

CHAPTER 6

STUDIES ON PHYSICO-CHEMICAL PROPERTIES WITH THE
RELAXATION PHENOMENA OF SOME NORMAL ALIPHATIC ALCOHOLS
IN NONPOLAR SOLVENT UNDER GIGA HERTZ ELECTRIC FIELD AT A
SINGLE TEMPERATURE

6. STUDIES ON PHYSICO CHEMICAL PROPERTIES WITH THE RELAXATION PHENOMENA OF SOME NORMAL ALIPHATIC ALCOHOLS IN NONPOLAR SOLVENT UNDER GIGA HERTZ ELECTRIC FIELD AT A SINGLE TEMPERATURE

6.1. INTRODUCTION

Relaxation mechanism of polar molecules in non polar solvents under high frequency electric field is of special interest as it provides one with useful tool to study structural configuration and molecular associations in the formation of monomer [1] and dimer [2,3] through measured relaxation parameters like relaxation time τ and dipole moment μ obtained by any conventional method [4,5]. The technique also gives valuable information regarding stability or unstability [6] of the systems undergoing relaxation phenomena. Also τ_j obtained from the ratio of slopes of individual variations of $\chi''_{ij} - \omega_j$ and $\chi'_{ij} - \omega_j$ are conveniently used to shed more light on structural and associational aspects [7] in addition to physico-chemical properties of the polar molecules.

Glasser et al [8] measured the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of complex hf dielectric relative permittivity ϵ^*_{ij} together with static and hf relative permittivity ϵ_{0ij} and $\epsilon_{\infty ij}$ of some normal alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol at various mole fractions under different electric field frequencies in n-heptane at 25°C. The purpose of their study was to observe triple relaxation phenomena in them under different concentrations characterized by relaxation times τ_1, τ_2, τ_3 which arise respectively due to hydrogen bonded structure, orientational motion of the molecules and rotation of -OH groups about C-C bond. The alcohols under study are of special importance for their wide applications in the fields of biological research, medicine and industry.

But the modern trend is to study relaxation phenomena in polar-nonpolar liquid mixtures in terms of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} rather than permittivity ϵ^*_{ij} or conductivity σ^*_{ij} . As all types of polarizations are associated with ϵ^*_{ij} , while σ^*_{ij} includes within it transport of bound molecular charges, so it is more reasonable to work with χ_{ij} 's as it is directly linked with orientational polarization of the molecules. Moreover, the present study have

been carried out in modern concept of internationally accepted symbols of dielectric terminology and parameter in SI units because of its unified, coherent and rationalized nature. Under such context we have derived a straight line equation in terms of real χ'_{ij} and imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} together with low frequency real dielectric susceptibility χ_{oij} to have τ_1 and τ_2 of alcohol molecules in n-heptane at 25°C under GHz electric field. The frequency 24.33 GHz has been found out to be the most effective dispersive region of the alcohol molecules. When χ''_{ij} of the molecules are plotted against frequency (f) they showed peak in the neighbourhood of 24 GHz which is probably due to dielectric reorientation of polar molecules [9]. At this frequency the alcohol molecules absorb electrical energy much more strongly to show reliable τ_1 and τ_2 from intercept and slope of the least squares fitted straight line equation of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij} / χ'_{ij} signifying the material property of the systems. The data of χ'_{ij} , χ''_{ij} and χ_{oij} so obtained are entered in Table 6.1

*Table—6.1 Concentration variation of measured real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex dielectric relative permittivity ϵ^*_{ij} , static and hf dielectric permittivity ϵ_{oij} and $\epsilon_{\infty ij}$ along with real χ'_{ij} and imaginary χ''_{ij} parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} , low frequency susceptibility χ_{oij} for alcohols in n-heptane at 25°C under different GHz electric field*

Systems with serial number & Mol.wt(Mj) in Kg.(in n-heptane)	Frequency f in GHz	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij} (= $\epsilon'_{ij} - \epsilon_{\infty ij}$)	χ''_{ij} (= ϵ''_{ij})	χ_{oij} (= $\epsilon_{oij} - \epsilon_{\infty ij}$)
I. 1-butanol Mj =0.074	a) 24.33	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
		0.2072	2.1440	0.0818	2.6210	2.0200	0.1240	0.0818	0.6010
	b) 9.25	0.0291	1.9630	0.0059	1.9710	1.9280	0.0350	0.0059	0.0430
		0.0451	1.9850	0.0121	2.0000	1.9450	0.0400	0.0121	0.0550
		0.0697	2.0150	0.0220	2.0500	1.9580	0.0570	0.0220	0.0920
		0.1163	2.0660	0.0416	2.1750	1.9780	0.0880	0.0416	0.1970
		0.1652	2.1210	0.0637	2.3810	2.0000	0.1210	0.0637	0.3810
		0.2072	2.1720	0.0956	2.6210	2.0200	0.1520	0.0956	0.6010
		0.2072	2.1720	0.0956	2.6210	2.0200	0.1520	0.0956	0.6010

Systems with serial number & Mol.wt(Mj) in Kg.(in n-heptane)	Frequency f in GHz	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij} (= $\epsilon_{ij}' - \epsilon_{\infty ij}$)	χ''_{ij} (= ϵ_{ij}'')	χ_{oij} (= $\epsilon_{oij} - \epsilon_{\infty ij}$)	
II. 1-hexanol Mj = 0.102	c) 3.00	0.0291	1.9700	0.0044	1.9710	1.9280	0.0420	0.0044	0.0430	
		0.0451	1.9940	0.0114	2.0000	1.9450	0.0490	0.0114	0.0550	
		0.0697	2.0300	0.0188	2.0500	1.9580	0.0720	0.0188	0.0920	
		0.1163	2.1010	0.0460	2.1750	1.9780	0.1230	0.0460	0.1970	
		0.1652	2.1800	0.0782	2.3810	2.0000	0.1800	0.0782	0.3810	
		0.2072	2.2440	0.1119	2.6210	2.0200	0.2240	0.1119	0.6010	
	a) 24.33	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	
		b) 9.25	0.0458	1.9700	0.0083	1.9880	1.9440	0.0260	0.0083	0.0440
			0.0703	1.9900	0.0121	2.0150	1.9520	0.0380	0.0121	0.0630
			0.1028	2.0150	0.0226	2.0640	1.9700	0.0450	0.0226	0.0940
			0.1687	2.0740	0.0454	2.1960	1.9890	0.0850	0.0454	0.2070
			0.2335	2.1280	0.0688	2.3600	2.0020	0.1260	0.0688	0.3580
0.2901			2.1790	0.1000	2.5800	2.0180	0.1610	0.1000	0.5620	
c) 3.00		0.0458	1.9770	0.0065	1.9880	1.9440	0.0330	0.0065	0.0440	
		0.0703	2.0030	0.0117	2.0150	1.9520	0.0510	0.0117	0.0630	
	0.1028	2.0400	0.0214	2.0640	1.9700	0.0700	0.0214	0.0940		
	0.1687	2.1120	0.0446	2.1960	1.9890	0.1230	0.0446	0.2070		
	0.2335	2.1860	0.0755	2.3600	2.0020	0.1840	0.0755	0.3580		
	0.2901	2.2500	0.1097	2.5800	2.0180	0.2320	0.1097	0.5620		
III. 1-heptanol Mj = .116	a) 24.33	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	
		b) 9.25	0.0564	1.9750	0.0084	1.9850	1.9320	0.0430	0.0084	0.0530
	0.0735		1.9850	0.0129	2.0080	1.9450	0.0400	0.0129	0.0630	
	0.1175		2.0170	0.0232	2.0660	1.9570	0.0600	0.0232	0.1090	
	0.1909		2.0790	0.0438	2.1950	1.9890	0.0900	0.0438	0.2060	
	0.2465		2.1140	0.0609	2.3150	2.0020	0.1120	0.0609	0.3130	
	0.2970		2.1570	0.0774	2.4640	2.0080	0.1490	0.0774	0.4560	
	c) 3.00	0.0735	1.9980	0.0111	2.0080	1.9450	0.0530	0.0111	0.0630	
		0.1175	2.0430	0.0216	2.0660	1.9570	0.0860	0.0216	0.1090	
		0.1909	2.1170	0.0456	2.1950	1.9890	0.1280	0.0456	0.2060	
		0.2465	2.1750	0.0651	2.3150	2.0020	0.1730	0.0651	0.3130	
		0.2970	2.2250	0.0864	2.4640	2.0080	0.2170	0.0864	0.4560	

Systems with serial number & Mol.wt(Mj) in Kg.(in n-heptane)	Frequency f in GHz	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij} (= $\epsilon_{ij}' - \epsilon_{\infty ij}$)	χ''_{ij} (= ϵ_{ij}'')	χ_{oij} (= $\epsilon_{oij} - \epsilon_{\infty ij}$)
IV. 1-decanol Mj = .158	a) 24.33	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
	b) 9.25	0.0572	1.9680	0.0090	1.9760	1.9400	0.0280	0.0090	0.0360
		0.0857	1.9770	0.0146	2.0030	1.9520	0.0250	0.0146	0.0510
		0.1351	2.0110	0.0228	2.0500	1.9640	0.0470	0.0228	0.0860
		0.2140	2.0550	0.0386	2.1470	1.9900	0.0650	0.0386	0.1570
		0.2640	2.0770	0.0484	2.2200	2.0080	0.0690	0.0484	0.2120
		0.3353	2.1230	0.0656	2.3460	2.0300	0.0930	0.0656	0.3160
	c) 3.00	0.0572	1.9720	0.0041	1.9760	1.9400	0.0320	0.0041	0.0360
		0.0857	1.9950	0.0086	2.0030	1.9520	0.0430	0.0086	0.0510
		0.1351	2.0310	0.0194	2.0500	1.9640	0.0670	0.0194	0.0860
		0.2140	2.0880	0.0371	2.1470	1.9900	0.0980	0.0371	0.1570
		0.2640	2.1290	0.0496	2.2200	2.0080	0.1210	0.0496	0.2120
		0.3353	2.1860	0.0690	2.3460	2.0300	0.1560	0.0690	0.3160

together with measured permittivities ϵ_{ij} 's. The validity of straight line equations of Fig.6.1 is tested by correlation coefficient(r) and % of errors which are entered in Table 6.2 along with estimated τ_1 and τ_2 . In absence of reliable τ_j 's of these normal alcohols the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j at $w_j \rightarrow 0$ as seen in Figs.6.2 and 6.3 were utilised to get hf τ_j to compare them with those of Murthy et al [10] of Fig.6.4 and Gopala Krishna's method [11].

The theoretical weighted contributions c_1 and c_2 towards dielectric dispersions in terms of measured τ_1 and τ_2 were worked out from Fröhlich's equations [12] to compare them with the experimental ones by graphical variation of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} with w_j at $w_j = 0$ of Figs. 6.5 and 6.6. They are shown in Table 6.3. The symmetric γ and asymmetric δ distribution parameters were obtained from graphical extrapolation techniques of Figs. 6.5 and 6.6 in the limit $w_j = 0$ and from variation of $(1/\phi)\log(\cos\phi)$ against $\bar{\phi}$ of Fig. 6.7 respectively. Symmetric relaxation time τ_s from γ and

characteristic relaxation time τ_{cs} from δ and ϕ , were however, estimated to conclude about symmetric relaxation behaviour of polar molecules. τ_s and τ_{cs} so obtained are placed in Table 6.2 to compare them with τ_1 , τ_2 and τ_j .

The dipole moment's μ_1 and μ_2 in terms of b_1 and b_2 involved with estimated τ_1 and τ_2 and linear coefficient β 's of χ'_{ij} against ω_j curves of Fig. 6.3 were worked out to present them in Table 6.4 to compare with reported μ_j 's (Gopala Krishna) and μ_{theo} obtained from bond angles and reduced bond moments [13] of substituent polar groups attached to parent molecules. The comparison however suggests that the flexible part of the molecules rotate internally under GHz electric field [14,15]. The slight disagreement between experimental and theoretical μ 's establishes the very existence of strong internal hydrogen bonding among -OH groups of long straight chain alcohol molecules. Physico-chemical aspects of different solute molecules in nonpolar solvent can be explained by non linear variation of both τ_2 and μ_2 against frequency (f) of the applied electric field as shown in Fig. 6. 8.

6.2. EXPERIMENTAL

The dielectric constants ϵ'_{ij} and losses ϵ''_{ij} of the alcohols in n-heptane at different mole fractions of solutes were measured [8] with a Boonton RX meter corrected by a heterodyne beat method. Refractive indices ($n_{Dij} = \sqrt{\epsilon'_{ij}}$) of the solution were estimated by a Pulfrich refractometer for sodium D-line. The alcohols 1-butanol, 1-hexanol, 1-heptanol and 1-decanol were obtained from various commercial sources dried for a period over "Drierite" (anhydrous calcium sulphate) and fractionally distilled at atmospheric pressure. Commercial n-heptane was dried over sodium wire prior to its use and its relative permittivity ($\epsilon_i = 1.917$) was checked in agreement with literature value at 25°C.

6.3. THEORETICAL FORMULATION TO ESTIMATE DOUBLE RELAXATION

TIMES τ_1 , τ_2 AND C_1 , C_2

The hf complex dielectric relative permittivity ϵ^*_{ij} of polar-nonpolar liquid mixtures is associated with a number of non interacting Debye type dispersions in accordance with Budo's relation[16]

$$\frac{\varepsilon_{ij}^* - \varepsilon_{\infty ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = \sum \frac{c_k}{1 + j\omega\tau_k} \quad (6.1)$$

where $j = \sqrt{-1}$, is a complex number and c_k is the relative contribution for the k th type of relaxation process.

But when ε_{ij}^* consists of two Debye type dispersions Budo's relation reduces to Bergmann's equations [17]. $\varepsilon_{\infty ij}$ includes within it fast polarization and frequently appears as a subtracted term in Bergmann's equations. Thus to avoid the clumsiness of algebra and to use the modern concept of dielectric terminology and parameter one gets

$$\chi'_{ij} = (\varepsilon'_{ij} - \varepsilon_{\infty ij}), \quad \chi''_{ij} = \varepsilon''_{ij}, \quad \chi_{0ij} = (\varepsilon_{0ij} - \varepsilon_{\infty ij})$$

The Bergmann's equations thus becomes

$$\frac{\chi'_{ij}}{\chi_{0ij}} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad (6.2)$$

$$\frac{\chi''_{ij}}{\chi_{0ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (6.3)$$

The relative weighted factors c_1 and c_2 are such that $c_1 + c_2 = 1$, χ'_{ij} and χ''_{ij} are the real and imaginary parts of hf complex dielectric orientational susceptibility χ_{ij}^* and χ_{0ij} is low frequency dielectric susceptibility which is real. The introduction of χ 's in Bergmann's equations are then concerned with the molecular orientational polarization alone.

Putting $\omega\tau_1 = \alpha_1$ and $\omega\tau_2 = \alpha_2$ eqs. (6.2) and (6.3) are solved to get

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{0ij}(\alpha_2 - \alpha_1)} \quad (6.4)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{0ij}(\alpha_2 - \alpha_1)} \quad (6.5)$$

provided $\alpha_2 - \alpha_1 \neq 0$.

As $c_1 + c_2 = 1$, we have

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

or, $\chi'_{ij}\alpha_2 + \chi'_{ij}\alpha_2\alpha_1^2 - \chi''_{ij} - \chi''_{ij}\alpha_1^2 + \chi''_{ij} + \chi''_{ij}\alpha_2^2 - \chi'_{ij}\alpha_1 - \chi'_{ij}\alpha_1\alpha_2^2 = \chi_{oij}(\alpha_2 - \alpha_1)$

or, $\chi'_{ij}(\alpha_2 - \alpha_1) - \chi'_{ij}\alpha_1\alpha_2(\alpha_2 - \alpha_1) + \chi''_{ij}(\alpha_2^2 - \alpha_1^2) = \chi_{oij}(\alpha_2 - \alpha_1)$

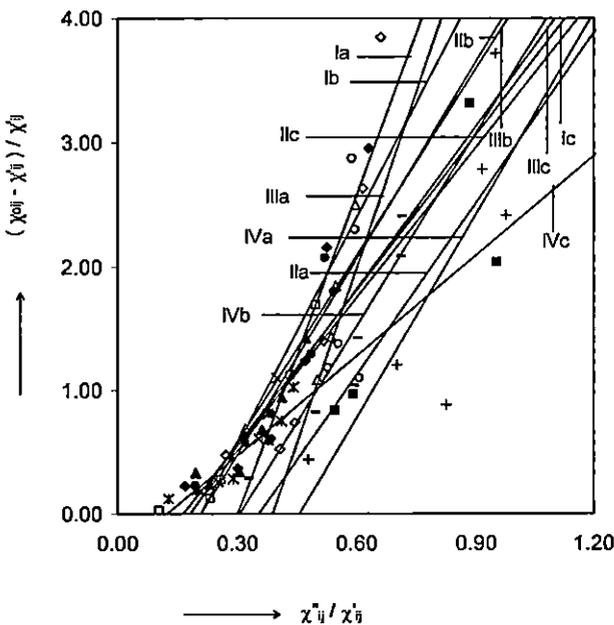
or, $\chi'_{ij} - \chi'_{ij}\alpha_1\alpha_2 + \chi''_{ij}(\alpha_2 + \alpha_1) = \chi_{oij}$

or, $\chi''_{ij}(\alpha_1 + \alpha_2) - \chi'_{ij}\alpha_1\alpha_2 = \chi_{oij} - \chi'_{ij}$

$$\text{or, } \frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = (\alpha_1 + \alpha_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \alpha_1\alpha_2$$

substituting $\alpha_1 = \omega\tau_1$ & $\alpha_2 = \omega\tau_2$ we have

$$\text{or } \frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2\tau_1\tau_2 \tag{6.6}$$



which is a straight line equation between the variables $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ and χ''_{ij} / χ'_{ij} with slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2\tau_1\tau_2$. where $\omega = 2\pi f$, f being frequency of the applied electric field in GHz range. The above equation is, however, satisfied by experimental points as seen in Fig.6.1 for different weight fractions τ_i 's of solute at 25°C

Fig 6.1 .Linear variation of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ with χ''_{ij} / χ'_{ij} for alcohols in n-heptane at 25°C of Ia. 1-butanol (\diamond) at 24.33 GHz, Ib. 1-butanol (\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa. 1-hexanol (\blacksquare) at 24.33 GHz, IIb. 1-hexanol (\blacktriangle) at 9.25 GHz IIc. 1-hexanol (\blacktriangle) at 3.00 GHz, IIIa. 1-heptanol (\circ) at 24.33 GHz, IIIb. 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz, IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

under electric field frequencies of 24.33, 9.25 and 3.00 GHz. The eq.(6.6) has been used to estimate τ_1 and τ_2 in order to place them in Table 6.2.

*Table 6.2:-- The relaxation times τ_1 and τ_2 , from the slope and intercept of straight line eq.(6.6), correlation coefficient r 's and % of error in regression technique, measured τ_j from the slope of χ_{ij}'' vs χ_{ij}' of eq.(6.16) 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. (6.17), reported τ_s symmetric and characteristic relaxation times τ_s and τ_{cs} for different straight chain aliphatic alcohols in *n*-heptane at 25°C under different GHz electric field.*

System with Sl. No.& Molecular weight M_j in Kg	Freque ncy (f) in GHz	Slope and inter-cept of eq.(6.6)		estimated τ_1 & and τ_2 in psec		Corrl. Coeff. (r)	% of error	Estimated τ_j in psec from method of Murti et al & ratio of individual slope)		Report -ed τ_j in psec	τ_s in psec	τ_{cs} in psec
		Slope	Inter cept	τ_1	τ_2							
I. 1-butanol $M_j = 0.074$	24.33	8.66	2.60	2.04	54.56	0.9973	0.000032	4.95	3.42	17.44	0.98	15.41
	9.25	6.13	1.28	3.72	101.78	0.9988	0.000014	12.52	6.79	43.86	1.40	4.61
	3.00	4.15	0.68	9.09	211.22	0.9980	0.000024	30.18	15.80	147.92	-	-
II. 1-hexanol $M_j = 0.102$	24.33	4.59	1.63	2.54	27.46	0.9573	0.000619	7.69	72.85	15.66	1.08	13.99
	9.25	5.17	1.08	3.75	85.16	0.9960	0.000048	11.42	7.79	42.45	10.50	163.63
	3.00	4.02	0.67	9.17	204.07	0.9983	0.000020	27.09	9.81	154.07	3.89	334.83
III. 1- heptanol $M_j = 0.116$	24.33	9.44	3.67	2.65	59.09	0.9891	0.000143	3.88	3.03	21.04	5.04	21.39
	9.25	5.01	0.92	3.29	82.96	0.9890	0.000132	11.02	26.84	48.86	1.31	3.03
	3.00	4.34	0.79	10.05	220.31	0.9970	0.000040	24.86	20.66	173.36	4.16	-
IV. 1- decanol $M_j = 0.158$	24.33	5.43	2.48	3.29	32.22	0.9940	0.000072	7.63	10.20	18.19	1.91	1.15
	9.25	5.16	1.57	5.60	83.06	0.9847	0.000184	14.00	11.10	51.02	3.19	13.43
	3.00	2.69	0.33	6.88	135.54	0.9993	0.000008	28.02	22.25	184.45	1.78	-

The theoretical weighted contributions c_1 and c_2 were, then obtained from eqs. (6.4) and (6.5) with the variables χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} of Fröhlich's eqs. (6.7) and (6.8) in terms of known τ_1 and τ_2 of Table 6.2.

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \quad (6.7)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} [\tan^{-1}(\omega \tau_2) - \tan^{-1}(\omega \tau_1)] \quad (6.8)$$

c_1 and c_2 so obtained are entered in Table 6.3 in order to compare them with the experimental ones obtained from eqs. (6.4) and (6.5) with graphically extrapolated values of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} in the limit $\omega \rightarrow 0$ of Figs. 6.5 and 6.6 respectively.

6.4. THEORETICAL FORMULATION TO ESTIMATE SYMMETRIC AND CHARACTERISTIC RELAXATION TIMES τ_s and τ_{cs}

The molecules under present investigation appear to behave like non-rigid ones having symmetric and asymmetric distribution parameters γ and δ involved with eqs. (6.9) and (6.10)

$$\frac{\chi^*_{ij}}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (6.9)$$

$$\frac{\chi^*_{ij}}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (6.10)$$

The former one is associated with symmetric relaxation time τ_s while the later one with characteristic relaxation times τ_{cs} . On separating the real and imaginary parts of eqs. (6.9) and (6.10) and rearranging them in terms of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} at $\omega \rightarrow 0$ as seen in Figs 6.5 and 6.6, the γ and τ_s were obtained as

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}}{\chi''_{ij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad (6.11)$$

And

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{(\chi'_{ij} / \chi''_{ij}) \cos(\gamma\pi/2) - \sin(\gamma\pi/2)} \right]^{1/(1-\gamma)} \quad (6.12)$$

Similarly δ and τ_{cs} can be had from eq.(6.10) as

$$\tan(\phi\delta) = \frac{(\chi''_{ij} / \chi_{oij})_{\omega_j \rightarrow 0}}{(\chi'_{ij} / \chi_{oij})_{\omega_j \rightarrow 0}} \quad (6.13)$$

and $\tan\phi = \omega\tau_{cs}$ (6.14)

As ϕ can not be evaluated directly, an arbitrary theoretical curve between $(1/\phi) \log(\cos\phi)$ against ϕ in degree was drawn in Fig. 6.7 from which

$$(1/\phi) \log(\cos\phi) = \frac{\log \{(\chi'_{ij} / \chi_{oij}) / (\cos\phi\delta)\}}{\phi\delta} \quad (6.15)$$

can be known. The known value of $(1/\phi) \log(\cos\phi)$ is used to know ϕ from Fig. 6.7. With known ϕ eqs. (6.13) and (6.14) can be used to obtain δ and τ_{cs} respectively. τ_s and τ_{cs} in Table 6.2 can be compared with τ_j 's by Murthy et al[10], τ_j 's by the method of ratio of individual slope, Gopala Krishna [11] and τ_1, τ_2 by double relaxation method. Estimated values of γ and δ are seen in Table 6.3.

Table-6.3: Fröhlich's parameter A, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion with χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} estimated from Fröhlich's eqs. (6.7) and (6.8) and those by graphical technique of Figs.6.5 and 6.6, symmetric and asymmetric distribution parameters γ and δ of some normal alcohols in n-heptane at 25°C under different gigahertz electric field.

Systems with Sl. No.	Frequency (f) in GHz	A = ln (τ_2/τ_1)	Theoretical values of χ'_{ij} / χ_{oij} & χ''_{ij} / χ_{oij} from eqs (6.7) & (8)		Theoretical values of c_1 and c_2		Experimental values of χ'_{ij} / χ_{oij} & χ''_{ij} / χ_{oij} at $\omega_j \rightarrow 0$ of Figs 6.5 & 6.6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
					c_1	c_2	c_1	c_2	γ	δ		
I. 1-butanol	24.33	3.286	0.366	0.350	0.370	2.069	0.799	0.195	0.884	-0.474	0.357	0.21
	9.25	3.308	0.465	0.360	0.439	1.637	0.973	0.132	1.033	-0.499	0.043	0.51
	3.00	3.146	0.556	0.367	0.498	1.203	1.112	0.069	1.178	-0.537	-0.688	-
II.1-hexanol	24.33	2.381	0.415	0.406	0.404	1.197	0.796	0.211	0.946	-0.479	0.323	0.23
	9.25	3.122	0.489	0.370	0.454	1.423	0.697	0.158	0.729	0.031	0.552	0.15
	3.00	3.103	0.560	0.369	0.500	1.171	0.840	0.109	0.875	-0.157	0.538	0.09
III.1-heptanol	24.33	3.103	0.313	0.346	0.335	2.101	0.475	0.312	0.537	1.140	0.289	0.46
	9.25	3.227	0.511	0.365	0.470	1.398	0.980	0.122	1.031	-0.346	0.025	0.70
	3.00	3.088	0.535	0.372	0.484	1.244	1.003	0.108	1.061	-0.376	-0.088	-
IV. 1-decanol	24.33	2.281	0.341	0.396	0.364	1.283	0.870	0.404	1.100	-0.193	-0.079	2.49
	9.25	2.696	0.427	0.390	0.411	1.355	0.862	0.259	0.959	-0.118	0.125	0.44
	3.00	2.981	0.664	0.359	0.561	0.846	1.007	0.037	1.063	-0.290	-0.145	-

6.5. THEORETICAL FORMULATION O OBTAIN RELAXATION TIME τ_j AND hf

DIPOLE MOMENT μ_j

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

$$\epsilon'_{ij} = \epsilon_{oij} + (1/\omega\tau) \epsilon''_{ij}$$

$$\text{or, } (\epsilon'_{ij} - \epsilon_{oij}) = (1/\omega\tau) \epsilon''_{ij}$$

$$\text{or, } \chi'_{ij} = (1/\omega\tau) \chi''_{ij}$$

$$\text{or, } (d\chi''_{ij} / d\chi'_{ij}) = \omega\tau_j \quad (6.16)$$

χ''_{ij} 's are found to vary almost linearly[10] with χ'_{ij} as seen in Fig.6.4, the slope $\omega\tau_j$ is

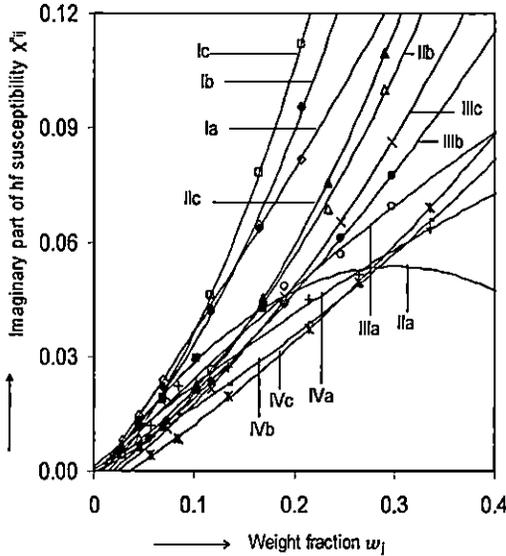


Fig 6.2 .Variation of imaginary part of hf susceptibility χ''_{ij} with weight fraction w_j for alcohols in n-heptane at 25°C of Ia.1-butanol(\diamond) at 24.33 GHz,Ib.1-butanol(\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa.1-hexnol (\blacksquare) at 24.33 GHz,IIb.1-hexnol (\triangle) at 9.25 GHz IIc.1-hexnol (\blacktriangle) at 3.00 GHz,IIIa.1-heptanol (\circ) at 24.33 GHz,IIIb 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz,IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

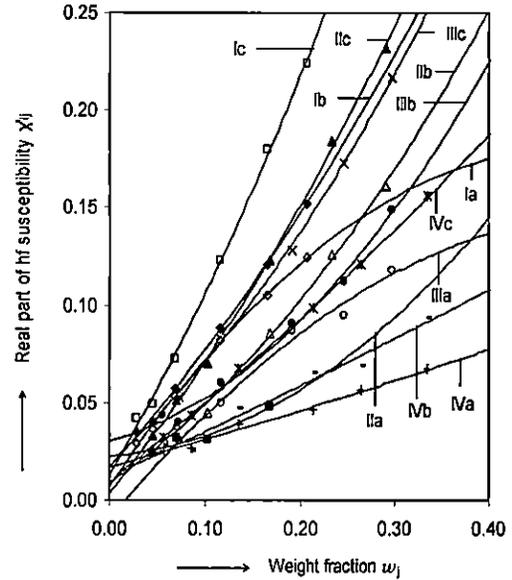


Fig 6.3 .Variation of real part of hf susceptibility χ'_{ij} with weight fraction w_j for alcohols in n-heptane at 25°C of Ia.1-butanol(\diamond) at 24.33 GHz,Ib.1-butanol(\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa.1-hexnol (\blacksquare) at 24.33 GHz,IIb.1-hexnol (\triangle) at 9.25 GHz IIc.1-hexnol (\blacktriangle) at 3.00 GHz,IIIa.1-heptanol (\circ) at 24.33 GHz,IIIb 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz,IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

used to obtain τ_j as seen in the 9th column of Table 6.2.

But earlier investigation on some isomers of anisidines and toluidines [15] and the present investigation on normal alcohols shows that variation of χ''_{ij} against χ'_{ij} as seen in Fig. 6.4 are strictly not linear. The ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j 's in Figs 6.2 and 6.3 is a better representation of eq. (6.16) to get τ_j where polar-polar interactions are almost avoided [15]. Thus

$$\frac{(d\chi''_{ij} / dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij} / dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (6.17)$$

The Imaginary part χ''_{ij} of χ^*_{ij} can be represented [18,19] as

$$\chi''_{ij} = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\epsilon_{ij} + 2)^2 w_j \quad (6.18)$$

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

$$(d\chi''_{ij} / d\omega_j)_{\omega_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{27 \varepsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\varepsilon_i + 2)^2 \quad (6.19)$$

Now in comparison to earlier works presented elsewhere[6,13] the approximation that $\chi_{ij} \cong \chi''_{ij}$ like $\sigma_{ij} \cong \sigma''_{ij}$ is not necessary to obtain μ_j from τ_j where σ''_{ij} is the imaginary part of complex hf conductivity and σ_{ij} is the total hf conductivity of polar – nonpolar liquid mixture. From eqs. (6.17) and (6.19) one gets

$$\omega \tau_j (d\chi'_{ij} / d\omega_j) = \frac{N\rho_i \mu_j^2}{27 \varepsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\varepsilon_i + 2)^2$$

$$\text{or, } \omega \tau_j \beta = \frac{N\rho_i \mu_j^2}{27 \varepsilon_0 M_j k_B T} \omega \tau_j b (\varepsilon_i + 2)^2$$

$$\text{or, } \beta = \frac{N\rho_i \mu_j^2}{27 \varepsilon_0 M_j k_B T} b (\varepsilon_i + 2)^2$$

$$\text{or, } \mu_j = \left[\frac{27 \varepsilon_0 M_j k_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 b} \right]^{1/2} \quad (6.20)$$

which is directly interrelated with the measured τ 's through b, 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

$\beta = d\chi'_{ij} / d\omega_j$ = Linear coefficient of $\chi'_{ij} - \omega_j$ curves of Fig.6.3 at $\omega_j \rightarrow 0$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent n-heptane at 25°C = 680.15 Kg.m⁻³

ϵ_i = Relative permittivity of the solvent n-heptane = 1.917

$b = 1 / (1 + \omega^2 \tau^2)$ = a dimensionless parameter involved with estimated τ_1 & τ_2 of eq. (6.6) and τ_j of eq. (6.17).

Dipole moments μ_1 and μ_2 obtained with the knowledge of b_1 and b_2 involved with estimated τ_1 and τ_2 by double relaxation method are entered in the 8th and 9th column of Table 6.4. They are, however, compared to μ_j with τ_j of eq. (6.17) and reported μ 's (Gopala Krishna) and μ_{theo} as seen in 10th, 12th and 13th columns.

Table-6.4: Linear coefficient β of χ'_{ij} Vs w_j curves of Fig. 6.3, dimensionless parameters b_1 , b_2 from τ_1 & τ_2 of eq. (6.6), correlation coefficient (r) and % of errors, estimated dipole moment μ_1 , μ_2 from eq. (6.20), computed dipole moment μ_j from τ_j of eq. (6.17), reported dipole moment (Gopala Krishna's method), all are expressed in Coulomb-metre for different straight chain alcohols in n-heptane at 25°C under different GHz electric field.

System with Sl. No. & mol. weight M _j in kg	Frequ- ency (f) in GHz	Linear coeffi- cient of χ'_{ij} vs w_j curves of fig 6.3 β	Dimensionless parameters		Correlation coefficient of $\chi'_{ij} - w_j$ & χ''_{ij} - w_j curves	% of errors of both $\chi'_{ij} - w_j$ & $\chi''_{ij} - w_j$ curves	Estimated Dipole moments $\mu \times 10^{30}$ in coulomb metre			$\mu_1 =$ $\mu_2 (C_1/C_2)^{1/2}$ in c.m	Reported $\mu \times 10^{30}$ in C.m by	μ_{theo} $\times 10^{30}$ in C.m
			b_1	b_2			μ_1	μ_2	μ_j			
I.1-butanol (M _j = 0.074)	24.33	0.719	0.911	0.0142	0.997347	0.000032	3.02	24.25	3.26	10.25	3.58	
	9.25	0.539	0.955	0.0278	0.998805	0.000014	2.56	14.99	2.69	7.77	3.80	3.74
	3.00	0.830	0.971	0.0593	0.998034	0.000024	3.14	12.72	3.23	8.19	4.30	
II.1-hexanol (M _j =0.102)	24.33	0.034	0.869	0.0537	0.957348	0.000619	0.79	3.18	8.25	1.85	3.35	
	9.25	0.330	0.955	0.0392	0.996042	0.000048	2.35	11.59	2.52	6.55	3.87	3.49
	3.00	0.609	0.971	0.0633	0.998317	0.000020	3.16	12.39	3.17	8.10	4.27	
III.1- heptanol (M _j = 0.116)	24.33	0.588	0.859	0.0121	0.989149	0.000143	3.52	29.69	3.60	11.86	3.59	
	9.25	0.131	0.965	0.0412	0.989026	0.000132	1.57	7.59	2.86	4.40	3.60	3.73
	3.00	0.447	0.965	0.0548	0.996990	0.000040	2.90	12.17	3.06	7.59	4.27	
IV.1- decanol (M _j =0.158)	24.33	0.142	0.798	0.0395	0.994031	0.000072	2.10	9.43	3.47	5.03	3.55	
	9.25	0.227	0.904	0.0411	0.984662	0.000184	2.49	11.67	2.82	6.42	3.83	3.68
	3.00	0.388	0.983	0.1328	0.999324	0.000008	3.12	8.50	3.36	6.92	4.33	

6.6. RESULTS AND DISCUSSIONS

The least square fitted straight line eq. of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij} / χ'_{ij} for

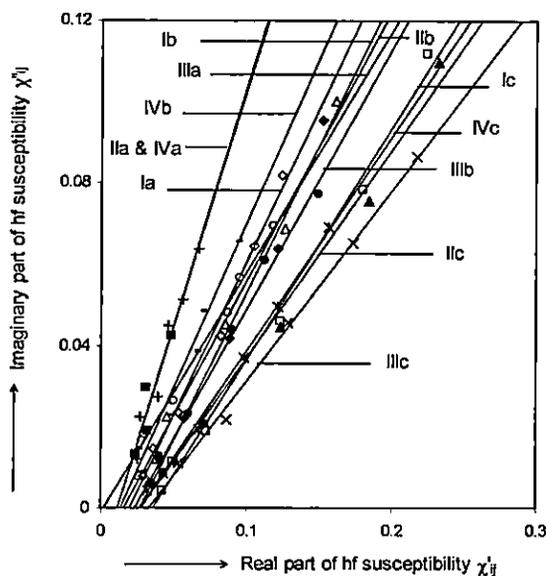


Fig 6.4 Variation of imaginary part of hf susceptibility χ''_{ij} with real part of hf susceptibility χ'_{ij} of alcohols in n-heptane at 25°C of Ia. 1-butanol (\diamond) at 24.33 GHz, Ib. 1-butanol (\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa. 1-hexanol (\blacksquare) at 24.33 GHz, IIb. 1-hexanol (\triangle) at 9.25 GHz, IIc. 1-hexanol (\blacktriangle) at 3.00 GHz, IIIa. 1-heptanol (\circ) at 24.33 GHz, IIIb. 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz, IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

different weight fractions w_j 's of solute at 25°C in n-heptane under different GHz electric field frequency are shown graphically in Fig. 6.1 together with experimental points placed on them. The real χ'_{ij} and imaginary χ''_{ij} parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} and low frequency real dielectric susceptibility χ_{oij} are, however, derived from measured [8] permittivities $\epsilon\epsilon'_{ij}$, ϵ''_{ij} , ϵ_{oij} and ϵ_{ooij} of

Table 6.1. The linearity of all curves of Fig. 6.1 are confirmed by correlation coefficients r 's and percentage of errors placed in the 7th and 8th columns of Table 6.2. The relaxation times τ_1 and τ_2 estimated from eq. (6.6) are placed in the 5th and 6th columns of Table 6.2. It is seen that both τ_1 and τ_2 are of low values at 24.33 GHz and tends to increase with the lower frequencies of 9.25 and 3.00 GHz electric fields. It may be explained on the basis of the fact that at higher frequencies the rate of hydrogen bond rupture is maximum in such long chain alcohols to reduce τ for each rotating unit [20].

In absence of reliable τ_j of such molecules it was tried to calculate τ_j from the least square fitted straight line eq. of χ''_{ij} against χ'_{ij} in Fig. 6.4 as claimed by Murthy et al [10] to place them in the 9th column of Table 6.2. But the experimental points are found to deviate from linearity as seen in Fig. 6.4 which is probably due to various associational aspects of polar molecules in non polar solvent [13]. The

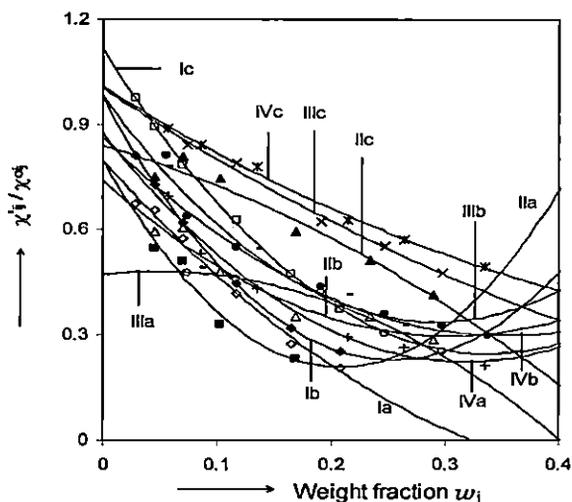


Fig 6.5 i. Variation χ''_{ij} / χ'_{oj} with weight fraction ω_j for alcohols in n-heptane at 25°C of Ia. 1-butanol (\diamond) at 24.33 GHz, Ib. 1-butanol (\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa. 1-hexanol (\blacksquare) at 24.33 GHz, IIb. 1-hexanol (\triangle) at 9.25 GHz IIc. 1-hexanol (\blacktriangle) at 3.00 GHz, IIIa. 1-heptanol (\circ) at 24.33 GHz, IIIb. 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz, IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

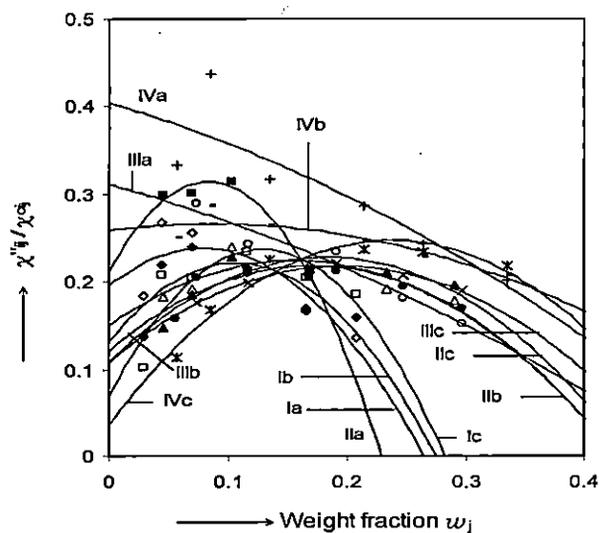


Fig 6.6 . Variation χ''_{ij} / χ'_{oj} with weight fraction ω_j for alcohols in n-heptane at 25°C of Ia. 1-butanol (\diamond) at 24.33 GHz, Ib. 1-butanol (\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa. 1-hexanol (\blacksquare) at 24.33 GHz, IIb. 1-hexanol (\triangle) at 9.25 GHz IIc. 1-hexanol (\blacktriangle) at 3.00 GHz, IIIa. 1-heptanol (\circ) at 24.33 GHz, IIIb. 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz, IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

individual plots of χ''_{ij} and χ'_{ij} against ω_j of normal alcohols are not linear as seen in Figs 6.2 and 6.3 which confirms the probable solute-solute (dimer) and solute-solvent (monomer) molecular associations. The reliability of both $\chi''_{ij} - \omega_j$ and $\chi'_{ij} - \omega_j$ variations are confirmed by correlation coefficients r 's and

% of errors as placed in Table 6.4. This fact at once inspired us to evaluate τ_j from the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with ω_j at $\omega_j \rightarrow 0$. τ_j so obtained shows close agreement with τ_1 from double relaxation and Gopala krishna's method

[11]. This approach further confirms that polar – polar interactions are fully avoided

[6,15] in the later method. Thus hf dielectric susceptibility measurement yields the

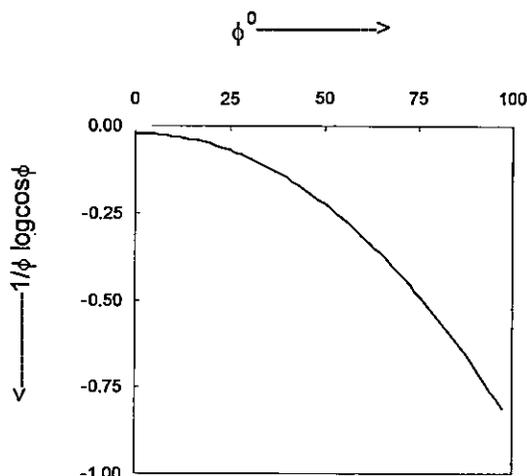


Figure 7. Variation of $(1/\phi) \log(\cos\phi)$ against ϕ^0

Fig 6.7

and asymmetric distribution parameters γ and δ of such molecules from eqs. (6.11) and (6.13) with graphical extrapolation values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $\omega_j = 0$ of Figs.

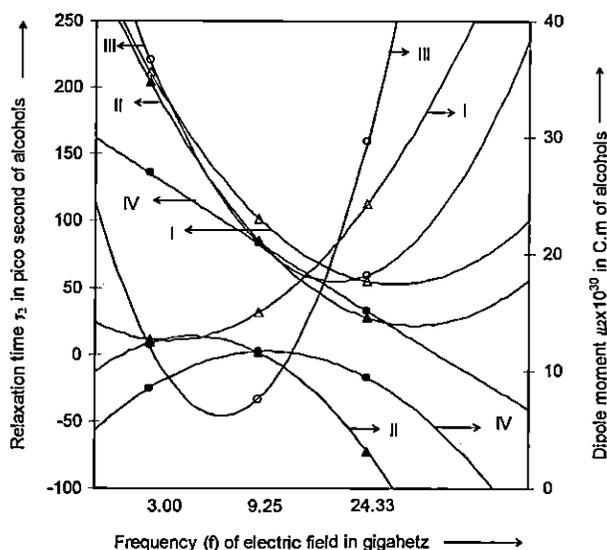


Fig 6.8 Variation of Relaxation time and Dipole moment against frequency(f) of the applied electric field for some alcohols in n-heptane at 25°C I.1-butanol(Δ) II.1-hexanol (\blacktriangle) III.1-heptanol (\circ) IV. 1-decanol (\bullet)

accurate microscopic τ due to orientational polarization whereas double relaxation method gives both microscopic and macroscopic τ 's [15,20].

Higher values of τ_2 's results in bigger size of rotating unit ($\tau_j T / \eta^\gamma$) which is due to solute-solvent (monomer) associations under GHz electric field. Distribution of τ 's between two limiting values τ_1 & τ_2 prompts one to estimate the symmetric

and asymmetric distribution parameters γ and δ of such molecules from eqs. (6.11) and (6.13) with graphical extrapolation values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $\omega_j = 0$ of Figs. 6.5 and 6.6. Values of γ so obtained is used to evaluate τ_s from eq. (6.12). The arbitrary curve of $(1/\phi) \log(\cos\phi)$ against ϕ in degree is essential to know ϕ for known value of $(1/\phi) \log(\cos\phi)$ from eq. (6.15). Known ϕ from Fig. 6.7 was however used to evaluate δ and τ_{cs} from eqs. (6.13) and (6.14). τ_s and τ_{cs} thus so estimated are entered in the 12th and 13th columns of Table 6.2 to compare them

with τ_1 , τ_2 and τ_j . Both γ and δ are placed in 12th and 13th columns of Table 6.3. The value of γ establishes the non-rigid behaviour of the molecules signifying the applicability of Debye–Smyth model of dielectric relaxation to some extent in such normal alcohols in n-heptane under GHz electric field.

Symmetric relaxation time τ_s obtained from eq. (6.12) with known γ agrees well with τ_1 's by double relaxation and τ_j 's by Gopala Krishna's method except at 3.00 GHz electric field frequency. This discrepancy may be explained on the basis of the fact that at lower frequency the rate of hydrogen bond rupture is small resulting in higher value of τ for each rotating unit. High value of τ_{cs} eventually rules out the possibility of occurring asymmetric relaxation behaviour for the alcohols. Fig. 6.8 represents the plot of both τ_2 and μ_2 against frequency (f) of the applied electric field. It is evident from the plot that τ_2 of the alcohols decreases with frequency. It is due to the fact that at higher frequency the rate of hydrogen bond rupture is maximum, reducing thereby τ_2 for each rotating unit [20]. For system II and IV the variation of μ_2 against frequency is convex in nature having zero μ_2 values at two frequencies due to strong symmetry attained by the molecules. 1-butanol (system I) and 1-heptanol (system III) shows minimum μ_2 for their symmetry attained between 3.00 and 9.25 GHz electric field frequency. Beyond 9.25 GHz μ_2 increases with f showing asymmetric nature of the molecules. All types of symmetries and asymmetries arises probably due to various types of molecular associations between solute and solvent molecules which are supposed to be physico-chemical behaviour of the systems [19].

The relative contributions c_1 and c_2 towards dielectric dispersions as seen in the 6th and 7th columns of Table 6.3 have been evaluated from eqs. (6.4) and (6.5) for fixed τ_1 and τ_2 as predicted from eq. (6.6) and with estimated χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} from Fröhlich's eq. (6.7) and (6.8). The same are, however, obtained experimentally from the graphical variation of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} with ω_j of Figs. 6.5 and 6.6 at $\omega_j = 0$. They are also shown in 10th and 11th column of Table 6.3 to compare with the former ones. The Fröhlich's parameter A is the temperature variation of the width of distribution of τ and is equal to $\ln(\tau_2/\tau_1)$.

Variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with ω_j as seen in Figs. 6.5 and 6.6 are concave and convex in nature which are in accordance with Bergmann's eqs. (6.2) and (6.3) as observed elsewhere [14,21]. The estimated c_2 is greater than c_1 for almost all the alcohols in Fröhlich's method, while the reverse is true for graphical technique. Formation of internal hydrogen bonding among -OH groups in polar alcohol molecules gives rise to inertia [15,20] of the flexible part with respect to whole molecule which results in negative c_2 satisfying the condition $c_1 + c_2 \cong 1$ in graphical technique. For Fröhlich method $c_1 + c_2 > 1$, indicating the possibility of occurrence of more than two relaxation processes [8] in them.

Dipole moments μ_1 and μ_2 estimated from dimensionless parameters b_1 and b_2 for measured τ_1 & τ_2 and linear coefficient β 's of $\chi'_{ij} - \omega_j$ curves of Fig. 6.3 are shown in the 8th and 9th columns of Table 6.4. Correlation coefficient 'r' and % of errors involved in $\chi'_{ij} - \omega_j$ variations are placed in 6th and 7th columns of Table 6.4 only to show how far χ'_{ij} 's are correlated with ω_j 's. Values of r's and % of errors in terms of r's gives reliable β to yield accurate μ_1 and μ_2 . Almost all the curves of Fig. 6.3 shows a tendency to become closer within the limit $0.00 \leq \omega_j \leq 0.05$ probably due to the same polarity of the molecules arising out of monomer and dimer formations [13,15].

The theoretical dipole moments μ_{theo} were, however, obtained from bond angles and bond moments of a number of dipolar groups like $\text{H}_3 \rightarrow \text{C}$, $\text{C} \rightarrow \text{O}$ and $\text{O} \leftarrow \text{H}$ of 1.23×10^{-30} , 3.33×10^{-30} and 1.30×10^{-30} Coulomb metre [13] and are entered in 13th column of Table 6.4. The -OH group in all the alcohols making an angle 105° with the C-C bond plays an important role to yield theoretical dipole moment μ_{theo} . In absence of reliable μ_j values Gopala Krishna's method were employed to get μ_j (Reported data) to compare with μ_1 's estimated from the relation $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$ assuming two relaxation processes are equally probable in them. But the agreement is poor as seen in the 11th and 12th columns of Table 6.4, probably due to the fact that sum of c_1 and c_2 as estimated from Fröhlich's method is not strictly equal to one. The close agreement between μ_1 from double relaxation method, μ_{theo} and reported μ 's establishes the basic soundness of the method [19] for getting hf μ_j in addition to the fact that a part of the molecule is rotating [15]

under GHz electric field. Slight disagreement between μ_{theo} and μ_1 arises due to the formation of H bonds among the –OH groups in dipolar liquid molecules which results in solute – solute molecular association increasing thereby the value of μ_{theo} 's.

6.7. CONCLUSIONS

The methodology so far developed in SI units with internationally accepted symbols of dielectric terminologies and parameters appears to be simple, straightforward and topical one to predict relaxation parameters as χ 's are directly linked with molecular orientational polarization. The significant and interesting equations to evaluate relaxation parameters gives deep insight into the solute–solute and solute–solvent molecular interactions in a solution. The simple straight line eq. (6.6) provides one with microscopic and macroscopic relaxation times. Evaluation of τ_j from eq. (6.17) by ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} against ω_j in the limit $\omega_j = 0$ is a better representation of eq. (6.16) of Murthy et al as it eliminates polar–polar interactions in a solution. The results obviously show that the former method in long straight chain hydrogen bonded associative alcohol molecules may be applicable to get the accurate τ 's of the molecules only due to orientational polarization. Validity of the method so far advanced to evaluate hf τ_j and μ_j is also supported by τ_j and μ_j values estimated from freshly calculated Gopala Krishna's method. The close agreement between measured τ_j and τ_{cs} confirms the non-rigid behaviour of the molecules which at once invites the applicability of Debye-Smyth model of dielectric relaxation in such alcohol molecules. Molecular association is however confirmed by conformational structure in which internal H bonding plays the prominent role. Graphical variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with ω_j as seen in Figs. 6.5 and 6.6 to estimate c_1 and c_2 are concave and convex in nature which are inaccordance with Bergmann's equations. Reliable τ_1 and τ_2 obtained for alcohols at three electric field frequencies indicate the fact that double relaxation is a material property of the system. Although Figs. 6.1 to 6.6 appear to be crowded, they provides a clear comparison between the results obtained for different systems. Some experimental points are found not to

fall on the smooth curves of different Figs. probably due to various molecular associations between solute and solvent molecules which supports the physico-chemical behaviour of the systems. Concave and convex nature of curves of Fig. 6.8 shows that stability and instability of the alcohol molecules depends on frequency of the applied electric field ever shown. Thus the correlation between the conformational structures [19] with the observed results enhances the scientific content to add a new horizon of understanding to the existing knowledge of dielectric relaxation phenomena in addition to physico-chemical properties of the polar liquid molecules.

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