

CHAPTER 5

THE PHYSICO-CHEMICAL ASPECTS OF SOME LONG STRAIGHT CHAIN
ALCOHOLS FROM SUSCEPTIBILITY MEASUREMENT UNDER A 24 GHz
ELECTRIC FIELD AT 25⁰C

5. THE PHYSICO-CHEMICAL ASPECTS OF SOME LONG STRAIGHT CHAIN ALCOHOLS FROM SUSCEPTIBILITY MEASUREMENT UNDER A 24 GHz ELECTRIC FIELD AT 25°C

5.1 INTRODUCTION

The relaxation process of dipolar liquid or solid material (DRL or DRS) is very encouraging to study the physico-chemical molecular behaviour and structures through the different experimental techniques [1,2]. The methods consist of the measurements of high frequency (hf) conductivity [3], hf susceptibility [4], thermally stimulated depolarization current density (TSDC) [5], isothermal frequency domain of AC spectroscopy (IFDS) [6] etc. Although the latter two methods are very important as they provide one with the necessary information of dielectric relaxations, but these methods are very lengthy and often needs a tedious computer simulation work in comparison to the former methods. The hf conductivity or susceptibility measurement techniques are very simpler, straightforward and unique one within the framework of Debye model [7] to give the firm answer to the problem with which the present research group is usually dealing with.

Straight chain alcohols behave almost like polymers in dispersion regions. The strong dipole of $-OH$ group rotates about $>C=O$ bond without disturbing $-CH_3$ and $-CH_2$ groups. They thus have the possibility to exhibit intramolecular as well as intermolecular rotations. Glasser et al [8], and Crossley et al [9], however, measured the real ϵ'_{ij} and imaginary ϵ''_{ij} , parts of hf complex relative permittivity ϵ^*_{ij} along with the static ϵ_{oij} and optical ϵ_{oij} relative permittivities of alcohols at 25°C under different gigahertz electric field frequencies. As evident from Table 5.1 the available relative permittivities ϵ''_{ij} 's if plotted against frequency 'f' will show the sharp peak [10] at 24 GHz electric field frequency. At this resonance frequency the alcohol molecules in solvent n-heptane absorbs electric energy much more strongly to give exact and reliable values of relative permittivities. This at once suggests that 24 GHz electric field frequency is the most effective dispersive region of such normal and octyl alcohols and prompted the present workers to study the physico-chemical aspects of long straight chain alcohols in terms of hf susceptibilities χ'_{ij} , χ''_{ij} and χ_{oij} as the datas are available only at 25°C. The datas are, however, collected in Table 5.1 upto four decimal places. The hf dielectric

susceptibilities could, on the other hand, be obtained by the subtraction of either 1 or infinitely hf permittivity $\epsilon_{\alpha ij}$ from the real part ϵ'_{ij} and static ϵ_{oij} relative permittivities. If 1 is subtracted, the susceptibilities due to all operating polarization processes result, while if $\epsilon_{\alpha ij}$ is subtracted [11], the susceptibility due to only orientational polarization results. The imaginary part χ''_{ij} is numerically equal to ϵ''_{ij} as shown in Table 5.1.

Table-5.1. Measured relative permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} , $\epsilon_{\alpha ij}$, real χ'_{ij} , imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} and low frequency susceptibility χ_{oij} of some dipolar alcohols at 25°C for different weight fractions w_j of solutes under 24 GHz electric field in solvent n-heptane.

Systems with Mol.wt(Mj) in Kg.(in n-heptane)	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\alpha ij}$	χ'_{ij} (= $\epsilon'_{ij} - \epsilon_{\alpha ij}$)	χ''_{ij} (= ϵ''_{ij})	χ_{oij} (= $\epsilon_{oij} - \epsilon_{\alpha ij}$)
I. 1-butanol (Mj= 0.074)	0.0291	1.9570	0.0079	1.9710	1.9280	0.0290	0.0079	0.0430
	0.0451	1.9810	0.0147	2.0000	1.9450	0.0360	0.0147	0.0550
	0.0697	2.0110	0.0236	2.0500	1.9580	0.0530	0.0236	0.0920
	0.1163	2.0600	0.0425	2.1750	1.9780	0.0820	0.0425	0.1970
	0.1652	2.1050	0.0644	2.3810	2.0000	0.1050	0.0644	0.3810
	0.2072	2.1440	0.0818	2.6210	2.0200	0.1240	0.0818	0.6010
II. 1-hexanol (Mj= 0.102)	0.0458	1.9680	0.0131	1.9880	1.9440	0.0240	0.0131	0.0440
	0.0703	1.9840	0.0190	2.0150	1.9520	0.0320	0.0190	0.0630
	0.1028	2.0010	0.0296	2.0640	1.9700	0.0310	0.0296	0.0940
	0.1687	2.0370	0.0425	2.1960	1.9890	0.0480	0.0425	0.2070
	0.2335	2.0880	0.0569	2.3600	2.0020	0.0860	0.0569	0.3580
	0.2901	2.1340	0.0748	2.5800	2.0180	0.1160	0.0748	0.5620
III. 1-heptanol (Mj = 0.116)	0.0564	1.9680	0.0147	1.9850	1.9320	0.0360	0.0147	0.0530
	0.0735	1.9750	0.0182	2.0080	1.9450	0.0300	0.0182	0.0630
	0.1175	2.0070	0.0265	2.0660	1.9570	0.0500	0.0265	0.1090
	0.1909	2.0760	0.0482	2.1950	1.9890	0.0870	0.0482	0.2060
	0.2465	2.0970	0.0567	2.3150	2.0020	0.0950	0.0567	0.3130
	0.2970	2.1260	0.0693	2.4640	2.0080	0.1180	0.0693	0.4560
IV. 1-decanol (Mj = 0.158)	0.0572	1.9650	0.0120	1.9760	1.9400	0.0250	0.0120	0.0360
	0.0857	1.9790	0.0223	2.0030	1.9520	0.0270	0.0223	0.0510
	0.1351	2.0030	0.0273	2.0500	1.9640	0.0390	0.0273	0.0860
	0.2140	2.0360	0.0449	2.1470	1.9900	0.0460	0.0449	0.1570
	0.2640	2.0640	0.0513	2.2200	2.0080	0.0560	0.0513	0.2120
	0.3353	2.0970	0.0637	2.3460	2.0300	0.0670	0.0637	0.3160
V. 2-methyl 3-heptanol (Mj = 0.130)	0.0437	1.9600	0.0156	1.9710	1.9300	0.0300	0.0156	0.0410
	0.1299	2.0220	0.0361	2.0590	1.9660	0.0560	0.0361	0.0930
	0.2522	2.0950	0.0565	2.1720	2.0070	0.0880	0.0565	0.1650
	0.4081	2.1690	0.0809	2.3300	2.0540	0.1150	0.0809	0.2760

Systems with Mol.wt(Mj) in Kg.(in n- heptane)	Weight fraction w_j of solute	ϵ_{ij}'	ϵ_{ij}''	ϵ_{0ij}	$\epsilon_{\alpha ij}$	χ_{ij}' (= $\epsilon_{ij}' -$ $\epsilon_{\alpha ij}$)	χ_{ij}'' (= ϵ_{ij}'')	χ_{0ij} (= $\epsilon_{0ij} -$ $\epsilon_{\alpha ij}$)
VI. 3-methyl 3-heptanol (Mj = 0.130)	0.0450	1.9650	0.0137	1.9740	1.9340	0.0310	0.0137	0.0400
	0.1334	2.0280	0.0393	2.0690	1.9660	0.0620	0.0393	0.1030
	0.2538	2.1030	0.0674	2.1800	2.0040	0.0990	0.0674	0.1760
	0.4085	2.1680	0.0928	2.3340	2.0570	0.1110	0.0928	0.2770
VII. 4-methyl 3-heptanol (Mj = 0.130)	0.0466	1.9640	0.0146	1.9760	1.9360	0.0280	0.0146	0.0400
	0.1326	2.0250	0.0375	2.0650	1.9690	0.0560	0.0375	0.0960
	0.2590	2.1040	0.0616	2.1850	2.0110	0.0930	0.0616	0.1740
	0.4124	2.1800	0.0849	2.3520	2.0650	0.1150	0.0849	0.2870
VIII. 5-methyl 3-heptanol (Mj = 0.130)	0.1228	2.0080	0.0296	2.0480	1.9560	0.0520	0.0296	0.0920
	0.2489	2.0750	0.0511	2.1680	2.0040	0.0710	0.0511	0.1640
	0.3898	2.1480	0.0676	2.3150	2.0400	0.1080	0.0676	0.2750
IX. 4-octanol (Mj = 0.130)	0.1201	2.0000	0.0265	2.0400	1.9480	0.0520	0.0265	0.0920
	0.2445	2.0670	0.0449	2.1480	1.9970	0.0700	0.0449	0.1510
	0.3838	2.1400	0.0659	2.2820	2.0310	0.1090	0.0659	0.2510
X. 2-octanol (Mj = 0.130)	0.1236	2.0010	0.0245	2.0490	1.9540	0.0470	0.0245	0.0950
	0.2479	2.0680	0.0513	2.1950	1.9960	0.0720	0.0513	0.1990
	0.3844	2.1410	0.0680	2.4100	2.0360	0.1050	0.0680	0.3740

The commercially available alcohols were dried over anhydrous calcium sulphate and fractionally distilled . The portions were collected with their known boiling points before use. The solvent n-heptane was dried over sodium wire prior to its use to make solutions. The real ϵ'_{ij} and the imaginary ϵ''_{ij} parts of the hf complex relative permittivity ϵ^*_{ij} of the solutions were measured by an apparatus as described elsewhere [9,11] with a Boonton RX meter corrected by a hetrodyne beat method. The refractive index n_{Dij} (where $n^2_{Dij} = \epsilon_{\alpha ij}$) of the solutions was measured by Pulfrich refractometer using the sodium D line [11]. This may introduce some errors in the desired results. The weight fractions w_j 's is given by .

$$w_j = \frac{f_j M_j}{f_i M_i + f_j M_j} \quad (5.1)$$

in terms of mole fractions f_j 's of all the alcohols are defined [12] as the weight of the solute per unit weight of the solution upto four decimal places in Table 5.1.

All the alcohols may be supposed to possess three relaxation times. They may be attributed to the rotation of $-OH$ group, orientational motion of the molecular species while the 3rd one is associated with the hydrogen bonded structures. All these long straight chain hydrogen bonded polymer type dipolar alcohol molecules have wide applications in the fields of biological research, medicine and industry. Moreover, they can be used as good solvents to clean the desired parts of the instruments, in lubrication chemistry, viscosity modifiers, in the preparation of emulsifying agent, waxes etc.

Bergmann et al [13] proposed 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 for τ_1 and τ_2 were also estimated. The single frequency measurement to get the double relaxation times is not a reliable one. Bhattacharyya et al [14] subsequently attempted to get τ_1 , τ_2 and c_1 , c_2 for a polar liquid from the relative permittivity measurements at least at two different frequencies in GHz range. The graphical analysis made by Higashi et al [15] on polar-nonpolar liquid mixtures suffers from a crude approximation.

Saha et al [16] and Sit et al [17], however, advanced an analytical treatment to study the single frequency measurements of the double relaxation times τ_1 and τ_2 from the measured relative permittivities. 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. The aspect of molecular orientational polarization is, however, achieved by χ_{ij} 's because ϵ_{oij} includes the fast polarization and it frequently appears as a subtracted term in Bergmann's equations [15]. Thus to avoid the clumsiness of algebra and to exclude the fast polarization; Bergmann's equations [13] are simplified by the established symbols of χ'_{ij} , χ''_{ij} and χ_{oij} of Table 5.1 in S.I. units, into the following forms:

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad (5.2)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (5.3)$$

assuming two broad Debye-type dispersions for which $c_1 + c_2 = 1$.

The eqs (5.2) and (5.3) are then solved to get:

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2\tau_1\tau_2 \quad (5.4)$$

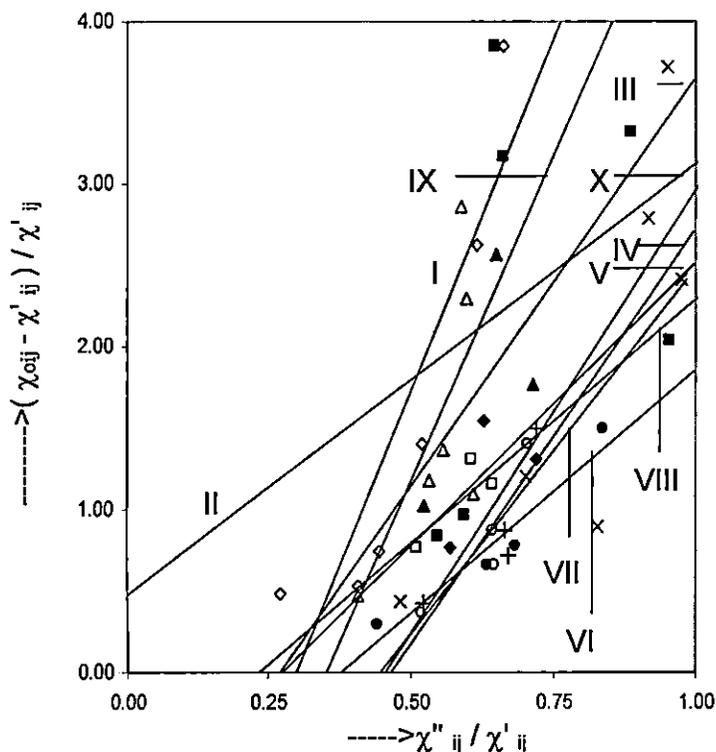


Fig.5.1 .Linear variation of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ with χ''_{ij} / χ'_{ij} for different long straight chain dipolar alcohols in n-heptane at 25°C under 24 GHz electric field frequency I. 1-butanol (—◇—), II. 1-hexanol (—■—), III. 1-heptanol (—△—), IV. 1-decanol (—x—), V. 2-methyl-3-heptanol (—o—), VI. 3-methyl-3-heptanol(—●—), VII. 4-methyl-3-heptanol (—+—), VIII. 5-methyl-3-heptanol (—◆—), IX.4-octanol (—□—), X. 2-octanol (—▲—)

which is a linear equation between the variables $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ and χ''_{ij} / χ'_{ij} having intercept $-\omega^2\tau_1\tau_2$ and slope $\omega(\tau_1 + \tau_2)$ as illustrated in Fig. 5.1 for all the alcohols.

The intercepts and slopes of all the alcohols were then used to get τ_1 & τ_2 for the flexible part and the whole molecular species with known $\omega (=2\pi f)$, where f being the frequency of the applied electric field. as presented in Table 5.2.

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex relative permittivity are related by

$$\epsilon'_{ij} = \epsilon_{oij} + \frac{1}{\omega\tau_j} \epsilon''_{ij} \quad (5.5)$$

As $\epsilon'_{ij} - \epsilon_{oij}$ and ϵ''_{ij} are numerically equal to real and imaginary parts of hf complex dimensionless di-electric orientational susceptibility χ^*_{ij}

respectively. So we get $\chi''_{ij} = (\omega\tau_j) \chi'_{ij}$ (5.6)

which is clearly a straight line [18] between χ''_{ij} and χ'_{ij} , the slope, $\omega\tau_j$ can be used to get τ_j of a polar unit. But for associative liquids like normal and octyl alcohols under investigation the nature of variation of χ''_{ij} with χ'_{ij} is not strictly linear as seen in Fig. 5.2. Non linear variation of both χ'_{ij} and χ''_{ij} with weight fractions w_j 's of solute are presented graphically in Figs. 5.3 and 5.4 respectively. In such cases

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (5.7)$$

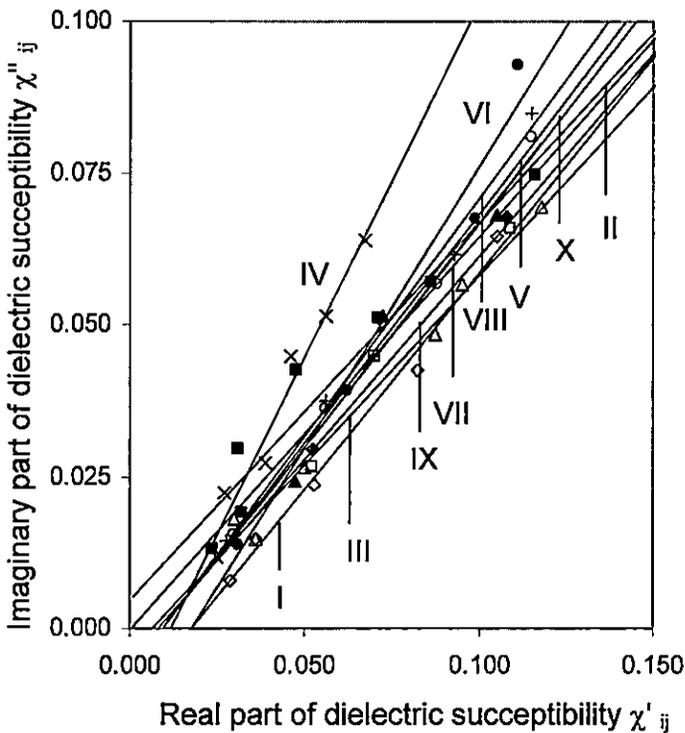


Fig 5.2. Linear variation of imaginary part χ''_{ij} of hf dielectric susceptibility against real part χ'_{ij} for different long straight chain dipolar alcohols in n - heptane at 25°C under 24GHz electric field frequency. I-butanol (--◇--), II. 1-hexanol (--■ - -), III. 1-heptanol (--△--), IV. 1-decanol (-- x --), V. 2 - methyl - 3 - heptanol (-- o --), VI. 3-methyl-3-heptanol (-- ● --), VII. 4-methyl-3-heptanol (-- + --), VIII. 5 - methyl - 3 - heptanol (-- ◆ --), IX. 4-octanol (-- □ --), X. 2-octanol (--▲ --)

is a better representation [19] of the slope of eq. (5.6) to get τ_j as it eliminates polar-polar interactions [20,21] in a given solution. τ_j 's from both eqs. (5.6) and (5.7) are placed in Table 5.2 to compare them with those obtained by the freshly calculated Gopala Krishna's [22] method.

The weighted contributions c_1 and c_2 towards dielectric relaxation in terms of estimated τ_1 and τ_2 are, however, worked out from Fröhlich's [23] theoretical equations are entered in Table 5.3 in order to compare them with the experimental ones obtained in terms of the intercepts of the variations of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j 's of Figs 5.5 and 5.6.

Both χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} at $\omega_j=0$ together with curve of $(1/\phi) \log \cos\phi$ against ϕ^0 as seen in Fig. 5.7 are used to get symmetric and asymmetric distribution parameters γ and δ and hence symmetric and characteristic relaxation times τ_s and τ_{cs} . Both τ_s and τ_{cs} are given in Table 5.2 and γ, δ are presented in Table 5.3.

The dipole moments μ_1 and μ_2 by hf susceptibility measurement technique are, however, estimated from linear coefficient β 's of χ'_{ij} vs ω_j curves of Fig. 5.3 along with the dimensionless parameters b_1 & b_2 involved with estimated τ_1 and τ_2 of Table 5.2. The dipole moments μ_1 and μ_2 due to rotation of the flexible polar groups and end over end rotations of the whole molecule respectively are placed in Table 5.4 along with μ_{theo} 's and reported μ 's (Gopala Krishna) for comparison.

5.2 WEIGHTED CONTRIBUTIONS c_1 AND c_2 FOR ESTIMATED τ_1 AND τ_2 :

Taking $\omega\tau_1 = \alpha_1$ and $\omega\tau_2 = \alpha_2$ and solving eqs. (5.2) and (5.3) obtains

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (5.8)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (5.9)$$

provided $\alpha_2 > \alpha_1$. c_1 and c_2 are estimated from known τ_1 and τ_2 by the double relaxation method. c_1 and c_2 can also be obtained with the known values of χ'_{ij} / χ_{oij} & χ''_{ij} / χ_{oij} from Fröhlich's [23] following theoretical equations with known τ_1 and τ_2 from eqs. (5.2) & (5.3).

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left[\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right] \quad (5.10)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} [\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)] \quad (5.11)$$

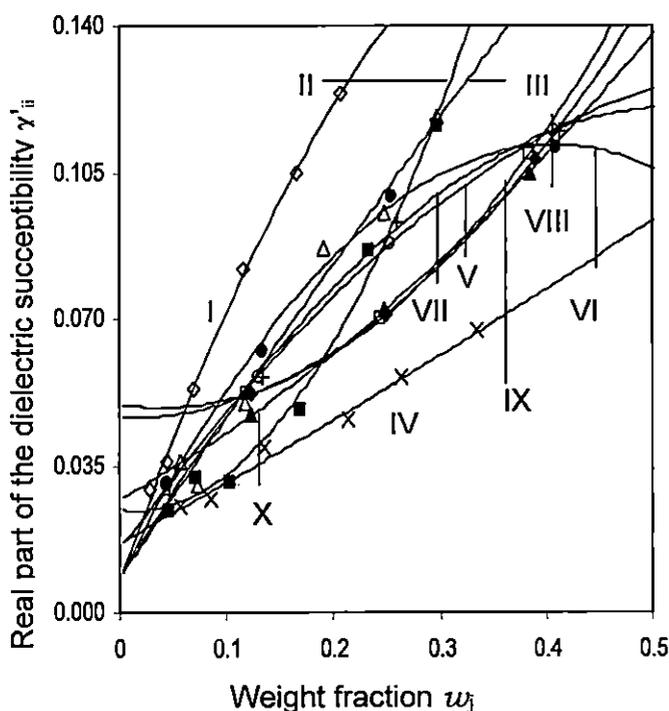


Fig 5. 3. Variation of real part χ'_{ij} of hf dielectric susceptibility with weight fraction w_j of some dipolar long straight chain alcohols in n-heptane at 25°C under 24GHz electric field frequency I.1-butanol (— \diamond —), II. 1-hexanol (— \blacksquare —), III. 1-heptanol (— \triangle —), IV. 1-decanol (— \times —), V. 2-methyl-3-heptanol (— \circ —), VI. 3-methyl-3-heptanol (— \bullet —), VII. 4-methyl-3-heptanol (— $+$ —), VIII. 5-methyl-3-heptanol (— \blacklozenge —), IX. 4-octanol (— \square —), X. 2-octanol (— \blacktriangle —)

c_1 and c_2 so estimated are placed in Table 5.3 for comparison with those worked out from intercept of the fitted polynomial plots of χ'_{ij} / χ_{oij} & χ''_{ij} / χ_{oij} against w_j curves of Figs. 5.5 and 5.6. Fröhlich's parameter A for each system are also placed in the same Table.

Table 5.2:-- The relaxation times τ_1 and τ_2 , from the slope and intercept of straightline equation.(4), correlation coefficient r 's and % of error in regression technique, measured τ_j from the slope of χ''_{ij} vs χ'_{ij} of eq (7) and the ratio of the individual slopes of χ''_{ij} vs ω_j and χ'_{ij} vs ω_j at $\omega_j \rightarrow 0$ of eq (7), reported τ , symmetric and characteristic relaxation times τ_s and τ_{cs} for different straight chain aliphatic alcohols in n-heptane under effective dispersive region of 24 GHz electric field at 25⁰C

System with St. No.	Slope and intercept of eq.(5.4)		Estimated τ_1 and τ_2 in psec		Corr. Coeff.	% of error	τ_j from (Murti et al) and (ratio of individual slope)		Reported τ_j in psec	τ_s in psec	τ_{cs} in pec
	Slope	Intercept	τ_1	τ_2							
I. 1-butanol (Mj= 0.074)	8.66	2.60	2.04	54.56	0.90	5.17	4.95	3.42	2.47	0.98	15.41
II. 1-hexanol (Mj= 0.102)	2.64	-0.47	-1.10	18.37	0.34	24.28	4.05	3.78	2.25	2.09	6.77
III. 1-heptanol (Mj = 0.116)	7.99	2.83	2.46	50.49	0.68	14.98	4.12	4.23	2.07	1.97	10.46
IV. 1-decanol (Mj = 0.158)	5.43	2.48	3.29	32.22	0.82	9.23	7.63	10.20	2.39	1.91	0.50
V. 2-methyl 3-heptanol (Mj = 0.130)	5.05	2.37	3.42	29.61	0.90	6.34	4.92	4.34	1.86	2.11	4.58
VI. 3-methyl 3-heptanol (Mj = 0.130)	3.00	1.14	2.91	16.68	0.96	2.33	6.06	4.30	2.26	1.65	5.29
VII. 4-methyl 3-heptanol (Mj = 0.130)	4.39	1.97	3.31	25.38	0.89	7.30	5.12	4.38	1.95	2.19	8.07
VIII. 5-methyl 3-heptanol (Mj = 0.130)	2.98	0.69	1.66	17.81	0.57	26.36	4.23	7.59	1.63	1.59	8.37
IX. 4-octanol (Mj = 0.130)	3.48	0.96	1.97	20.75	0.86	10.34	4.36	4.33	1.68	1.62	15.40
X. 2-octanol (Mj = 0.130)	5.02	1.37	1.89	30.94	0.63	23.30	4.82	15.91	1.93	2.33	37.08

Table-5.3: Fröhlich's parameter A, theoretical and experimental values of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} of Fröhlich eqs. (5.10) and (5.11) and from fitted curves of Figs. 5.5 and 5.6 at $\omega_j \rightarrow 0$, 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 some straight chain aliphatic alcohols in solvent n-heptane under effective dispersive region of 24 GHz electric field at 25°C.

Systems with Sl.No.	A = In (τ_2/τ_1)	Theoretical values of $\chi'_{ij} /$ χ_{oij} & χ''_{ij} / χ_{oij} from Eqs (5.10) & (5.11)		Theoretical values of c_1 and c_2		Experimental values of $\chi'_{ij} /$ χ_{oij} & χ''_{ij} / χ_{oij} at $\omega_j \rightarrow 0$ of Figs 5.5 & 5.6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
		χ_{oij}	χ''_{ij} / χ_{oij}	c_1	c_2	χ_{oij}	χ''_{ij} / χ_{oij}	c_1	c_2	γ	δ
I. 1-butanol	3.286	0.366	0.350	0.370	2.069	0.799	0.195	0.884	-0.474	0.357	0.21
II. 1-hexanol	—	—	—	—	—	0.740	0.348	0.598	1.412	0.128	0.55
III. 1-heptanol	3.023	0.347	0.359	0.358	1.878	0.721	0.298	0.816	0.247	0.230	0.39
IV. 1-decanol	2.281	0.341	0.396	0.364	1.283	0.870	0.404	1.100	-0.193	-0.079	2.49
V. 2-methyl 3-heptanol	2.157	0.345	0.404	0.369	1.198	0.776	0.386	0.995	-0.107	0.041	0.76
VI. 3-methyl 3-heptanol	1.746	0.474	0.446	0.435	0.837	0.814	0.319	1.000	-0.157	0.099	0.55
VII. 4-methyl 3-heptanol	2.036	0.374	0.417	0.386	1.084	0.729	0.358	0.920	-0.051	0.121	0.51
VIII. 5-methyl 3-heptanol	2.371	0.564	0.409	0.486	0.906	0.782	0.287	0.794	0.302	0.189	0.39
IX. 4-octanol	2.353	0.508	0.413	0.455	1.003	0.731	0.243	0.789	0.086	0.328	0.27
X. 2-octanol	2.797	0.451	0.387	0.426	1.351	0.683	0.193	0.741	-0.023	0.477	0.20

5.3 FORMULATIONS FOR SYMMETRIC AND CHARACTERISTIC RELAXATION TIMES AND ALSO SYMMETRIC AND ASYMMETRIC DISTRIBUTION PARAMETER:

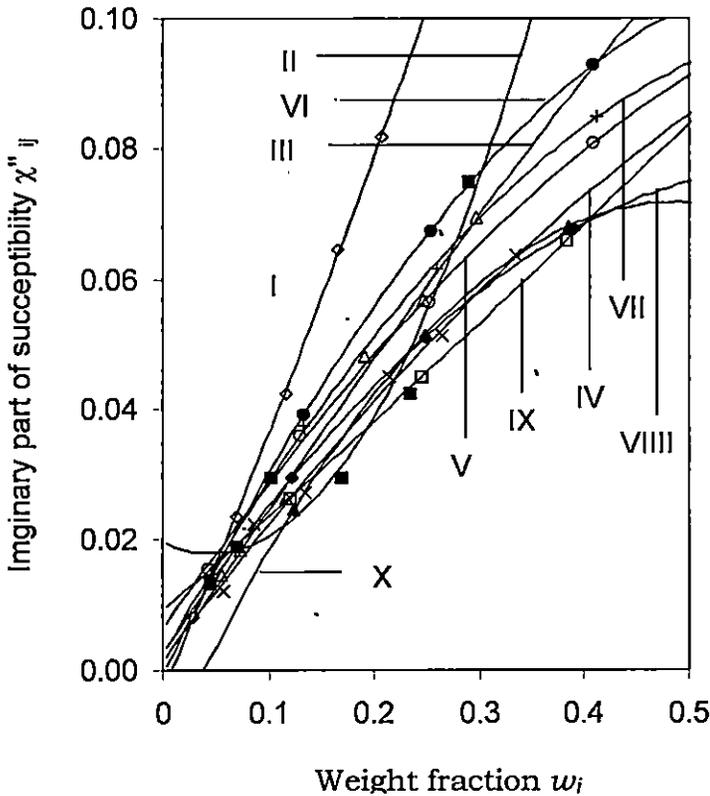


Fig 5.4. Variation of imaginary part χ''_{ij} of hf dielectric susceptibility with weight fraction w_i of some dipolar long straight chain alcohols in n-heptane at 25⁰ C under 24 GHz electric field frequency I. 1-butanol (-- \diamond --), II. 1-hexanol (-- \blacksquare --), III. 1-heptanol (-- \triangle --), IV. 1-decanol (-- x --), V. 2-methyl-3 - heptanol (-- o --), VI. 3-methyl-3 - heptanol (-- \bullet --), VII. 4-methyl-3-heptanol (-- + --), VIII. 5-methy - 3 - heptanol (-- \blacklozenge --), IX. 4-octanol (-- \square --), X. 2-octanol (-- \blacktriangle --)

The molecules under investigation appear to behave like nonrigid ones under 24 GHz electric field frequency having either symmetric or asymmetric relaxation behaviour characterized by either symmetric τ_s and characteristic τ_{cs} relaxation times involved with the following equations:

$$\frac{\chi^*_{ij}}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (5.12)$$

$$\frac{\chi^*_{ij}}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (5.13)$$

separating the real and imaginary parts of the above equations and rearranging them in terms of intercepts viz $(d\chi'_{ij}/dw_j)_{w_j=0}$ and $(d\chi''_{ij}/dw_j)_{w_j=0}$ of the graphically fitted plots of Figs. 5.5 and 5.6 one gets γ and τ_s as :

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}/\chi_{oij}}{\chi''_{ij}/\chi_{oij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad (5.14)$$

and

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\{(\chi'_{ij}/\chi_{oij}) / (\chi''_{ij}/\chi_{oij})\} \cos(\gamma\pi/2) - \sin(\gamma\pi/2)} \right]^{1/1-\gamma} \quad (5.15)$$

similarly, δ and τ_{cs} can be evaluated from equation (13):

$$\tan(\phi\delta) = \frac{(\chi''_{ij}/\chi_{oij})_{w_j=0}}{(\chi'_{ij}/\chi_{oij})_{w_j=0}} \quad (5.16)$$

$$\text{and } \tan \phi = \omega\tau_{cs} \quad (5.17)$$

since ϕ can not be estimated directly, a theoretical curve between $(1/\phi) \log \cos \phi$ against ϕ in degrees has been drawn in Fig. 5.7. The value of $(1/\phi) \log \cos \phi$ can be estimated from the following relation

$$(1/\phi) \log \cos \phi = \log \left[\frac{\chi'_{ij}/\chi_{oij}}{\cos \phi \delta} \right] / \phi \delta \quad (5.18)$$

The known value of $(1/\phi) \log \cos \phi$ is used to get ϕ from the curve. With the known ϕ , eqs. (5.16) and (5.17) were used to obtain δ and τ_{cs} . Estimated τ_s and τ_{cs} are placed in Table 5.2 to compare with τ_j 's obtained by ratio of slopes of individual variations of χ'_{ij} & χ''_{ij} with w_j , τ_j 's by the method of Murthy et al [18], reported τ_j (Gopala Krishna) and τ_1 & τ_2 by the double relaxation method. Also γ and δ are shown in Table 5.3.

5.4. THEORETICAL FORMULATIONS TO OBTAIN hf DIPOLE MOMENT μ_j

The imaginary part χ''_{ij} of hf complex χ^*_{ij} is [4,20,24]

$$\chi''_{ij} = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\epsilon_{ij} + 2)^2 \omega_j \quad (5.19)$$

which on differentiation with respect to ω_j and at $\omega_j = 0$ yields that

$$\left(\frac{d\chi''_{ij}}{d\omega_j} \right)_{\omega_j=0} = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\epsilon_{ij} + 2)^2 \omega_j \quad (5.20)$$

From eqs. (5.7) and (5.19) one obtains

$$\omega \tau_j (d\chi'_{ij} / d\omega_j)_{\omega_j \rightarrow 0} = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\epsilon_{ij} + 2)^2 \quad (5.21)$$

or

$$\omega \tau_j \beta = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\epsilon_{ij} + 2)^2$$

or

$$\mu_j = \left[\frac{27 \epsilon_0 M_j k_B T \beta}{N\rho_{ij} (\epsilon_{ij} + 2)^2} \right]^{1/2} \quad (5.22)$$

where

ϵ_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹

M_j = Molecular weight of solute in kilogramme

k_B = Boltzmann Constant = 1.38×10^{-23} J mole⁻¹ K⁻¹

T = Temperature in absolute scale

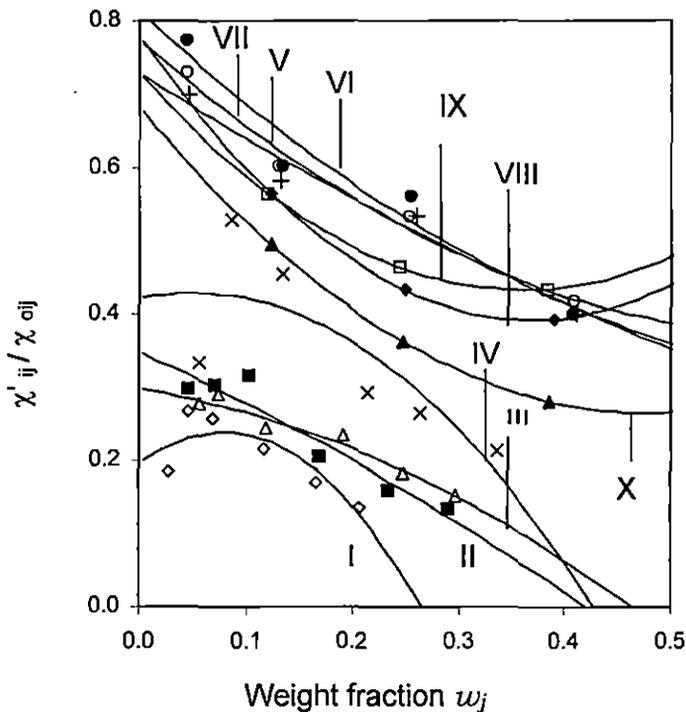
$\beta = (d\chi'_{ij} / dw_j) w_{j \rightarrow 0} =$ Linear coefficient of $\chi'_{ij} - w_j$ curve of Fig. 5.3 at $w_j \rightarrow 0$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent n-heptane = 680.15 Kg.m⁻³

ϵ_1 = Dielectric relative permittivity of the solvent = 1.917

$b = 1 / (1 + \omega^2 \tau_j^2)$ = a dimensionless parameter involved with estimated τ_j .



When $j = 1$ & 2 the dipole moments μ_1 & μ_2 associated with rotation of flexible polar groups and rotation of the whole molecule are evaluated in terms of b_1 & b_2 involved with τ_1 & τ_2 and are placed in Table 5.4 to compare them with μ_{theo} 's and reported μ 's (Gopala Krishna).

Fig 5.5. Plot of χ'_{ij} / χ_{oij} against weight fraction w_j of some dipolar long straight chain alcohols in n - heptane at 25°C under 24 GHz electric field frequency I. 1-butanol(-- \diamond --), II. 1-hexanol (-- \blacksquare --), III.1-heptanol (-- \triangle --), IV. 1-decanol (-- x --), V. 2-methyl-3 - heptanol (-- o --), VI. 3-methyl-3 - heptanol (-- \bullet --), VII. 4-methyl - 3 - heptanol (-- + --), VIII. 5-methy - 3 - heptanol (-- \blacklozenge --), IX. 4-octanol (-- \square --), X. 2-octanol (-- \blacktriangle --)

Table-5.4: linear coefficient β of χ'_{ij} Vs ω_j curves of Fig 5.3, dimensionless parameters b_1 , b_2 from τ_1 & τ_2 of eq.(5.4), correlation coefficient and % of error of χ'_{ij} - ω_j estimated dipole moment μ_1 , μ_2 from eq. (5.22), computed dipole moment μ_j from τ_j of eq. (5.7), reported dipole moment (Gopala Krishna's method), all are expressed in Coulomb metre for different straight chain alcohols in solvent n-heptane at 25°C under 24 GHz electric field.

Systems with Sl.No. and Mol.Wt.M _j in Kg (in n- heptane)	Linear coeffi.of χ'_{ij} vs ω_j curves of Fig. 5.3 β	Dimensionl ess parameters b_1 b_2		Correl. Coeffi. of χ'_{ij} - ω_j curves	% of errors	Estimated Dipole moments $\mu \times 10^{30}$ in coulomb metre			Report ed $\mu \times$ 10^{30} in C.m	μ^*_{theo} X 10^{30} in C.m
		μ_1	μ_2			μ_j				
I. 1-butanol (M _j = 0.074)	0.719	0.911	0.014	0.997	0.00003	3.02	24.25	3.26	3.58	3.74
II. 1-hexanol (M _j = 0.102)	0.371	0.973	0.112	0.969	0.00037	2.47	7.25	2.81	3.35	3.49
III. 1-heptanol (M _j = 0.116)	0.392	0.879	0.017	0.987	0.00015	2.84	20.49	3.16	3.59	3.73
IV. 1-decanol (M _j = 0.158)	0.142	0.798	0.040	0.994	0.00007	2.10	9.43	3.47	3.55	3.68
V. 2-methyl 3-heptanol (M _j = 0.130)	0.359	0.785	0.047	0.998	0.00003	3.05	12.53	3.24	1.33	1.86
VI. 3-methyl 3-heptanol (M _j = 0.130)	0.508	0.835	0.133	0.985	0.00023	3.52	8.81	3.85	1.18	2.11
VII. 4-methyl 3-heptanol (M _j = 0.130)	0.429	0.796	0.062	0.996	0.00006	3.31	11.83	3.55	3.42	1.95
VIII. 5-methyl 3-heptanol (M _j = 0.130)	0.211	0.939	0.119	0.967	0.00056	2.14	6.01	3.17	3.54	1.39
IX. 4-octanol (M _j = 0.130)	0.217	0.917	0.090	0.985	0.00025	2.20	7.00	2.52	3.48	1.11
X. 2-octanol (M _j = 0.130)	0.143	0.923	0.043	0.977	0.00038	1.78	8.25	4.49	3.24	1.45

* Ghosh et al[10]

5.5. RESULTS AND DISCUSSION

The least squares fitted straight line equations : $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij} = \omega (\tau_1 + \tau_2) \chi''_{ij} / \chi'_{ij} - \omega^2 \tau_1 \tau_2$ have been shown graphically in Fig. 5.1 for some normal and octyl alcohols with the symbols showing the experimental points in solvent n-heptane at 25°C under 24 GHz electric field frequency. The real χ'_{ij} and imaginary parts χ''_{ij} of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} and static or low frequency real dielectric susceptibility χ_{oij} have been derived from the measured relative permittivities [8,9] ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$. They are carefully collected in Table 5.1. The slopes and intercepts of eq. (5.4) used to get τ_1 & τ_2 are placed in the 2nd and 3rd columns of Table

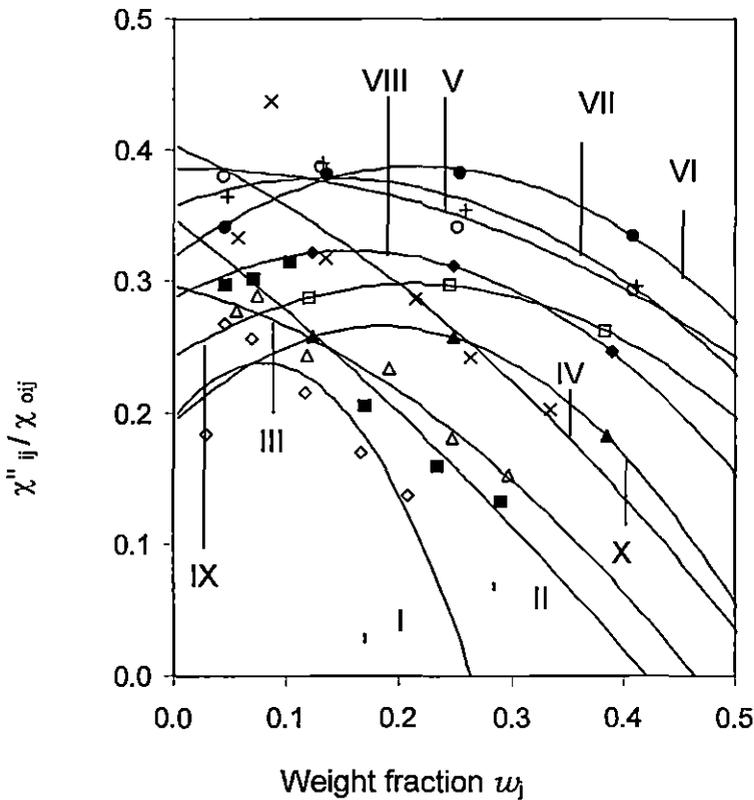


Fig 5. 6. Plot of χ''_{ij} / χ'_{ij} against weight fraction w_j of some dipolar long straight chain alcohols in n-heptane at 25°C under 24 GHz electric field frequency I. 1-butanol (--◇--), II. 1-hexanol (--■--), III. 1-heptanol (--△--), IV. 1-decanol (--x--), V. 2-methyl-3-heptanol (--o--), VI. 3-methyl-3-heptanol (--●--), VII. 4-methyl-3-heptanol (--+--), VIII. 5-methyl-3-heptanol (--◆--), IX. 4-octanol (--□--), X. 2-octanol (--▲--)

5.2 along with the estimated τ_1 & τ_2 in the 4th and 5th columns. Correlation coefficients (r) and % of errors of curves of Fig. 5.1 have been calculated and are placed in the 6th and 7th columns of Table 5.2 only to show how far the variables $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ and χ''_{ij} / χ'_{ij} are correlated with each other. It is seen that 'r' is very low and corresponding % of errors is very high for 5-methyl-3-heptanol and 2-octanol, which may be probably due to errors introduced in their permittivity ϵ_{ij} measurements. This fact

is further confirmed by remarkable deviations of experimental points from the fitted linear curves as seen in Fig. 5.1.

In absence of reliable τ_j values, the slopes of the linear curves [18] of Fig. 5.2 of the variables χ''_{ij} and χ'_{ij} are utilized to get τ_j . But for associative liquids like normal and octyl alcohols the variation of χ''_{ij} against χ'_{ij} is not strictly linear as seen in Fig. 5.2. Under such context, the ratio of slopes of individual variations of both χ'_{ij} and χ''_{ij} with ω_j 's is a better representation [20,21] of the method of Murthy et al [18] as it eliminates polar-polar interactions in a given solution [4]. τ_j 's estimated so far by this method are entered in the 9th column of Table 5.2 along with τ_j 's due to method of Murthy et al and reported ones as seen in the 8th and 10th columns. Non linear variation of both χ'_{ij} and χ''_{ij} against ω_j 's as seen in Figs 5.3 and 5.4 arises due to solute-solvent and solute-solute molecular associations which is supposed to be a physico-chemical property [21] of the solutes under consideration. Symmetric and characteristic relaxation times τ_s and τ_{cs} estimated from eqs (5.15) and (5.17) respectively in terms of γ and δ are seen in the 11th and 12th column of Table 5.2. It is observed that in comparison to τ_{cs} , τ_s is the same order of magnitude of τ_j 's from eq. (5.7) and reported (Gopala Krishna)

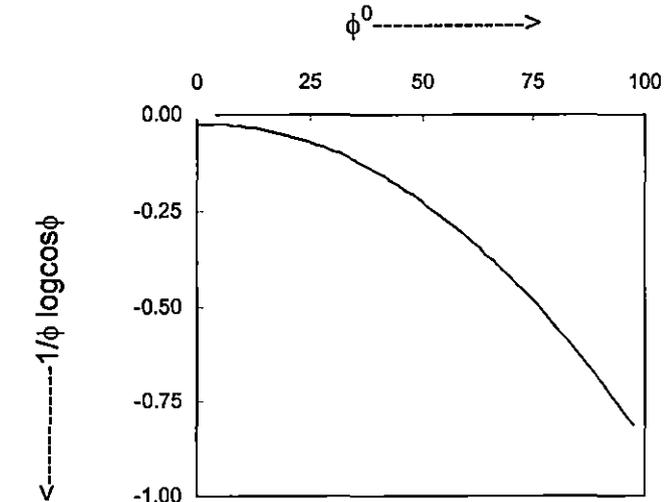


Figure 5.7. Variation of $(1/\phi) \log(\cos\phi)$ against

ones. This fact at once establishes the very basic soundness of our method [20,21] employed to get hf τ_j and also the symmetric relaxation behaviour [19] obeyed by the molecules. Larger τ_2 values arises for bigger size of rotating units $\tau_j T / \eta^j$ due to solute-solvent and solute solute molecular associations, supposed to be physico-chemical property of the solutes which is further supported by non linear variations of both χ'_{ij} and χ''_{ij} with ω_j 's as seen in Figs. 5.3 and 5.4.

The theoretical weighted contributions c_1 and c_2 towards dielectric relaxations from eqs.(5.8) and

(5.9) are, however, worked out with χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} values of eqs (5.10) & (5.11) and also with estimated τ_1 & τ_2 of Table 5.2. They are placed in the 5th and 6th columns of Table 5.3 in order to compare them with the experimental c_1 & c_2 estimated in terms of $(\chi'_{ij} / \chi_{oij}) w_{j \rightarrow 0}$ and $(\chi''_{ij} / \chi_{oij}) w_{j \rightarrow 0}$ of the graphically fitted plots of Figs. 5.5 and 5.6 and are placed in the 9th and 10th columns. Theoretical c 's for 1-hexanol could not be estimated as τ_1 is found to be negative probably due to errors [19] in the measurement of ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$. Both theoretical and experimental c_1 & c_2 shows that $c_1 + c_2 \approx 1$, which confirms the validity of eq. (5.4) to get τ_1 & τ_2 . It is seen that for some systems experimental c_2 is negative. This can, however, be explained on the basis of the fact that internal hydrogen bonding among -OH groups in dipolar alcohol molecules gives rise to inertia [25] of the flexible polar groups with respect to the whole molecule. Solute-solvent and solute-solute molecular interaction being a physico-chemical aspect is also supported by slight deviations of experimental points from the curves of Figs 5.5 and 5.6. The dipole moments μ_1 & μ_2 of the flexible polar groups and the whole molecules were estimated in terms of dimensionless parameters b_1 & b_2 involved with estimated τ_1 & τ_2 and linear coefficient β of $\chi'_{ij} - w_j$ curves of Fig. 5.3. They are entered in the 5th and 6th columns of Table 5.4 to compare them with μ_j 's estimated with τ_j 's of eq. (5.7), reported μ 's due to Gopala Krishna [22] and theoretical μ 's obtained with available bond angles and bond moments of the polar groups assuming the molecules to be planar ones, sketched here. Correlation coefficient's r 's and % of errors of $\chi'_{ij} - w_j$ curves of Fig. 5.3 were made by careful regression analysis of the measured data, are seen in the 5th and 6th columns of Table 5.4 only to suggest how far the variables $\chi'_{ij} - w_j$ are correlated with each other. Almost all the $\chi'_{ij} - w_j$ curves show a tendency to be closer within the range $0.00 \leq w_j \leq 0.10$, which is due to same polarity [4,25] of the molecules in addition to solute-solvent and solute-solute molecular interaction which is assumed to be physico-chemical behaviour [20,21] of the solutes in n-heptane. The close agreement of the estimated μ_1 & μ_2 with reported (Gopala Krishna) and theoretical μ 's establishes the very basic soundness of the present method to get hf μ_j 's in addition to the fact that a part of the molecule is rotating under GHz electric field [19]. It is seen that estimated μ_1 & μ_j 's are lower than that of μ_{theo} 's for normal alcohols while the reverse is true in octyl alcohols. It is probably due to the fact that strong hydrogen bonding among -OH groups in normal alcohols (1-butanol, 1-hexanol, 1-heptanol and 1-decanol) offers higher resistance due to

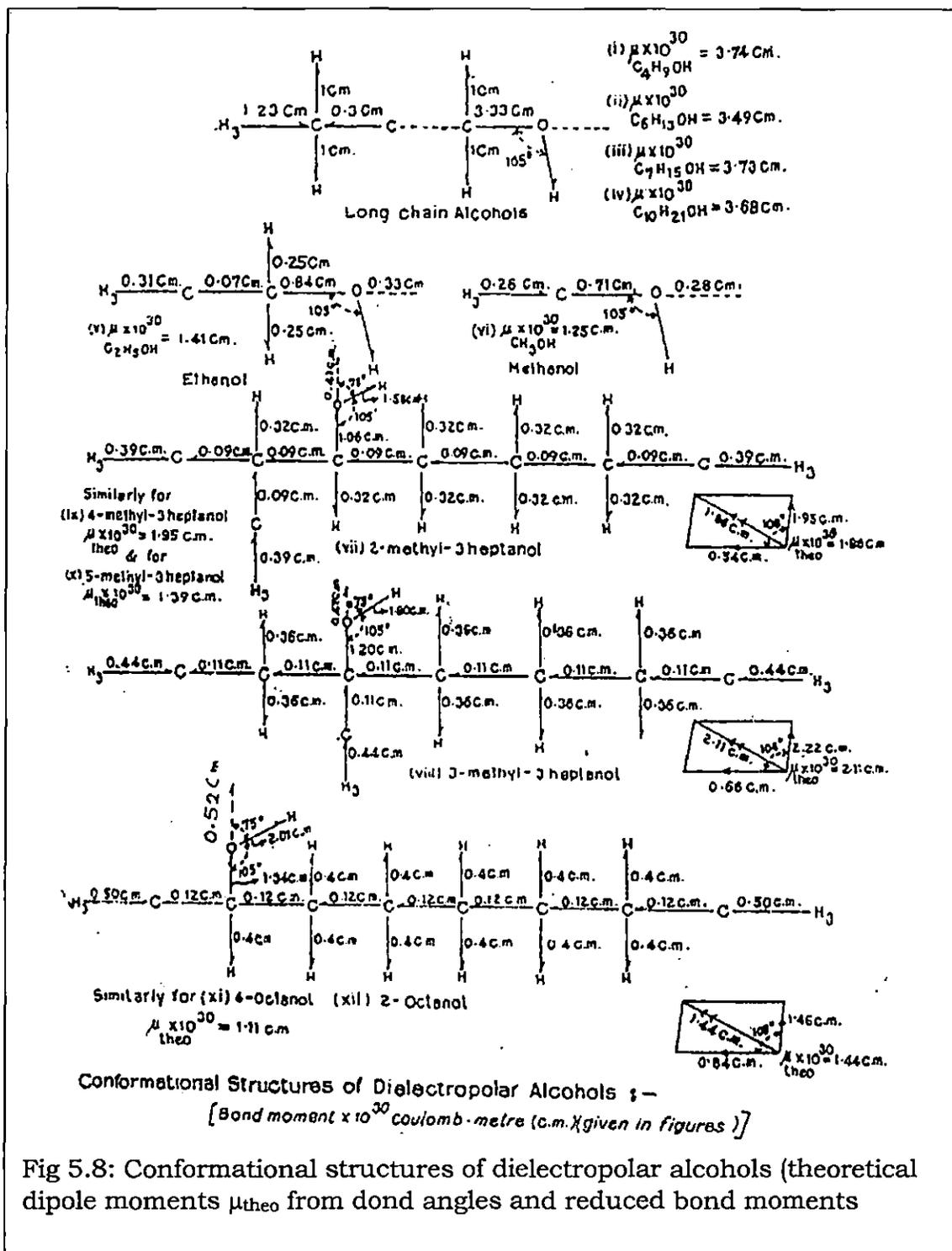


Fig 5.8: Conformational structures of dielectropolar alcohols (theoretical dipole moments μ_{theo} from bond angles and reduced bond moments

–OH groups to rotate under hf electric field to give lower μ_1 & μ_j values. In octyl alcohols hydrogen, on the otherhand, bonding between –OH groups is not so strong giving μ_1 's & μ_j 's higher than that of μ_{theo} 's as they are screened by a large number –CH₃ and –CH₂ groups. The conformations are presented in Fig. 5.8 in excellent agreement of the measured values in order to account of the mesomeric and electromeric effects of the substituted polar groups in alcohols by multiplying available bond moments by a factor $\mu_s / \mu_{\text{theo}}$ where μ_s is the low frequency or static dipole moment estimated elsewhere[10].

5.6. CONCLUSION

Theoretical formulations developed so far in SI unit within the frame work of Debye-Smyth model appears to be simpler straightforward and topical one to get the many interesting equations which are worked out in terms of χ_{ij} 's. They are useful to explain various physico-chemical aspects of several dipolar alcohol molecules in solvent n-heptane at 25^oC under 24 GHz (Q-band microwave) electric field frequency. The derived straight line eq. (5.4) have significant contribution in the field of dielectric relaxation as it gives microscopic τ_1 and macroscopic τ_2 due to both rotations of the flexible polar groups and the whole molecule while eq. (5.7) gives microscopic τ only [20,21]. Both theoretical and graphical experimental c_1 & c_2 confirm the validity of eq. (5.4). As seen in Table 5.3 that $c_1 + c_2 \cong 1$ is due to the fact that under 24 GHz electric field the rotations of the straight chained molecules are influenced by the moment of inertia of the flexible groups attached to the parent ones. $\epsilon_{\alpha ij} \cong 1$ to $1.5 n_{Dij}^2$. But $\epsilon_{\alpha ij} \cong n_{Dij}^2$ may introduce some errors in getting τ_1 & τ_2 and c_1 & c_2 also. Correlation coefficients r 's and % of errors between several variables involved in curves of Figs 5.1 and 5.3 are worked out only to establish the statistical validity [20,21] of eq. (5.4) and χ'_{ij} vs ω_j equations.. The close agreement of estimated relaxation parameters viz τ 's and μ 's with the reported ones confirms the very basic soundness of the theoretical formulations so far developed. The physico chemical properties of the systems are, however, inferred in terms of solute-solvent (monomer) and solute-solute (dimer) associations as supported by slight deviations of measured parameters from their reported and standard values and also observed by deviation of experimental points from the fitted polynomial plots of several Figs..

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