	0.1137	2.09	0.093
	0.1683	2.377	1.8988	0.1722	2.24	0.126
			0.2360	2.34	0.190	
(V) Trifluoro- ethanol in benzene $M_j=0.1000$ Kg	0.0030	2.284	2.1994	0.0113	2.332	0.007
	0.0060	2.301	2.2132	0.0215	2.396	0.041
	0.0226	2.405	2.3061	0.0313	2.458	0.073
	0.0311	2.456	2.3537	0.0416	2.515	0.118
	0.0411	2.525	2.4109	0.0523	2.638	0.189
(VI) Trifluoroacetic acid in benzene $M_j=0.1140$ Kg	0.0066	2.327	2.2370	0.0130	2.315	0.035
	0.0130	2.368	2.2731	0.0271	2.350	0.056
	0.0271	2.411	2.3082	0.0391	2.377	0.069
	0.0391	2.449	2.3452	0.0515	2.398	0.084
	0.0515	2.484	2.3671	0.0630	2.420	0.100
	0.0630	2.519	2.3940			
(VII) Octanoyl chloride in benzene $M_j=0.1625$ Kg	0.0183	2.369	2.2218	0.0181	2.306	0.033
	0.0349	2.444	2.2176	0.0358	2.350	0.076
	0.0497	2.526	2.2142	0.0516	2.393	0.111
	0.0648	2.582	2.2110	0.0702	2.439	0.147
	0.0808	2.661	2.2080	0.0802	2.486	0.184

agree with μ_s and μ_{theo} . A systematic comparison of τ_j 's with the reported τ 's and the estimated τ_1 and τ_2 of the molecules by double relaxation method [9.9] enables one to conclude either a part or a whole molecule is rotating under GHz electric field.

μ_{theo} 's were, however, obtained from available bond angles and bond moments of the substituent polar groups attached to the parent molecule [9.9-9.10]. Earlier investigations on different polar molecules [9.5] showed that a part of the molecule is rotating under hf electric field of nearly 3 cm wavelength. The purpose of the present paper is thus to observe how the apparently rigid aliphatic polar molecules behave under static or low frequency and 9.8 GHz electric fields.

The static or low frequency μ_s 's were measured from the linear coefficient of the variation of X_{ij} 's with w_j 's of a polar solute. The variables X_{ij} is, however, related with ϵ_{oij} and $\epsilon_{\infty ij}$ of the polar liquids. μ_s 's are estimated from the measured data of Table 9.1 and placed in Table 9.3 in order to compare with the hf μ_j 's involved with τ_j 's measured from Eqs.(9.9) and (9.10) as derived later on. The concentration variation of X_{ij} 's are displayed in Fig.9.1 by Newton-Raphson's method with the experimental points placed upon them.

The percentage of errors in getting $X_{ij}-w_j$ curves was computed from correlation coefficients ' r ' for all the systems. The errors introduced in α_1 's are very low because r 's are very close to unity establishing the fact X_{ij} 's are correlated almost exactly with w_j 's of Table 9.1. The μ_s 's of Table 9.3 are found to be almost equal with hf μ_j 's except systems V (-O-) and VI (-Δ-). μ_j 's are estimated from the linear coefficient β 's of the curves of hf conductivity σ_{ij} 's against w_j 's of polar liquids at infinite dilution and the estimated τ_j 's. τ_j 's are, however, obtained from the linear slope of $\sigma_{ij}''-\sigma_{ij}'$ curves of Fig.9.2 and the ratio of individual slopes of σ_{ij}'' and σ_{ij}' with w_j curves

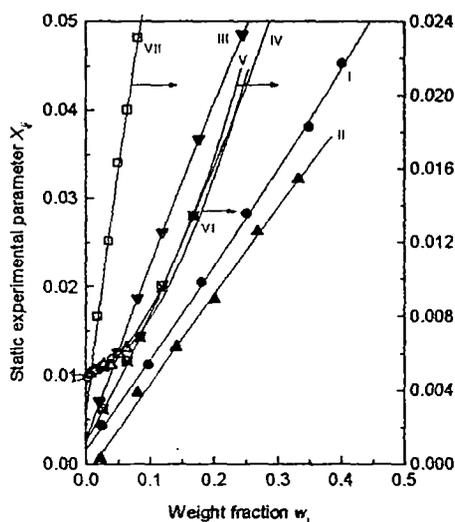


Figure 9.1: Variation of measured experimental parameter X_{ij} with weight fraction w_j of solutes,

I Chloral in benzene (-●-); II Chloral in *n*-heptane (-▲-); III Ethyltrichloroacetate in benzene (-▼-); IV Ethyltrichloroacetate in *n*-hexane (-⊗-); V Trifluoroethanol in benzene (-○-); VI Trifluoroacetic acid in benzene (-Δ-) and VII Octanoyl chloride in benzene (-□-).

at $w_j \rightarrow 0$ shown in Figs.9.3 and 9.4. τ_j 's are placed in Table 9.2 and were used to calculate μ_j 's of Table 9.3. μ_j 's from both the methods are found to agree excellently for all the systems except ethyltrichloroacetate and octanoyl chloride in benzene.

Table 9.2: Slope of $\sigma_{ij}''-\sigma_{ij}'$ curves, correlation coefficients r , percentage of error in regression technique, relaxation time τ_j using Eq.(9.9), ratio of slopes of $\sigma_{ij}''-w_j$ and $\sigma_{ij}'-w_j$ curves at $w_j \rightarrow 0$, percentage of error in $\sigma_{ij}''-w_j$ and $\sigma_{ij}'-w_j$ curves, corresponding τ_j using Eq.(9.10) and reported τ for chloral, ethyltrichloroacetate at 30°C, trifluoroethanol, trifluoroacetic acid at 25°C and octanoyl chloride at 35°C in different non-polar solvents under 9.8 GHz electric field.

System with sl.no	Slope of $\sigma_{ij}''-\sigma_{ij}'$ curve	Corrl .coef r	% of error	$\tau_j \times 10^{12}$ sec from Eq (9.9)	Ratio of slopes of $\sigma_{ij}''-w_j$ & $\sigma_{ij}'-w_j$ curves at $w_j \rightarrow 0$	% of error in regression technique		$\tau_j \times 10^{12}$ sec from Eq.(9.10)	Rept $\tau \times 10^{12}$ sec
						$\sigma_{ij}''-w_j$ curve	$\sigma_{ij}'-w_j$ curve		
(I)Chloral in benzene	6.8735	0.9987	0.07	2.36	6.5416	0.08	0.11	2.48	1.78*
(II) Chloral in <i>n</i> -heptane	8.9472	0.9881	0.65	1.82	8.8940	0.02	1.53	1.83	0.46*
(III) Ethyltrichloro acetate in benzene	2.2289	0.9820	0.98	7.29	1.3768	0.03	0.79	11.80	6.5**
(IV) Ethyltrichloro acetate in <i>n</i> -hexane	2.5845	0.9826	0.95	6.28	3.1959	0.27	0.95	5.08	5.7**
(V)Trifluoroethanol in benzene	1.6508	0.9982	0.11	9.84	3.2082	0.50	0.16	5.06	13.85 ⁺
(VI)Trifluoroacetic acid in benzene	1.6337	0.9973	0.16	9.94	2.1001	0.05	0.14	7.73	9.23 ⁺
(VII) Octanoyl chlo ride in benzene	1.2019	0.9989	0.07	3.51	0.8443	0.31	0.38	19.24	18.60 ⁺⁺

*= Cole-Cole plot,

**= Gopalakrishna's method,

⁺= Calculated by Gopalakrishna's method,

⁺⁺= Higasi's method.

μ_j 's thus obtained are compared with the theoretical dipole moment μ_{theo} 's derived from the available bond angles and bond moments of the substituent polar groups of the molecules [9.9-9.10] and presented in Table 9.3. In Fig.9.6 conformations of five dipolar molecules are displayed by taking into account of the reduced bond length by a factor μ_s / μ_{theo} due to inductive, mesomeric and electromeric effects of the substituent polar groups attached to the parent molecules.

9.2. Theoretical Formulation of X_{ij} to Estimate Static μ_s :

The low frequency or static dipole moment μ_s of a polar solute (j) in a non-polar solvent (i) at any temperature T K is given by [9.12]:

$$\frac{\epsilon_{oij} - 1}{\epsilon_{oij} + 2} - \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} = \frac{\epsilon_{oi} - 1}{\epsilon_{oi} + 2} - \frac{\epsilon_{\infty oi} - 1}{\epsilon_{\infty oi} + 2} + \frac{N\mu_s^2 c_j}{9\epsilon_o k_B T} \quad \dots(9.1)$$

where ϵ_{oij} and $\epsilon_{\infty ij}$ are the dimensionless low and infinite frequency relative permittivities of solution (ij) of Table 9.1. The molar concentration c_j can be expressed by weight fraction w_j of the polar solute:

$$c_j = \frac{\rho_{ij} w_j}{M_j}$$

k_B is the Boltzmann constant, N is the Avogadro's number and $\epsilon_o =$ permittivity of the free space = 8.854×10^{-12} Farad.metre⁻¹.

The weight W_i and volume V_i of a non-polar solvent is mixed with a polar solute of weight W_j and volume V_j to give the solution density ρ_{ij} , where,

$$\begin{aligned} \rho_{ij} &= \frac{W_i + W_j}{V_i + V_j} = \frac{W_i + W_j}{\frac{W_i}{\rho_i} + \frac{W_j}{\rho_j}} = \frac{\rho_i \rho_j}{\frac{W_i \rho_j}{W_i + W_j} + \frac{W_j \rho_i}{W_i + W_j}} \\ &= \frac{\rho_i \rho_j}{\rho_j w_i + \rho_i w_j} = \rho_i (1 - \gamma w_j)^{-1} \quad \dots(9.2) \end{aligned}$$

The weight fraction w_i and w_j of solvent and solute are:

$$w_i = \frac{W_i}{W_i + W_j} \quad \text{and} \quad w_j = \frac{W_j}{W_i + W_j}$$

such that $w_i + w_j = 1$ and $\gamma = (1 - \rho_i / \rho_j)$ where ρ_i and ρ_j are densities of pure solvent and pure solute respectively in SI units.

Now Eq.(9.1) may be written as :

$$\frac{\epsilon_{oij} - \epsilon_{\infty ij}}{(\epsilon_{oij} + 2)(\epsilon_{\infty ij} + 2)} = \frac{\epsilon_{oi} - \epsilon_{\infty oi}}{(\epsilon_{oi} + 2)(\epsilon_{\infty oi} + 2)} + \frac{N\rho_i \mu_s^2}{27\epsilon_o M_j k_B T} w_j (1 - \gamma w_j)^{-1}$$

or,

$$X_{ij} = X_i + \frac{N\rho_i \mu_s^2}{27\epsilon_o M_j k_B T} w_j + \frac{N\rho_i \mu_s^2}{27\epsilon_o M_j k_B T} \gamma w_j^2 + \dots \quad \dots(9.3)$$

The above equation can be expressed as a best fitted polynomial equation of w_j like

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \dots \quad \dots(9.4)$$

Now equating the coefficients of first power of w_j of Eqs.(9.3) and (9.4) one gets ;

$$\mu_s = \left(\frac{27 \epsilon_0 M_j k_B T a_1}{N \rho_i} \right)^{1/2} \quad \dots(9.5)$$

where a_1 is the slope of $X_{ij}-w_j$ curve of Fig.9.1. But μ_s from the coefficients of higher powers of w_j of Eqs.(9.3) and (9.4) are not reliable as they are involved with various effects of solvent, relative density, solute-solute association, internal field, macroscopic viscosity etc. μ_s from Eq.(9.5) along with a_1 are placed in Table 9.3 to compare with $hf \mu_j$'s as well as μ_1 and μ_2 from double relaxation method and μ_{theo} from the available bond angles and bond moments.

Table 9.3: Values of coefficients of $X_{ij} = a_0 + a_1 w_j + a_2 w_j^2$ and $\sigma_{ij} = \alpha + \beta w_j + \xi w_j^2$ curves, static and hf dipole moment μ_s , and μ_j , theoretical dipole moment μ_{theo} , reported dipole moment μ and estimated μ_1 and μ_2 of the flexible part and the whole molecule by double relaxation method for chloral, ethyltrichloroacetate at 30°C, trifluoroethanol, trifluoroacetic acid at 25°C and octanoyl chloride at 35°C in different non-polar solvents under 9.8 GHz electric field.

System with sl.no. & mol.wt	Coeff. of $X_{ij}-w_j$ curve a_0, a_1, a_2	Coeff. of $\sigma_{ij}-w_j$ curve α, β, ξ	$\mu_s \times 10^{30}$ in C.m	$\mu_j^a \times 10^{30}$ in C.m	$\mu_j^b \times 10^{30}$ in C.m	$\mu_{theo} \times 10^{30}$ in C.m	Rept $\mu \times 10^{30}$ in C.m	$\frac{\mu_s}{\mu_{theo}}$	Corre $\mu_{theo} \times 10^{30}$ in C.m	$\mu_1 \times 10^{30}$ in C.m	$\mu_2 \times 10^{30}$ in C.m
(I) Chloral in benzene $M_j = 0.1475$ Kg	0.0017 0.0992 0.0207	1.2206 0.9559 0.5611	5.28	5.27	5.27	10.02	4.87	0.53	5.31	5.27	19.32
(II) Chloral in <i>n</i> -heptane $M_j = 0.1475$ Kg	-0.0013 0.1053 -0.0144	1.0419 0.5311 1.1538	6.17	4.85	4.85	10.02	6.00	0.62	6.21	4.83	9.07
(III) Ethyltrichloroacetate in benzene $M_j = 0.1915$ Kg	0.0028 0.2049 -0.0719	1.2468 0.9425 1.0703	8.65	6.46	7.29	10.50	6.50	0.82	8.61	-	11.07
(IV) Ethyltrichloroacetate in <i>n</i> -hexane $M_j = 0.1915$ Kg	0.0027 0.1299 0.1231	1.0198 1.1260 -0.0323	7.96	8.71	8.52	10.50	8.67	0.76	7.97	8.13	14.53
(V) Trifluoroethanol in benzene $M_j = 0.1000$ Kg	0.0047 0.0144 0.2276	1.2535 1.3716 41.238	1.64	5.93	5.31	2.78	9.98	0.59	1.64	-	-
(VI) Trifluoroacetic acid in benzene $M_j = 0.1140$ Kg	0.0049 0.0077 0.2279	1.2430 1.5621 -5.3871	1.28	6.77	6.40	8.47	5.58	0.15	1.27	-	8.77
(VII) Octanoyl chloride in benzene $M_j = 0.1625$ Kg	0.0028 0.2870 -0.4601	1.2396 0.8981 6.9372	9.54	6.99	8.33	11.62	9.14	0.82	9.55	-	7.02

$\mu_j^a = hf$ dipole moment by using τ_j of Eq.(9.9) $\mu_j^b = hf$ dipole moment by using τ_j of Eq.(9.10)

9.3. Formulation of hf Conductivity σ_{ij} to Estimate τ_j and $hf \mu_j$:

The complex relative dielectric permittivity ϵ_{ij}^* under hf electric field is:

$$\epsilon_{ij}^* = \epsilon_{ij}' - j\epsilon_{ij}''$$

where ϵ_{ij}' and ϵ_{ij}'' are the real and imaginary parts of ϵ_{ij}^* . The hf complex conductivity σ_{ij}^* of a polar-nonpolar liquid mixture for a given weight fraction w_j is [9.12]

$$\sigma_{ij}^* = \sigma_{ij}' + j\sigma_{ij}''$$

or,

$$\sigma_{ij}^* = \omega\epsilon_o\epsilon_{ij}'' + j\omega\epsilon_o\epsilon_{ij}' \quad \dots(9.6)$$

where $\omega\epsilon_o\epsilon_{ij}'' = \sigma_{ij}'$ and $\omega\epsilon_o\epsilon_{ij}' = \sigma_{ij}''$ are the real and imaginary parts of complex conductivity, $\epsilon_o =$ permittivity of free space $= 8.854 \times 10^{-12}$ F.m⁻¹ and j is a complex number $= \sqrt{-1}$.

The total hf conductivity σ_{ij} is given by:

$$\sigma_{ij} = \omega\epsilon_o(\epsilon_{ij}''^2 + \epsilon_{ij}'^2)^{1/2} \quad \dots(9.7)$$

Again, σ_{ij}'' is related to σ_{ij}' by

$$\sigma_{ij}'' = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma_{ij}' \quad \dots(9.8)$$

$\sigma_{\infty ij}$ is the constant conductivity at infinite dilution of $w_j \rightarrow 0$ and τ_j is the relaxation time of a dipolar liquid. Eq.(9.8) on differentiation w.r.to σ_{ij}' yields

$$\frac{d\sigma_{ij}''}{d\sigma_{ij}'} = \frac{1}{\omega\tau_j} \quad \dots(9.9)$$

which provides a convenient method to obtain τ_j of a polar molecule. It is, however, better to use the ratio of the individual slopes of variation of σ_{ij}'' and σ_{ij}' with w_j in order to avoid the polar-polar interaction at $w_j \rightarrow 0$ in a given solvent to get τ_j from:

$$\frac{(d\sigma_{ij}''/dw_j)_{w_j \rightarrow 0}}{(d\sigma_{ij}'/dw_j)_{w_j \rightarrow 0}} = \frac{1}{\omega\tau_j} \quad \dots(9.10)$$

where $\omega = 2\pi f$ and f is the frequency of the applied hf electric field.

In hf region of GHz range, it is generally observed $\sigma_{ij}'' \approx \sigma_{ij}'$ as evident from Figs.9.3 and 9.5 hence Eq.(9.8) becomes

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

$$\beta = \frac{1}{\omega\tau_j} \left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} \quad \dots(9.11)$$

Here $\beta = (d\sigma_{ij}/dw_j)_{w_j \rightarrow 0}$ is the slope of $\sigma_{ij}-w_j$ curves of Fig.9.5 at $w_j \rightarrow 0$.

The real part σ'_{ij} of a polar-nonpolar liquid mixture of w_j at T K is [9.12] given by:

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

$$\left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{3M_j k_B T} \left(\frac{\epsilon_i + 2}{3} \right)^2 \left(\frac{\omega^2\tau}{1+\omega^2\tau^2} \right) \quad \dots(9.12)$$

Now, comparing Eqs.(9.11) and (9.12) one gets the $hf \mu_j$ from :

$$\mu_j = \left[\frac{27M_j k_B T \beta}{N\rho_i (\epsilon_i + 2)^2 \omega b} \right]^{1/2} \quad \dots(9.13)$$

wherer,

$$b = 1/(1+\omega^2\tau_j^2) \quad \dots(9.14)$$

is a dimensionless parameter involved with τ_j 's obtained from Eqs.(9.9) and (9.10). The other symbols used in Eq.(9.13) are N = Avogadro's number, ρ_i = density of the solvent, ϵ_i = relative permittivity of the solvent, M_j = molecular weight of the solute and k_B = Boltzmann constant. All are expressed in SI units. All the computed $hf \mu_j$'s in terms of β 's and b 's are presented in Table 9.3. They are compared with μ_1 and μ_2 of the flexible part and the whole molecule by the double relaxation method [9.9] as entered in Table 9.3. The computed τ_j 's are, however, placed in Table 9.2 to compare with those by other methods and freshly calculated Gopalakrishna's method for the last three systems.

9.4. Results and Discussion :

The dipole moments μ_s 's of the polar molecule under static or low frequency electric field are estimated from the slope α_1 of the $X_{ij}-w_j$ curves of Fig.9.1. X_{ij} is related to static and infinite frequency relative permittivities ϵ_{oij} and $\epsilon_{\omega ij}$ of Eq.(9.1) at different w_j 's of polar solutes presented in Table 9.1. All the curves of X_{ij} against w_j were, however, drawn by best-fitted regression analysis made on available experimental data extracted from Table 9.1 in order to plot Fig.9.1. Each system consists of a polar solute in different non-polar solvents usually shows almost same slopes as seen in Fig.9.1. This signifies the almost same polarity of the molecules under investigation [9.13].

Polarisations are found to be slightly larger for ethyltrichloroacetate in benzene, *n*-hexane and octanoyl chloride in benzene in comparison to other molecules. The increase in polarisation is due to

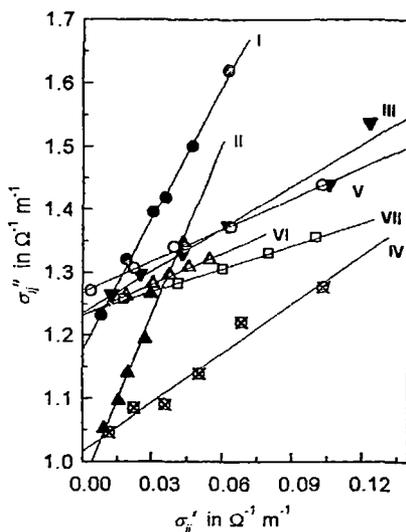


Figure 9.2: Linear plot of σ_{ij}'' against σ_{ij}' for different weight fraction w_j ,

I. Chloral in benzene (—●—); II. Chloral in *n*-heptane (—▲—); III. Ethyltrichloroacetate in benzene (—▼—); IV. Ethyltrichloroacetate in *n*-hexane (—⊗—); V. Trifluoroethanol in benzene (—○—); VI. Trifluoroacetic acid in benzene (—△—) and VII. Octanoyl chloride in benzene (—□—).

the increase in dipole moment which means that dimerisation takes place in such a manner that in the dimeric molecule, the dipoles are inclined at an angle less than 90° so that the dipole moment is more than that of the monomer. The correlation coefficients r 's in getting the coefficients of $X_{ij}-w_j$ curves of Fig.9.1 were very close to unity *i.e.*, 0.9993, 0.9978, 0.9999, 0.9998, 0.9693, 0.9574 and 0.9980 for seven systems of tables and figures respectively and hence percentage of errors in terms of r 's were very small.

The relaxation time τ_j of the molecules are estimated by using the linear slope of $\sigma_{ij}''-\sigma_{ij}'$ curve of Murthy *et al* [9.14] and the ratio of individual slopes of $\sigma_{ij}''-w_j$ and $\sigma_{ij}'-w_j$ at $w_j \rightarrow 0$. It is evident from Table 9.2 that τ_j 's agree well in both the methods except ethyltrichloroacetate (III), trifluoroethanol (V) and octanoyl chloride (VII) all in benzene. This behaviour is explained on the basis of solute-solute (dimer) molecular association in the higher concentration region which turn into solute-solvent (monomer) association due to rupture of dimer. In such case it is better to use the ratio of individual slopes of σ_{ij}'' and σ_{ij}' in $\Omega^{-1}\text{m}^{-1}$ against w_j at infinite dilution as seen in Figs.9.3 and 9.4 where polar-polar interaction is almost avoided completely to compute τ_j . The curves of $\sigma_{ij}''-\sigma_{ij}'$ in Fig.9.2 are not perfectly linear with the experimental data according to Eq.(9.9) for the systems III (—▼—), IV (—⊗—) and V (—○—). In such cases polar-polar interaction in the higher concentration region or solute-solvent association in the lower concentration region may be the cause for such non-linear behaviour. The almost parallel nature of the curves I and II ; III and IV in Fig.9.3 of $\sigma_{ij}''-w_j$ curves indicates the same polarity of the molecules of chloral and ethyltrichloroacetate in different solvents. The higher magnitude of σ_{ij}'' in $\Omega^{-1}\text{m}^{-1}$ in benzene for each solute of Fig.9.3 may reveal the solute-solute (dimer) interaction of the polar molecules. Curve VI (trifluoroacetic acid in benzene) of Fig.9.3 are found to increase

gradually to show maximum at $w_j = 0.1401$. This type of behaviour may be due to transition of phase [9.15] occurred after a certain concentration of the solute. Like systems II and IV in *n*-heptane and *n*-hexane, the other curves of Fig.9.3 for solvent benzene meet at a point on the ordinate axis $1.2206 \leq \sigma_{ij}'' \leq 1.2526$ at $w_j = 0$ exhibiting the probable solvation effect of polar solute in same non-polar solvent. It is evident from Fig.9.3 that all the curves are almost same as total *hf* conductivity σ_{ij} in $\Omega^{-1}\text{m}^{-1}$ plotted against w_j in Fig.9.5. This indicates the validity of the approximation $\sigma_{ij}'' \approx \sigma_{ij}$ in Eq.(9.11). All the curves of σ_{ij}' in Fig.9.4 increase gradually with w_j and become closer to yield $\sigma_{ij}' \approx 0$ at $w_j = 0$. Such nature of curves are explained on the basis of the fact that absorption of *hf* electric energy increases with concentration. The magnitude of absorption is maximum for trifluoroethanol in benzene (V) and minimum for chloral in *n*-heptane (II) although concentration of polar solute of the latter system is higher than the former.

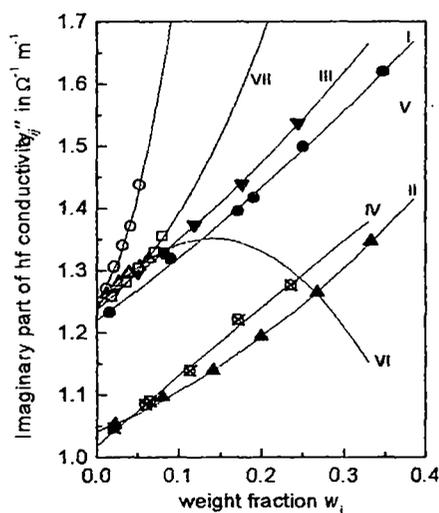


Figure 9.3: Variation of imaginary part of *hf* complex conductivity σ_{ij}'' with weight fraction w_j

I. Chloral in benzene (—●—); II. Chloral in *n*-heptane (—▲—); III. Ethyltrichloroacetate in benzene (—▼—); IV. Ethyltrichloroacetate in *n*-hexane (—⊖—); V. Trifluoroethanol in benzene (—○—); VI. Trifluoroacetic acid in benzene (—△—) and VII. Octanoyl chloride in benzene (—□—).

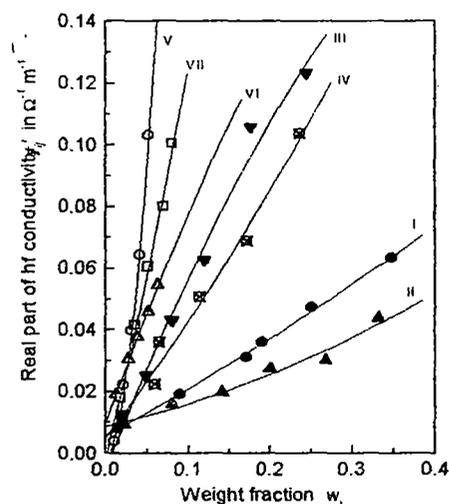


Figure 9.4: Variation of real part of *hf* complex conductivity σ_{ij}' with weight fraction w_j .

I. Chloral in benzene (—●—); II. Chloral in *n*-heptane (—▲—); III. Ethyltrichloroacetate in benzene (—▼—); IV. Ethyltrichloroacetate in *n*-hexane (—⊖—); V. Trifluoroethanol in benzene (—○—); VI. Trifluoroacetic acid in benzene (—△—) and VII. Octanoyl chloride in benzene (—□—).

The high frequency dipole moments μ_j of the polar liquids are estimated in terms of slope β of $\sigma_{ij}-w_j$ curve of Fig.9.5 and dimensionless parameter b 's in order to show them in Table 9.3. They are compared with μ_s , μ_1 , μ_2 and reported μ' 's respectively. All the curves of total *hf* conductivity σ_{ij} in $\Omega^{-1}\text{m}^{-1}$ against w_j of Fig.9.5 are parabolic as evident from the coefficients α , β and ξ of Table 9.3. This indicates that conductivity of the mixture with the absorption of *hf* electric energy increases with w_j 's of solute except system VI. These curve when extrapolated beyond the experimental data

exhibits maximum σ_{ij} at $w_j = 0.1401$ and then decreases gradually thereafter like $\sigma_{ij}''-w_j$ curves of Fig.9.3 probably due to transition of phase [9.15] occurred at that concentration. This type of behaviour invariably demands experimental measurement beyond this concentration of polar liquid already taken up.

The hf μ_j 's are found to agree well with the static μ_s for chloral, ethyltrichloroacetate and octanoyl chloride in benzene, *n*-heptane and *n*-hexane (system I, II, III, IV, and VII). It reveals the fact that dimerisation takes place both in static and high frequency electric field probably the available data of relative permittivities are in higher concentration regions. μ_j 's of trifluoroethanol and trifluoroacetic acid are higher than μ_s indicating the strong solute-solvent association due to hydrogen bonding. μ_j 's when compared with μ_1 and μ_2 by double relaxation method indicate that chloral in benzene, *n*-heptane and ethyltrichloroacetate in *n*-hexane show double relaxation phenomena in X-band electric field. This is due to rotations of the whole molecules as well as the flexible parts attached to the parent molecules. The other systems show the mono relaxation behaviour due to their solvation effect with benzene.

Assuming the planar structure of the molecules the theoretical dipole moments μ_{theo} 's for the polar molecules were estimated from the available bond angles and bond moments of C←Cl, C←C, C→F, C←O, C→OH and C→OCH₃ of 5.00, 0.30, 4.67, 8.00, 4.67 and 4.40 times of 10⁻³⁰ Coulomb.metre (C.m) making angles 62° and 57° with the bond axis by C→OH and C→OCH₃ groups only and were shown elsewhere [9.9-9.10]. μ_{theo} 's thus obtained are placed in Table 9.3. A little disagreement among the estimated μ_s and μ_j with μ_{theo} occurs due to inductive, mesomeric and electromeric effects of the substituent polar groups attached to the parent molecules under static or hf electric field. The so called mesomeric moments have significant values. This is caused by the permanent polarisation of different substituent groups acting as pusher or puller of electron towards

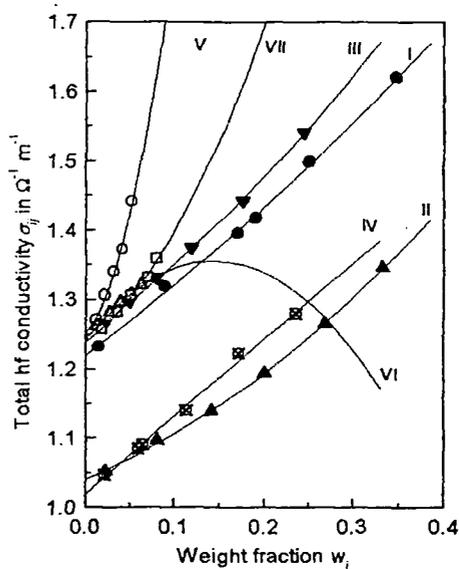


Figure 9.5: Variation of total hf conductivity σ_{ij} with weight fraction w_j

I Chloral in benzene (—●—); II. Chloral in *n*-heptane (—▲—); III. Ethyltrichloroacetate in benzene (—▼—); IV. Ethyltrichloroacetate in *n*-hexane (—⊗—); V. Trifluoroethanol in benzene (—○—); VI. Trifluoroacetic acid in benzene (—△—) and VII. Octanoyl chloride in benzene (—□—).

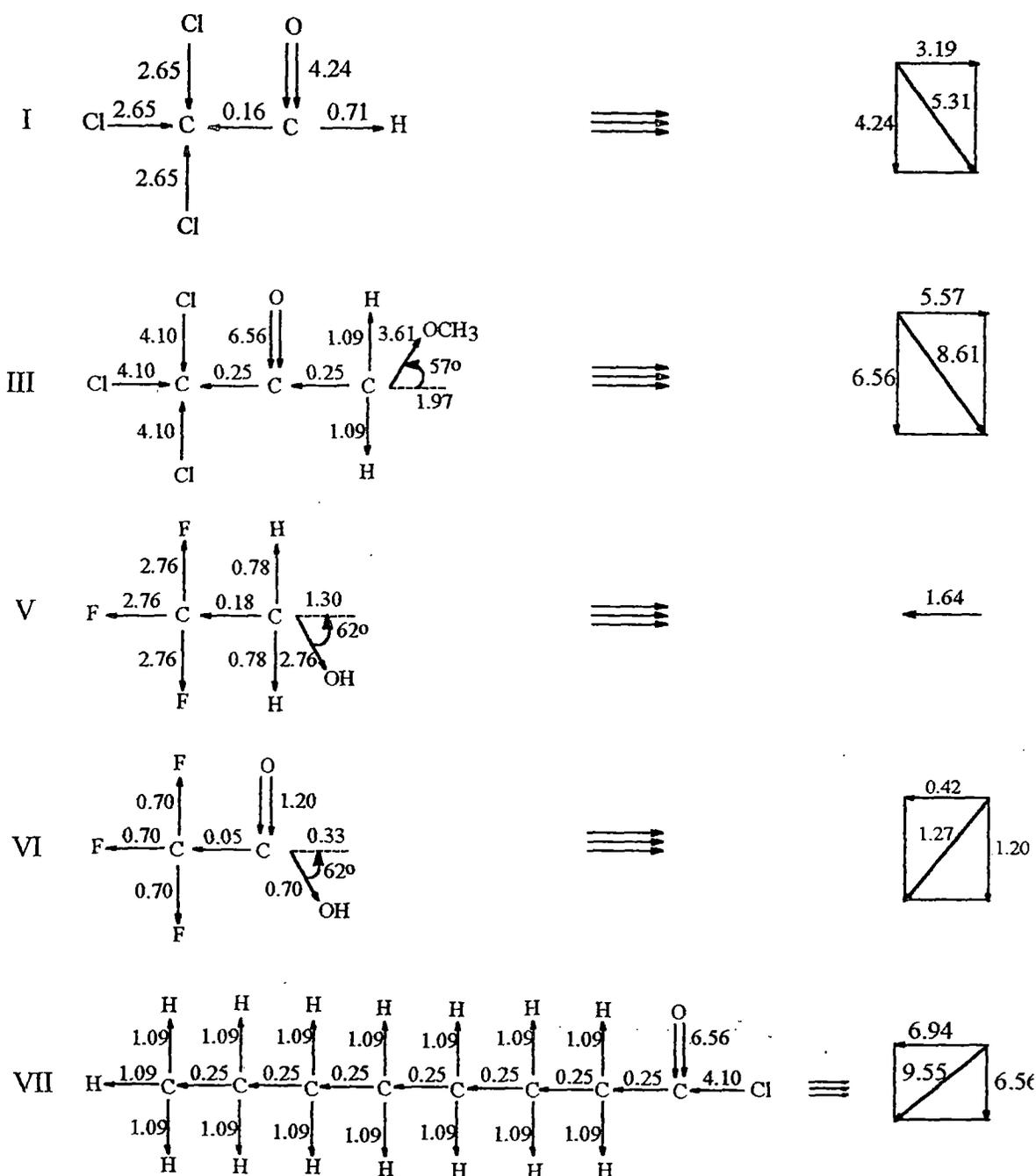


Figure 9.6: Conformational structures of the molecules by taking into account the reduced bond moments in multiple of 10^{-30} Coulomb metre.

I. Chloral, III. Ethyltrichloroacetate, V. Trifluoroethanol, VI. Trifluoroacetic acid, VII. Octanoyl chloride

or away from C-atoms of the compounds. The larger values of μ_{theo} 's from the available bond angles and bond moments in comparison to μ_s indicate that the bond length of the substituent polar groups of the dipolar molecules are reduced by a factor μ_s/μ_{theo} . The reduction in bond moments

evidently occurs in all polar liquids by a factor μ_s/μ_{theo} lying in the range 0.5 to 0.8 except trifluoroacetic acid (0.15) to conform to the exact μ_s . The structural conformations of five compounds with reduced bond lengths, in agreement with μ_j or μ_s are sketched in Fig.9.6.

9.5. Conclusion :

A convenient and useful method is thus suggested to calculate the relaxation time τ_j and hence hf dipole moment μ_j under the most effective dispersive region of 10 GHz electric field along with the static μ_s in SI units of some non-spherical rigid aliphatic polar molecules in non-polar solvents. The existing method by using the slope of hf $\sigma_{ij}''-\sigma_{ij}'$ curves of Murthy *et al* (1998) to obtain τ_j when compared with those from the ratio of the slopes of the individual variations of $\sigma_{ij}''-w_j$ and $\sigma_{ij}'-w_j$ at $w_j \rightarrow 0$ reveals the fact that both the methods yield almost the same τ_j 's both in higher and lower concentration of dipolar molecules. The latter method to get τ_j is a significant improvement over the former one as it eliminates the polar-polar interaction almost completely in a given solvent. The slope β 's of hf $\sigma_{ij}-w_j$ curves could, however, be used to calculate hf μ_j 's in terms of τ_j 's by the latter method. The comparison of μ_j and μ_s with μ_1 and μ_2 of the flexible part and the whole molecules by double relaxation method and μ_{theo} from available bond angles and bond moments of the substituent polar groups seems to be interesting phenomenon to offer deep insight into the dielectric relaxation mechanism. The μ_j 's and μ_s are almost equal in some cases revealing the fact that μ_s are little affected by frequency of the electric field in higher concentration region while lower μ_s 's than μ_j 's in the lower concentration region support monomer and dimer formation in the static and hf electric field respectively. Moreover, the $X_{ij}-w_j$ curves can be used to taste the accuracies of the measurement of all the relative permittivities. The X_{ij} 's are involves with the low and infinitely hf ϵ_{oij} and $\epsilon_{\infty ij}$ permittivities of a given polar-nonpolar liquid mixtures. The computation of τ_j , μ_j and μ_s from σ_{ij} and X_{ij} measurement of a polar unit in a given solvent appears to be more simple, straightforward and unique to locate their correlation coefficient r 's and percentage of errors involved. In this method it is claimed that τ_j , μ_j and μ_s are claimed to be accurate within 10% and 5% respectively. Both μ_j and μ_s are found to agree with μ_1 only to show that a part of the molecule is rotating under GHz electric field. μ_s/μ_{theo} 's are almost constant for all the molecule under study revealing the material property of the systems. The reduction in bond moments of the substituent polar groups by the factor μ_s/μ_{theo} exhibits the presence of mesomeric, inductive and electromeric moments in them under static or low and hf electric fields.

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