

## CHAPTER 6

# DOUBLE RELAXATION OF STRAIGHT CHAIN ALCOHOLS UNDER HIGH FREQUENCY ELECTRIC FIELD

## 6.1. Introduction

The dielectric relaxation phenomena of highly nonspherical polar liquids in nonpolar solvents under the ultra high frequency (uhf) electric fields have gained much attention [1,2] as they reveal various types of molecular interactions like solute - solute (dimer) and solute - solvent (monomer) formations in liquid mixtures. They also provide one with valuable information regarding sizes, shapes, structures and different thermodynamic parameters due to relaxation of the polar liquids [3].

The relaxation phenomena of pure primary alcohols are very interesting as they were found to possess three distinct low frequency Debye type processes predicting inherently the single relaxation time [4,5]. The dilution of polar alcohols with nonpolar solvents, however, increases the relative contributions towards dielectric dispersions in the hf electric field [6]. The straight chain mono - alcohols, on the other hand, are almost like polymers having  $-CH_3$  and  $-OH$  groups in their structures. Obviously, there exist many possibilities of internal and molecular rotations, bending, twisting etc each with a characteristic relaxation time. In averaging to the macroscopic condition, a distribution of relaxation time may also be possible. Mishra et al [7] claimed that it is not possible to resolve dielectric dispersion in three relaxation processes from the measured relaxation data under a single frequency electric field.

Again, to detect the double relaxation phenomena of a polar solute, Bergmann et al [8] proposed a technique based on measured relaxation parameters of pure polar liquid like real  $\epsilon'$ , loss  $\epsilon''$ , of the complex dielectric constant  $\epsilon^*$  as well as static  $\epsilon_0$  and the high frequency dielectric constant  $\epsilon_\infty$  at different frequencies of the electric field. The term  $\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}$  was then plotted against  $\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty}$  following Cole - Cole semi-circle equation. A suitable chord joining the two fixed points on the semi-circle consistent with all the experimental points is then chosen to yield the relaxation time  $\tau_1$  and  $\tau_2$  of the flexible part and the whole molecule itself. Bhattacharyya et al [9] had subsequently modified the procedure of Bergmann et al [8] to get  $\tau_1$  and  $\tau_2$  of a pure polar liquid in terms of the relaxation parameters measured at two different frequencies of the electric field in the GHz range.

In such a context, we have studied the double relaxation phenomena of some straight chain aliphatic alcohols, namely 1-butanol, 1-hexanol, 1-heptanol and 1-decanol dissolved in n-heptane at 24.33, 9.25 and 3.00 GHz electric field together with methanol and ethanol dissolved in benzene at 9.84 GHz electric field respectively at a temperature of 25°C by the recently developed method [10]. It is usually made with the single frequency measurements of the dielectric relaxation parameters like  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{0ij}$ , and  $\epsilon_{\infty ij}$  of a polar solute (j) in a nonpolar solvent (i) for different weight fractions  $\omega_j$ 's of the polar solute as shown in Table 6.1.  $\tau_1$  and  $\tau_2$  are then obtained from the slope and the intercept of a straight line equation containing the dielectric relaxation data of which  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  should be accurately known [11]. The approach as suggested earlier [10], seems to be an effective tool to detect the double relaxation phenomena of the polar liquid in a nonpolar solvent within the framework of Debye and Smyth model. For such straight chain alcohols behaving almost like polymers, Onsager's equation may be a better choice due to the strong intermolecular force exerted by alcohols in solution owing to their high dipole moments. But the resulting expressions can not be solved so easily as has been done in [10], because of the presence of the quadratic term  $\epsilon^*_{ij}$ . The method [10] was already applied to mono-substituted anilines [12] in benzene in order to get the frequency dependence of  $\tau_1$  and  $\tau_2$  under three different electric fields of 22.06, 3.86 and 2.02 GHz respectively, showing either the double or the mono-relaxation behaviours. p-anisidine alone shows the mono-relaxation behaviour at all frequencies. When the data are extended to 9.945 GHz electric field, all of them, on the other hand, show the double relaxation phenomena [13]. No such rigorous study on monohydric alcohols has been made so far. So it seems worthwhile to make an extensive study on the available data of aliphatic alcohols [14] as well as ethanol and methanol [15,16] with special emphasis on possible occurrence of  $\tau_1$  and  $\tau_2$  in the hf electric field [6].

It is evident from Table 6.2 and Figure 6.1 that all the alcohols show the double relaxation phenomena in all the frequencies of GHz range except methanol at 9.84 GHz, indicating separate broad dispersions in them. Ethanol is a system with  $\tau_2 \gg \tau_1$  while methanol shows very high value of  $\tau_2$  only.  $\tau_1$  and  $\tau_2$  are compared with most probable

**Table 6.1** Dielectric relaxation data like  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{0ij}$ , and  $\epsilon_{\infty ij}$  of some normal alcohols in n-heptane at 25°C from high frequency absorption measurements.

Weight fraction ( $\omega_j$ ) of solute.	frequency in GHz	$\epsilon'_{ij}$	$\epsilon''_{ij}$	$\epsilon_{0ij}$	$\epsilon_{\infty ij}$
System I : 1- Butanol in n-heptane					
0.0292	24.33	1.957	0.0079		
	9.25	1.963	0.0059	1.971	1.928
	3.00	1.970	0.0044		
0.0451	24.331	1.981	0.0147		
	9.25	1.985	0.0121	2.000	1.945
	3.00	1.994	0.0114		
0.0697	24.33	2.011	0.0236		
	9.25	2.015	0.0220	2.05	1.958
	3.00	2.03	0.0188		
0.1163	24.33	2.060	0.0425		
	9.25	2.066	0.0416	2.175	1.978
	3.00	2.101	0.0460		
0.1652	24.33	2.105	0.0644		
	9.25	2.121	0.0637	2.381	2.000
	3.00	2.180	0.0782		
0.2072	24.33	2.144	0.0818		
	9.25	2.172	0.0956	2.621	2.020
	3.00	2.244	0.1119		

System II :- 1-Hexanol in n-heptane.

	24.33	1.968	0.0131		
0.0459	9.25	1.970	0.0083	1.988	1.944
	3.00	1.977	0.0065		
	24.331	1.984	0.019		
0.0703	9.25	1.990	0.0121	2.015	1.952
	3.00	2.003	0.0117		
	24.33	2.001	0.0296		
0.1028	9.25	2.015	0.0226	2.064	1.970
	3.00	2.04	0.0214		
	24.33	2.037	0.0425		
0.1688	9.25	2.074	0.0454	2.196	1.989
	3.00	2.112	0.0446		
	24.33	2.088	0.0569		
0.2335	9.25	2.128	0.0688	2.36	2.002
	3.00	2.186	0.0755		
	24.33	2.134	0.0748		
0.2901	9.25	2.179	0.1000	2.580	2.018
	3.00	2.250	0.1097		

System III:- 1 - heptanol in n-heptane.

	24.33	1.975	0.0182		
0.0735	9.25	1.985	0.0129	2.008	1.945
	3.00	1.998	0.0111		
	24.33	2.007	0.0265		
0.1175	9.25	2.017	0.0232	2.066	1.957
	3.00	2.043	0.0216		
	24.33	2.076	0.0482		
0.1909	9.25	2.079	0.0438	2.195	1.989
	3.00	2.117	0.0456		
	24.33	2.097	0.0567		
0.2465	9.25	2.114	0.0609	2.315	2.002
	3.00	2.175	0.0651		
	24.33	2.126	0.0693		
0.2970	9.25	2.157	0.0774	2.464	2.008
	3.00	2.225	0.0864		

System IV: - 1 - Decanol. in n-heptane.

	24.33	1.965	0.012		
0.0572	9.25	1.968	0.009	1.976	1.94
	3.00	1.972	0.0041		
	24.33	1.979	0.0223		
0.0857	9.25	1.977	0.0146	2.003	1.952
	3.00	1.995	0.0086		
	24.33	2.003	0.0273		
0.1351	9.25	2.011	0.0228	2.05	1.964
	3.00	2.031	0.0194		
	24.33	2.036	0.0449		
0.2140	9.25	2.055	0.0386	2.147	1.990
	3.00	2.088	0.0371		
	24.33	2.064	0.0513		
0.2640	9.25	2.077	0.0484	2.220	2.008
	3.00	2.129	0.0496		
	24.33	2.097	0.0637		
0.3553	9.25	2.123	0.0656	2.346	2.03
	3.00	2.186	0.0690		

System V :- Ethanol in benzene.

0.0664		2.4500	0.008166	3.3	2.2620
0.1393		2.4833	0.012416	4.3	2.1904
0.2077	9.84	2.5000	0.020833	5.4	2.1199
0.2953		2.5500	0.029750	7.0	2.0621
0.3638		2.5666	0.034213	8.2	2.0164

System VI :- Methanol in benzene.

0.0514		2.4666	0.00822	4.8	2.2141
0.0930		2.5000	0.00833	6.5	2.1550
0.1495	9.84	2.5166	0.01677	8.6	2.0851
0.2266		2.5500	0.02975	11.4	2.0164
0.3049		2.5833	0.03875	13.7	1.9600

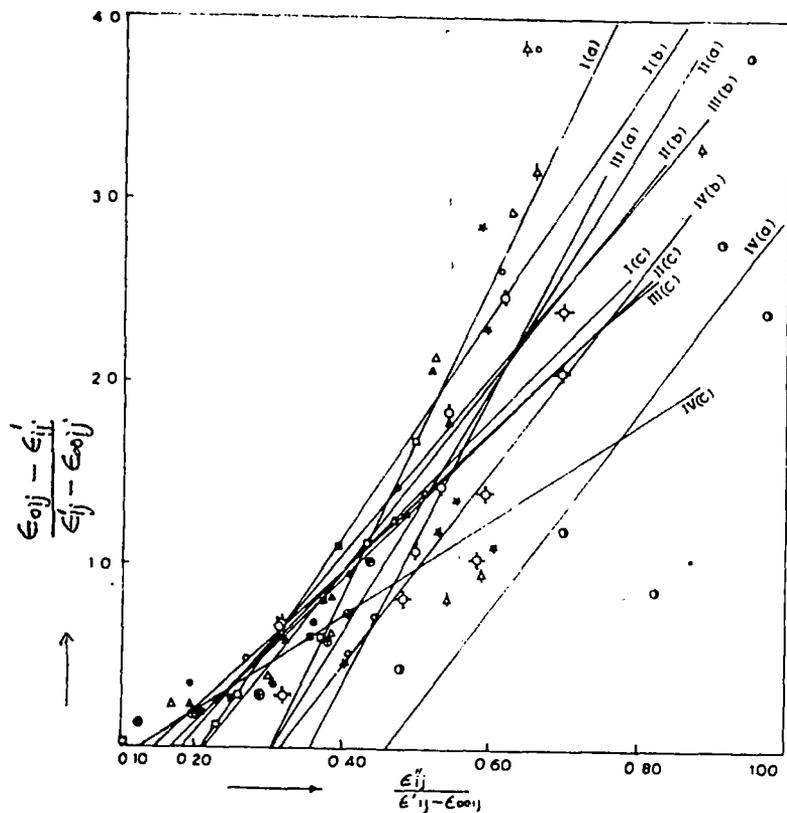


Figure 6.1 Straight line plot of  $(\epsilon_{0ij} - \epsilon'_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})$  against

$\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$  of monoalcohols at 25°C under different *uhf*

electric field

System-I (a): (-O-) for 1-Butanol at 24.33 GHz  
 System-I (b): (-Δ-) for 1-Butanol at 9.25 GHz  
 System-I (c): (□-) for 1-Butanol at 3.00 GHz

System-II (a): (-X-) for 1-Hexanol at 24.33 GHz  
 System-II (b): (-○-) for 1-Hexanol at 9.25 GHz  
 System-II (c): (-●-) for 1-Hexanol at 3.00 GHz

System-III (a): (-\*-) for 1-Heptanol at 24.33 GHz  
 System-III (b): (-▲-) for 1-Heptanol at 9.25 GHz  
 System-III (c): (-■-) for 1-Heptanol at 3.00 GHz

System-IV (a): (-●-) for 1-Decanol at 24.33 GHz  
 System-IV (b): (-○-) for 1-Decanol at 9.25 GHz  
 System-IV (c): (-⊙-) for 1-Decanol at 3.00 GHz

**Table 6.2** The estimated intercept and slopes of straight line equation  $[(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})]$  against  $[\epsilon''_{ij}/\epsilon'_{ij} - \epsilon_{\infty ij}]$  with errors and correlation coefficients together with measured  $\tau$ 's of some normal alcohols at 25°C under different ultra high frequency (- gigahertz) electric field.

System with SI. No. and molecular wt.	Frequency f in GHz	Intercept and slope of equation (6.8)		Correlation coefficient (r)	Percentage error in regression technique	Estimated values of $\tau_2$ and $\tau_1$ in p Sec		Measured $\tau$ , in p Sec	Most probable relaxation time $\tau_0 = \sqrt{\tau_1 \tau_2}$ in p Sec
I) I-Butanol in n-heptane $M_j = 74$ gm	a) 24.33	2.6046	8.6557	0.9013	5.16	54.60	2.04	1.96	10.55
	b) 9.25	1.2809	6.1343	0.9347	3.47	101.87	3.73	4.30	19.49
	c) 3.00	0.6825	4.1544	0.9328	3.57	211.41	9.10	16.98	43.86
II) I-Hexanol in n-heptane $M_j = 102$ gm	a) 24.33	2.045	6.7079	0.6195	18.58	41.81	2.10	2.74	9.37
	b) 9.25	1.0803	5.1697	0.9163	4.42	85.24	3.76	5.86	17.90
	c) 3.00	0.6651	4.0210	0.9308	3.67	204.26	9.17	13.14	43.28
III) I-Heptanol in n-heptane $M_j = 116$ gm	a) 24.33	2.8273	7.9933	0.6752	14.98	49.89	2.43	2.11	11.01
	b) 9.25	0.9233	5.0147	0.9433	3.03	83.03	3.30	5.78	16.55
	c) 3.00	0.6823	4.1075	0.9638	1.95	208.81	9.20	13.49	43.83
IV) I-Decanol in n-heptane $M_j = 158$ gm	a) 24.33	2.4813	5.4316	0.8153	9.23	32.25	3.30	2.69	10.32
	b) 9.25	1.5735	5.1553	0.9463	2.87	83.14	5.61	5.71	21.60
	c) 3.00	0.3316	2.6855	0.9228	4.08	135.66	6.89	14.37	30.57
V) Ethanol in benzene $M_j = 46$ gm	9.84	4.5211	288.7386	0.9416	3.42	4672.26	0.25	3.9	34.18
VI) Methanol in benzene $M_j = 32$ gm	9.84	-5.4003	198.2809	0.8952	5.99	3209.12	—	4.3	—

relaxation time  $\tau_0$  where  $\tau_0 = \sqrt{\tau_1 \tau_2}$  as shown in the last column of Table 6.2. In absence of accurate  $\tau$  for such alcohols,  $\tau$ 's are estimated from the slope of the imaginary part  $K''_{ij}$  and the real part  $K'_{ij}$  of the total uhf conductivity  $K^*_{ij}$  and placed in the 9th column of Table 6.2 for comparison with  $\tau_1$ ,  $\tau_2$  and  $\tau_0$ , respectively.

The relative contributions towards the dielectric relaxation i.e.  $c_1$  and  $c_2$  due to  $\tau_1$  and  $\tau_2$  are estimated by using Fröhlich's equations [17] as well as graphical method (Figures 6.2 and 6.3). They are also shown in Table 6.3.

The dipole moments  $\mu_1$  and  $\mu_2$  of the flexible part as well as of the whole molecule are then estimated in terms of  $\tau$  and slope  $\beta$  of the linear plot of  $K''_{ij}$  against  $\omega_j$  (Figure 6.4). They are shown in Table 6.4 in order to compare with  $\mu_0$  due to  $\tau_0$  and  $\mu_{theo}$  from bond angles and bond moments (Figure 6.5) respectively. The  $\mu_1$ 's in terms of  $c_1$ ,  $c_2$  and  $\mu_0$  are also calculated by assuming that the two relaxation processes are equally probable; and they are placed in the last column of Table 6.4 only to compare with  $\mu_1$  due to  $\tau_1$ .

### 6.2 Theoretical formulations to estimate $\tau_1$ , $\tau_2$ ; $c_1$ , $c_2$ and $\mu_1$ , $\mu_2$ .

The complex dielectric constant  $\epsilon^*_{ij}$  of a polar non-polar liquid mixture can be represented as the sum of a number of non-interacting Debye type dispersions in accordance with the Budo's [18] relation as:

$$\frac{\epsilon^*_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \sum_k \frac{c_k}{1 + j\omega\tau_k} \quad \dots\dots(6.1)$$

where  $j = \sqrt{-1}$  and  $\sum c_k = 1$ . The term  $c_k$  is the weight factor for the  $k$ -th type of relaxation mechanism. When the complex dielectric constant  $\epsilon^*_{ij}$  consist of two non-interacting Debye type dispersions, Budo's relation reduces to Bergmann's [8] equations:

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \dots\dots(6.2)$$

$$\text{and } \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2 \tau_2^2} \quad \dots\dots(6.3)$$

such that  $c_1 + c_2 = 1$ , where  $c_1$  and  $c_2$  are the relative contributions towards dielectric relaxations due to intra-molecular relaxation time  $\tau_1$  and molecular relaxation time  $\tau_2$ .

Putting  $\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = x$  and  $\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = y$  with  $\omega\tau = \alpha$  and using the abbreviations,

$a = \frac{1}{1+\alpha^2}$  and  $b = \frac{\alpha}{1+\alpha^2}$ , the above eqs. (6.2) and (6.3) can be written as

$$x = c_1 a_1 + c_2 a_2, \quad \dots\dots(6.4)$$

$$y = c_1 b_1 + c_2 b_2, \quad \dots\dots(6.5)$$

where suffices 1 and 2 with a and b are related to  $\tau_1$  and  $\tau_2$  respectively. From eqs. (6.4) and (6.5) since  $\alpha_2 - \alpha_1 \neq 0$  and  $\alpha_2 > \alpha_1$  we have

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots\dots(6.6)$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots\dots(6.7)$$

Now, using  $c_1 + c_2 = 1$ , one gets the following equation with the help of eqs. (6.6) and (6.7)

$$\frac{1-x}{y} = (\alpha_1 + \alpha_2) - \frac{x}{y} \alpha_1 \alpha_2$$

which, on substitution of the values of x, y and  $\alpha$  yields

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega (\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2 \quad \dots\dots(6.8)$$

Equation (6.8) is a straight line between  $\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}}$  and  $\frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}}$  with slope  $\omega (\tau_1 + \tau_2)$

and intercept  $-\omega^2 \tau_1 \tau_2$  respectively. Here,  $\omega$  = angular frequency of the applied electric field of frequency  $f$  in GHz. When the eq. (6.8) is fitted with the measured dielectric relaxation data  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{0ij}$ , and  $\epsilon_{\infty ij}$  for different weight fractions  $w_j$ 's of each alcohol in

n-heptane (at 25°C under 24.33, 9.25 and 3.00 GHz electric fields) as well as of methanol and ethanol in benzene (at 9.84 GHz), we get the slopes and intercepts as shown in Table 6.2 to yield  $\tau_1$  and  $\tau_2$ .

The relative contributions  $c_1$  and  $c_2$  towards the dielectric relaxations in terms of  $x, y$  and  $\tau_1, \tau_2$  for each alcohol are found out and shown in Table 6.3. The theoretical values of  $x$  and  $y$  are, however, calculated from Fröhlich's equations [17] as

$$x = \frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left( \frac{e^{2A} \omega^2 \tau_s^2 + 1}{1 + \omega^2 \tau_s^2} \right), \quad \dots\dots(6.9)$$

and

$$y = \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} \left[ \tan^{-1}(e^A \omega \tau_s) - \tan^{-1}(\omega \tau_s) \right], \quad \dots\dots(6.10)$$

where  $A = \text{Fröhlich parameter} = \ln(\tau_2/\tau_1)$  and  $\tau_s$  is called the small limiting relaxation time being given by  $\tau_s = \tau_1$ . A simple graphical extrapolation technique, on the other hand, has been adopted here to get the values of  $x$  and  $y$  at  $\omega_j \rightarrow 0$ , as illustrated graphically in Figures 6.2 and 6.3 respectively. This is really in accord with Bergmann's eqs. (6.2) and (6.3) when the once estimated  $\tau_1$  and  $\tau_2$  from eq (6.8) are substituted in the right hand sides of the above eqs. (6.2) and (6.3).

The dipole moments  $\mu_1$  and  $\mu_2$  of polar solutes in terms of  $\tau_1$  and  $\tau_2$  as obtained from the double relaxation method and slope  $\beta$  of the concentration variation of the experimental uhf conductivity  $K_{ij}$  are then estimated. The uhf conductivity  $K_{ij}$  is, however, given by Murphy and Morgan [19] as

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon''_{ij}{}^2 + \epsilon'_{ij}{}^2)^{1/2}, \quad \dots\dots(6.11)$$

which is a function of  $\omega_j$  of polar solute. Although  $\epsilon''_{ij} < \epsilon'_{ij}$  in the uhf electric field, still the term  $\epsilon''_{ij}$  offers resistance to polarisation. Thus, the real part  $K'_{ij}$  of the uhf conductivity of a polar-nonpolar liquid mixture at  $T^\circ\text{K}$  can be written according to Smyth [20] as:

**Table 6.3** Fröhlich parameter A, relative contributions  $c_1$  and  $c_2$  due to  $\tau_1$  and  $\tau_2$ , theoretical values of  $x$  and  $y$  due to Fröhlich equations (6.9) and (6.10) and those by our method at infinite dilution for monoalcohols under different uhf electric field at 25°C.

System with Sl. No. and molecular wt.	Frequency f in GHz	Fröhlich parameter $A=\ln(\tau_2/\tau_1)$	Theoretical values of $x$ and $y$ from eq. no. (6.9) and (6.10)		Theoretical values of $c_1$ and $c_2$ from eq. no. (6.4 ) and (6.5)		Estimated values of $x$ and $y$ at $\omega_j \rightarrow 0$ from Figs. (6.2) and (6.3)		Estimated values of $c_1$ and $c_2$ from graphical technique	
I) 1-Butanol in n-heptane $M_j = 74\text{gm}$	(a) 24.33	3.2871	0.3666	0.3495	0.3701	2.0678	0.83	0.218	0.9162	-0.3579
	(b) 9.25	3.3073	0.4651	0.3596	0.4394	1.6354	0.99	0.15	1.0483	-0.4076
	(c) 3.00	3.1455	0.5556	0.3670	0.4985	1.2024	1.11	0.13	1.1589	-0.2668
II) 1-Hexanol in n-heptane $M_j = 102\text{gm}$	(a) 24.33	2.9912	0.3924	0.3692	0.3885	1.6769	0.79	0.264	0.8694	-0.0725
	(b) 9.25	3.1211	0.4885	0.3704	0.4535	1.4215	0.70	0.130	0.7385	-0.1234
	(c) 3.00	3.1035	0.5600	0.3689	0.5004	1.1707	1.005	0.078	1.0618	-0.4113
III) 1-Heptanol in n-heptane $M_j = 116\text{ gm}$	(a) 24.33	3.0219	0.3464	0.3588	0.3580	1.8763	0.655	0.236	0.7464	-0.0586
	(b) 9.25	3.2253	0.5112	0.3647	0.4703	1.3973	0.835	0.130	0.8724	-0.1575
	(c) 3.00	3.1222	0.5560	0.3682	0.4983	1.1910	1.045	0.116	1.0942	-0.2853
IV) 1-Decanol in n-heptane $M_j = 158\text{ gm}$	(a) 24.33	2.2796	0.3412	0.3962	0.3644	1.2809	1.11	0.29	1.4687	-1.5413
	(b) 9.25	2.6960	0.4268	0.3899	0.4105	1.3544	0.955	0.17	1.0911	-0.7627
	(c) 3.00	2.9801	0.6640	0.3585	0.5611	0.8453	1.005	0.012	1.0716	-0.3678
V) Ethanol in benzene $M_j = 46\text{ gm}$	9.84	9.8357	0.4240	0.1577	0.4236	43.6436	0.24	0.0099	0.2400	1.7937

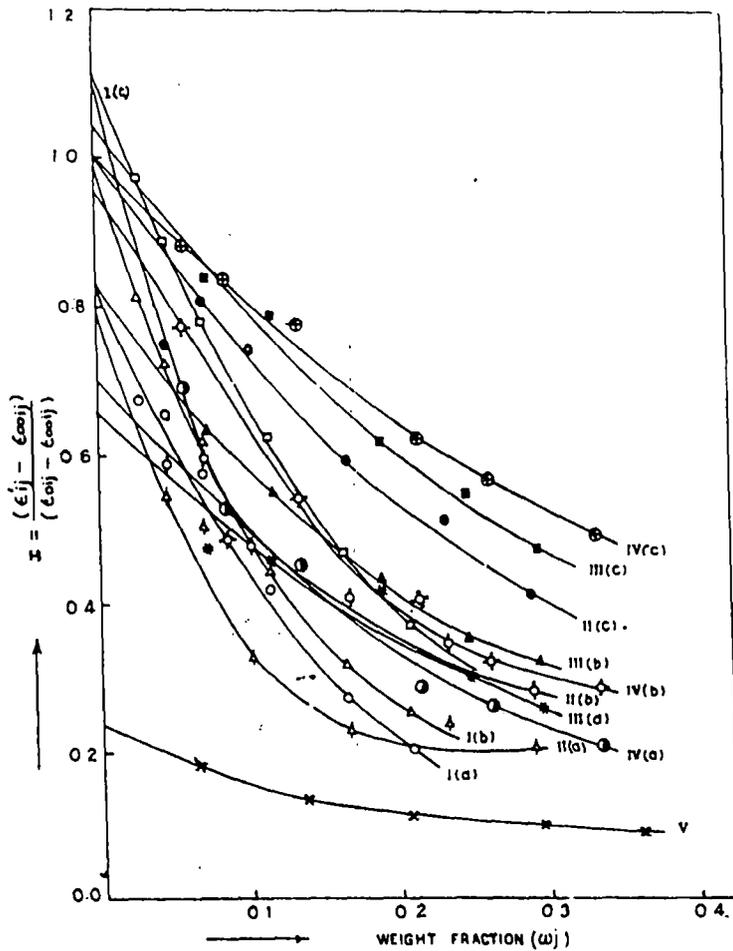
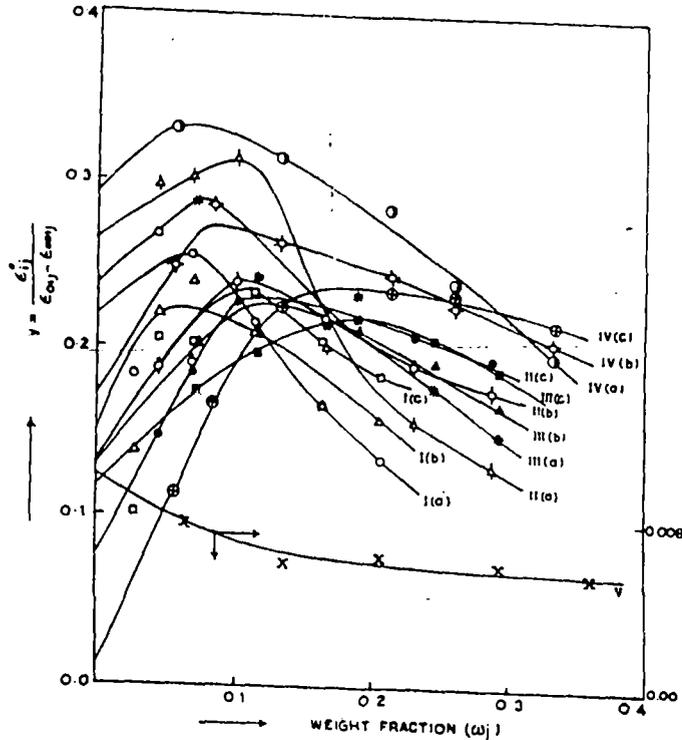


Figure 6.2 Variation of  $(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$  against weight fraction  $\omega_j$  for monoalcohols at different *uhf* electric field

- |                        |                             |
|------------------------|-----------------------------|
| System-I (a): (-O-)    | for 1-Butanol at 24.33 GHz  |
| System-I (b): (-Δ-)    | for 1-Butanol at 9.25 GHz   |
| System-I (c): (-□-)    | for 1-Butanol at 3.00 GHz   |
| System-II (a): (-△-)   | for 1-Hexanol at 24.33 GHz  |
| System-II (b): (-○-)   | for 1-Hexanol at 9.25 GHz   |
| System-II (c): (-●-)   | for 1-Hexanol at 3.00 GHz   |
| System-III (a): (-* -) | for 1-Heptanol at 24.33 GHz |
| System-III (b): (-▲-)  | for 1-Heptanol at 9.25 GHz  |
| System-III (c): (-■-)  | for 1-Heptanol at 3.00 GHz  |
| System-IV (a): (-⊙-)   | for 1-Decanol at 24.33 GHz  |
| System-IV (b): (-⊖-)   | for 1-Decanol at 9.25 GHz   |
| System-IV (c): (-⊗-)   | for 1-Decanol at 3.00 GHz   |
| System-V : (-X-)       | for 1-Ethanol at 9.84 GHz   |



**Figure 6.3** Variation of  $\epsilon'_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$  against weight fraction  $\omega_j$  for monoalcohols at different *uhf* electric field

- |  |                             |
|--|-----------------------------|
| System-I (a): (-O-)                    | for 1-Butanol at 24.33 GHz  |
| System-I (b): (- $\Delta$ -)           | for 1-Butanol at 9.25 GHz   |
| System-I (c): ( $\square$ -)           | for 1-Butanol at 3.00 GHz   |
| System-II (a): (- $\bar{\Delta}$ -)    | for 1-Hexanol at 24.33 GHz  |
| System-II (b): (- $\bar{O}$ -)         | for 1-Hexanol at 9.25 GHz   |
| System-II (c): (- $\bullet$ -)         | for 1-Hexanol at 3.00 GHz   |
| System-III (a): (-*\$-\$)              | for 1-Heptanol at 24.33 GHz |
| System-III (b): (- $\blacktriangle$ -) | for 1-Heptanol at 9.25 GHz  |
| System-III (c): (- $\blacksquare$ -)   | for 1-Heptanol at 3.00 GHz  |
| System-IV (a): (- $\odot$ -)           | for 1-Decanol at 24.33 GHz  |
| System-IV (b): (- $\odot$ -)           | for 1-Decanol at 9.25 GHz   |
| System-IV (c): (- $\oplus$ -)          | for 1-Decanol at 3.00 GHz   |
| System-V : (-X-)                       | for 1-Ethanol at 9.84 GHz   |

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT} \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \omega_j \quad \text{.....(6.12)}$$

Differentiating the above eq. (6.12) with respect to  $\omega_j$  and for  $\omega_j \rightarrow 0$ , the eq (6.12) reduces to

$$\left( \frac{dK'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad \text{.....(6.13)}$$

where,  $M_j$  is the molecular weight of a polar solute,  $N$  is the Avogadro's number,  $k$  is the Boltzman's constant, the local field  $F_{ij} = \frac{1}{9}(\epsilon_{ij} + 2)^2$  becomes  $F_i = \frac{1}{9}(\epsilon_i + 2)^2$  and the density  $\rho_{ij} \rightarrow \rho_i$  the density of solvent at  $\omega_j \rightarrow 0$ .

Again, the total uhf conductivity  $K_{ij} = \frac{\omega}{4\pi} \epsilon'_{ij}$  can now be written as :

$$K_{ij} = K_{\infty ij} + \frac{1}{\omega\tau} K'_{ij}$$

or

$$\left( \frac{dK'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \omega\tau \left( \frac{dK_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \omega\tau\beta, \quad \text{.....(6.14)}$$

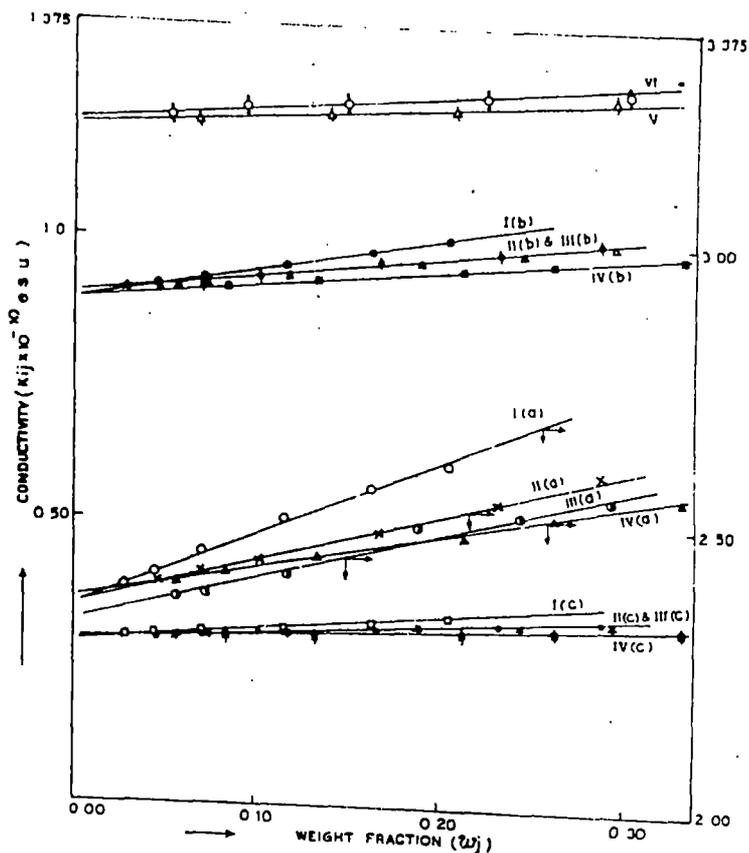
where  $\beta$  is the slope of  $K_{ij} - \omega_j$  curve at infinite dilution, From eqs. (6.13) and (6.14) we thus get

$$\mu_j = \left( \frac{3M_j k T \beta}{N \rho_i F_i \omega b} \right)^{1/2} \quad \text{.....(6.15)}$$

in order to obtain the dipole moment in terms of  $b$ , where  $b$  is a dimensionless parameter given by

$$b = \frac{1}{1 + \omega^2 \tau^2} \quad \text{.....(6.16)}$$

The computed  $\mu_1$ ,  $\mu_2$  and  $\mu_0$  together with  $b_1$ ,  $b_2$  and  $b_0$  and  $\beta$ 's of  $K_{ij} - \omega_j$  equations for all the alcohols are given in Table. 6.4.



**Figure 6.4** Straight line plots of  $K_{ij}$  against  $\omega_j$  under different uhf electric field at 25°C

System-I (a): (-O-)	for 1-Butanol at 24.33 GHz
System-I (b): (-*-)	for 1-Butanol at 9.25 GHz
System-I (c): (-□-)	for 1-Butanol at 3.00 GHz
System-II (a): (-X-)	for 1-Hexanol at 24.33 GHz
System-II (b): (-◐-)	for 1-Hexanol at 9.25 GHz
System-II (c): (-●-)	for 1-Hexanol at 3.00 GHz
System-III (a): (-⊙-)	for 1-Heptanol at 24.33 GHz
System-III (b): (-Δ-)	for 1-Heptanol at 9.25 GHz
System-III (c): (-*-)	for 1-Heptanol at 3.00 GHz
System-IV (a): (-▲-)	for 1-Decanol at 24.33 GHz
System-IV (b): (-■-)	for 1-Decanol at 9.25 GHz
System-IV (c): (-◼-)	for 1-Decanol at 3.00 GHz
System-V : (-△-)	for Ethanol at 9.84 GHz
System-VI : (-◊-)	for Methanol at 9.84 GHz

### 6.3. Results and discussions

The least - square - fitted straight line equations of  $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$  against  $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$  for different weight fractions  $\omega_j$ 's of 1-butanol, 1-hexanol, 1-heptanol and 1-decanol in n-heptane under alternating electric field of 24.33; 9.25 and 3.00 GHz at 25°C are shown in Figure 6.1, together with the experimental points on them as seen in Table 6.1. The straight line equations of methanol and ethanol in benzene at 9.84 GHz are:

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = 198.2809 \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} + 5.4003$$

and

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = 288.7386 \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - 4.5211 \text{ respectively.}$$

The experimental data of  $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$  for methanol and ethanol are so high that they can not be plotted in Figure 6.1. In absence of reliable values of  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  for methanol, it is not possible to show the applicability of simple mixing rule in determining relaxation data for this system. But the method has been applied to ethanol and it is found that the  $\tau$  value is 3207.57 p Sec which is in good agreement with the measured data as presented in Table 6.2. The weight fractions  $\omega_j$ 's of the respective solutes have been obtained from mole fractions  $x_i$  and  $x_j$  of the solvent and solute of molecular weights  $M_i$  and  $M_j$  respectively by a relation [21]

$$\omega_j = \frac{x_j M_j}{x_i M_i + x_j M_j} \quad \dots\dots(6.17)$$

The linearity of all the straight lines, as illustrated in Figure 6.1; is, however, tested by evaluating their correlation coefficient  $r$ . They are found to lie within the range of 0.9638 to 0.6195 as shown in Table 6.2. The corresponding percentage of errors in the fitting technique, can be had from the correlation coefficients. They are all shown in the 5-th and the 6-th columns of Table 6.2 respectively. The errors, are, however, large in magnitudes in the hf electric field of 24.33 GHz for 1-hexanol, 1-heptanol and 1-decanol respectively, probably due to unavoidable uncertainty in measurements of relaxation parameters for such higher frequency.

$\tau_1$  and  $\tau_2$  for each alcohol are estimated from the slope and the intercept of straight line eq (6.8) and are placed in the 7-th and the 8-th columns of Table 6.2 respectively. All the monoalcohols show  $\tau_1$  and  $\tau_2$  at all the frequencies with an exception for methanol which exhibits the monorelaxation behaviour [12].

The monorelaxation behaviour [12] can easily be evaluated on the basis of the relaxation parameters by putting  $c_1 = 0$  in eqs (6.2) and (6.3). The resulting equation becomes :

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega \tau_2 \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} \quad \dots\dots(6.18)$$

$\tau_2$  for methanol is found to be 5254.3 p Sec in approximate agreement with  $\tau_2$  as obtained by double relaxation method (Table 6.2).  $\tau_2$ 's and  $\tau_1$ 's as obtained from the double relaxation method are then compared with the most probable relaxation time  $\tau_0$  where  $\tau_0 = \sqrt{\tau_1 \tau_2}$  and the measured relaxation time  $\tau_s$ 's from the slope of the given relation :

$$K''_{ij} = K_{\infty ij} + \frac{1}{\omega \tau_s} K'_{ij}, \quad \dots\dots(6.19)$$

where  $K_{\infty ij}$  is the constant conductivity at infinite dilution. Both  $\tau_0$  and  $\tau_s$  are shown in the 10-th and the 9-th columns of Table 6.2 respectively.  $\tau_2$  and  $\tau_1$  for the double relaxation processes show low values at 24.33 GHz and increase gradually at the lower frequencies of 9.25 and 3.00 GHz respectively. This is explained on the basis of the fact that at higher frequency, the rate of hydrogen bond rupture in long chain alcohols may be maximum to reduce  $\tau$  for each rotating unit. This sort of behaviour is also observed in the estimated  $\tau_s$  and  $\tau_0$  respectively. Although the measured  $\tau_s$  and  $\tau_0$  are smaller in magnitudes,  $\tau_1$  agrees excellently with  $\tau_s$  (Table 6.2). This is perhaps due to the fact that the hf conductivity measurement always yields the average microscopic relaxation time whereas the double relaxation phenomena offers a better understanding of microscopic as well as macroscopic molecular relaxation times.

The relative contributions  $c_1$  and  $c_2$  towards dielectric relaxations for each alcohol have been evaluated from Bergmann's eqs. (6.2) and (6.3) for fixed values of  $\tau_1$  and  $\tau_2$  as

predicted by eqs. (6.8) with the estimated  $x$  and  $y$  from graphical technique as well as from Fröhlich's eqs. (6.9) and (6.10) respectively.  $c_1$  and  $c_2$  thus obtained by Fröhlich's method are placed in the 6-th and 7-th columns of Table 6.3. In the 10-th and the 11-th columns of the same Table 6.3 are shown  $c_1$  and  $c_2$  values with the fixed values of  $x$  and  $y$  at infinite dilutions of Figures 6.2 and 6.3. The variations of  $x$  and  $y$  with  $\omega_j$  are concave and convex in nature as illustrated graphically in Figures 6.2 and 6.3 in accordance with Bergmann's eqs (6.2) and (6.3) respectively. Ethanol is an exception whose  $y$  value changes in a similar way as  $x$ . This anomaly is perhaps due to nonavailability of the accurate  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  [11], and it thereby yields abnormally high  $\tau$  value like methanol, although the latter one exhibits monorelaxation behaviours as shown in Table 6.2. However, the estimated value of  $c_2$  is greater than  $c_1$  for each alcohol, under investigation, in Fröhlich's method, while the reverse is true for the graphical method. Eventually,  $c_2$  is -ve for most of the cases except l-hexanol at 24.33 GHz and ethanol at 9.84 GHz respectively in the latter case. This -ve value of  $c_2$  is due to inertia of the flexible part [10]. This type of behaviour may be explained on the basis of the fact that the latter one ascertains the nature of the flexible part in comparison to Fröhlich's method. It is also interesting to note that unlike Fröhlich's method, the latter method yields  $c_1 + c_2 < 1$  except for l-decanol at 24.33 GHz where  $c_1 + c_2 < 0$ , although  $|c_1 + c_2| > 1$  signifying more than two relaxation processes may be possible in them [14].

The dipole moments  $\mu_1$  and  $\mu_2$  of all the alcohols, as enlisted in Table 6.4 were estimated in terms of dimensionless parameters  $b_1$  and  $b_2$  and slopes  $\beta$  of  $K_{ij}$  versus  $\omega_j$  equations by using eq (6.15). The linear variation of uhf conductivities  $K_{ij}$  of all the alcohols as a function of  $\omega_j$ 's are shown in Figure 6.4. The correlation coefficient  $r$  and the corresponding percentage of error in the estimation of the slope  $\beta$  and hence all the  $\mu$ 's together with  $b$ 's are shown in Table 6.4. From Table 6.4,  $\mu_2$ 's are, however, found to be large at 24.33 GHz while in comparatively lower frequencies like 9.25 and 3.00 GHz, they are gradually smaller for each polar alcohol under our investigation. But  $\mu_1$ 's, on the other

hand, show the opposite trend. It is also interesting to note that the values of  $\mu_2$ 's for all the alcohols decrease with the increase of C-atoms in them. This type of behaviour may be explained by the fact that the long chain polymer type molecules having a large number of carbon atoms, in a nonpolar solvent, tend to break up in the hf electric field in order to reduce or even eliminate the absorption attributable to them. The proportion of smaller molecular species, on the other hand, have comparatively smaller number of C-atoms and the corresponding absorption will increase [14]. This is also confirmed by the fact that as  $\tau$  decreases with increasing  $\omega$ , the term  $\omega^2\tau^2$  is higher and therefore, eq (6.16) yields smaller  $b$  values to increase  $\mu$ 's according to eq. (6.15).

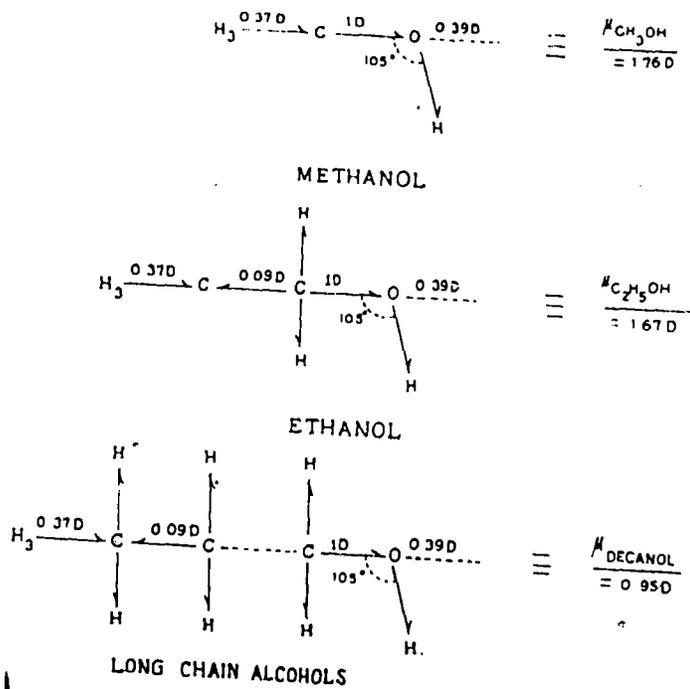
$\mu_1$ ,  $\mu_2$  and  $\mu_0$  are finally compared with  $\mu_{\text{theo}}$  for the orientational polarisation of all the associated liquids containing a large number of dipolar groups like  $\text{H}_3 \rightarrow \text{C}$ ,  $\text{C} \leftarrow \text{O}$  and  $\text{O} \leftarrow \text{H}$  when their individual monomeric moments are added vectorially as shown in Figure 6.5.  $\mu_{\text{theo}}$  may also be inferred from Fröhlich's equation having correlation factor which bears structural information for such liquids. But to a fair approximation, the structural conformation of such liquids, as shown diagrammatically in Figure 6.5 and placed in Table 6.4, from the bond moments of  $\text{H}_3 \rightarrow \text{C}$ ,  $\text{C} \leftarrow \text{O}$  and  $\text{O} \leftarrow \text{H}$  and the bond angle of  $105^\circ$  made by  $-\text{OH}$  groups with the main bond axis, have major contributions in yielding the theoretical dipole moment,  $\mu_{\text{theo}}$ . All the  $\mu$ 's are displayed in Table 6.4 with those of  $\mu_1$ ,

where  $\mu_1 = \mu_2 \left( \frac{c_1}{c_2} \right)^{1/2}$  assuming the two relaxation processes are equally probable. These  $\mu_1$ 's are slightly larger in magnitudes in comparison to  $\mu_{\text{theo}}$ ,  $\mu_1$  and  $\mu_0$  which are in close agreement among themselves.

#### 6.4. Conclusion

The methodology so far advanced for double and single broad dispersions of the polar-nonpolar liquid mixtures seems to be much simpler, straightforward and significant one to detect the existence of double and monorelaxation behaviours of polar liquids in nonpolar solvents. The correlation coefficients between the desired parameters as given in





**Figure 6.5** Conformational structures of methanol, ethanol and decanol

eqs. (6.8) and (6.18) could, however, be estimated to find out the percentage of errors entered in the dielectric relaxation data, to yield  $\tau_1$  and  $\tau_2$  of the polar liquids, because the relaxation times  $\tau$ 's are claimed to be accurate within  $\pm 10\%$ . The monohydric alcohols so far studied always yield, both  $\tau_1$  and  $\tau_2$  at all frequencies of the electric field. The corresponding dipole moments  $\mu_1$  and  $\mu_2$  can then be estimated from eq. (6.15) in terms of  $b_1$  and  $b_2$  (which are, however, related to  $\tau_1$  and  $\tau_2$  as estimated) to arrive at their conformations as shown in Figure 6.5

### Acknowledgment

The authors are thankful to Mr. A. R. Sit, BE (Electrical) for his interest in this work.

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