

## *CHAPTER 10*

**MATERIAL PROPERTY OF DIPOLAR LIQUID IN  
NONPOLAR SOLVENT THROUGH RELAXATION  
PHENOMENA UNDER HIGH FREQUENCY  
ELECTRIC FIELD - A NOVEL IDEA**

## 10.1. Introduction :

Relaxation phenomena is an important tool to measure relaxation time  $\tau_j$ , dipole moment  $\mu_j$ , shape, size as well as molecular interactions of a dipolar liquid molecule in a non-polar solvent under high frequency ( $hf$ ) electric field [10.1-10.2]. There are various established techniques [10.3-10.4] like thermally stimulated depolarisation current (TSDC) and isothermal frequency domain AC spectroscopy by which one can estimate  $\mu_j$  and  $\tau_j$  of a polar liquid molecule. Nevertheless, one can use Debye and Smyth model to determine  $\tau_j$  and  $\mu_j$  of a dipolar liquid molecule because of its simplicity and straightforwardness. Crossley *et al* [10.5] and Glasser *et al* [10.6] proposed that the normal and isomeric octyl alcohols were expected to show triple relaxation times under  $hf$  electric field of GHz range when they are diluted with non-polar solvent *n*-heptane. Alcohols show double relaxation times [10.7-10.8]  $\tau_2$  and  $\tau_1$  due to end over end rotation as well as rotation of the flexible part of the molecule at all frequencies of 3.00, 9.25 and 24.33 GHz electric field.

We, therefore, thought to study these alcohols again because of its diverse nature in different environments. The alcohols are hydrogen bonded polymer type molecules. Some of the octyl alcohols are isomers. They usually showed  $\alpha$ ,  $\beta$  and  $\gamma$  relaxation in  $hf$  electric field. It was observed [10.9] that  $\mu_j$ 's of alcohols vary slightly when measurements are done in terms of either relative permittivities  $\epsilon_{ij}$ 's or conductivity  $\sigma_{ij}$ 's in SI units. The other parameter  $\tau_j$ , however, remains same in both cases. Nowadays, it is the practice to study the relaxation phenomena in terms of orientation susceptibilities  $\chi_{ij}$ 's [10.10-10.11] rather than  $\epsilon_{ij}$ 's or  $\sigma_{ij}$ 's.  $\epsilon_{ij}$  includes all types of polarisations whereas  $\sigma_{ij}$  is concerned with the bound molecular charges.  $\chi_{ij}$ 's, on the other hand, are related to orientation polarisations of the molecule. The purpose of the present paper is to study the existence of double relaxation times of alcohols between two limiting  $\tau$ 's in terms of  $hf$   $\chi_{ij}$ 's. The chemical systems under consideration are identical and they are in same environment. If any system shows double relaxation times at one frequency it will show the same double relaxation times  $\tau_1$  and  $\tau_2$  at all the frequencies because the double relaxation phenomenon is the material property of the system. Saha *et al* and Sit *et al* [10.12-10.13] proposed a very simple and easy technique to measure the double relaxation times of a polar-nonpolar liquid mixture at a given experimental temperature under a single frequency of the electric field. The estimated  $\tau$ 's are different in different frequencies of the electric field. Moreover,  $\tau_1$  and  $\tau_2$  from the single frequency measurement technique is not so reliable [10.14-10.15].

In this context, we propose a graphical technique to estimate  $\tau_1$  and  $\tau_2$  of some alcohols (j) in a non-polar solvent (i) in terms of real  $\chi_{ij}'$  and imaginary  $\chi_{ij}''$  parts of  $hf$  complex dielectric orientation susceptibilities  $\chi_{ij}^*$  under 3.00, 9.25 and 24.33 GHz electric field and low frequency

Table 10.1: Concentration variation of the real part  $\chi_{ij}'$  and imaginary part  $\chi_{ij}''$  of dimensionless complex dielectric orientation susceptibility  $\chi_{ij}^*$  and the static dielectric orientation susceptibility  $\chi_{oj}$  which is real of some normal and isomeric octyl alcohols in *n*-heptane under 3.00, 9.25 and 24.33 GHz electric fields.

Frequency $f$ in GHz	Weight fraction $w_j$	$\chi_{ij}'$	$\chi_{ij}''$	$\chi_{oj}$	Weight fraction $w_j$	$\chi_{ij}'$	$\chi_{ij}''$	$\chi_{oj}$
		I. 1-Butanol			II. 1-Hexanol			
3.00	0.0451	0.049	0.0114	0.055	0.0459	0.033	0.0065	0.044
	0.0697	0.072	0.0188	0.093	0.0703	0.051	0.0117	0.063
	0.1163	0.123	0.0460	0.197	0.1028	0.070	0.0214	0.094
	0.1652	0.180	0.0782	0.381	0.1688	0.123	0.0446	0.207
	0.2072	0.224	0.1119	0.601	0.2335	0.184	0.0755	0.358
				0.2901	0.232	0.1097	0.562	
9.25	0.0451	0.040	0.0121	0.055	0.0459	0.026	0.0083	0.044
	0.0697	0.057	0.0220	0.093	0.0703	0.038	0.0121	0.063
	0.1163	0.088	0.0416	0.197	0.1028	0.045	0.0226	0.094
	0.1652	0.121	0.0637	0.381	0.1688	0.085	0.0454	0.207
	0.2072	0.152	0.0956	0.601	0.2335	0.126	0.0688	0.358
				0.2901	0.161	0.1000	0.562	
24.33	0.0451	0.036	0.0147	0.055	0.0459	0.024	0.0131	0.044
	0.0697	0.053	0.0236	0.093	0.0703	0.032	0.0190	0.063
	0.1163	0.082	0.0425	0.197	0.1028	0.031	0.0296	0.094
	0.1652	0.105	0.0644	0.381	0.1688	0.048	0.0425	0.207
	0.2072	0.124	0.0818	0.601	0.2335	0.086	0.0569	0.358
				0.2901	0.116	0.0748	0.562	
		III. 1-Heptanol			IV. 1-Decanol			
3.00	0.0735	0.053	0.0111	0.056	0.0572	0.032	0.0051	0.036
	0.1175	0.086	0.0216	0.109	0.1351	0.067	0.0194	0.086
	0.1909	0.128	0.0456	0.236	0.2140	0.098	0.0371	0.157
	0.2465	0.173	0.0651	0.313	0.2640	0.121	0.0496	0.212
	0.2970	0.217	0.0864	0.456	0.3353	0.156	0.0690	0.316
9.25	0.0735	0.040	0.0129	0.056	0.0572	0.028	0.0090	0.036
	0.1175	0.060	0.0232	0.109	0.1351	0.047	0.0228	0.086
	0.1909	0.090	0.0438	0.236	0.2140	0.065	0.0386	0.157
	0.2465	0.112	0.0609	0.313	0.2640	0.069	0.0484	0.212
	0.2970	0.149	0.0774	0.456	0.3353	0.093	0.0656	0.316
24.33	0.0735	0.030	0.0182	0.056	0.0572	0.025	0.0120	0.036
	0.1175	0.050	0.0265	0.109	0.1351	0.039	0.0273	0.086
	0.1909	0.087	0.0482	0.236	0.2140	0.046	0.0400	0.157
	0.2465	0.095	0.0567	0.313	0.2640	0.056	0.0513	0.212
	0.2970	0.118	0.0694	0.456	0.3353	0.067	0.0637	0.316
		V. 2-methyl 3-heptanol			VI. 3-methyl 3-heptanol			
3.00	0.0437	0.040	0.0040	0.041	0.0450	0.040	0.0043	0.040
	0.1299	0.086	0.0137	0.093	0.1334	0.099	0.0131	0.103
	0.2522	0.143	0.0309	0.165	0.2538	0.162	0.0272	0.176
	0.4081	0.215	0.0583	0.276	0.4085	0.242	0.0489	0.277
9.25	0.0437	0.037	0.0088	0.041	0.0450	0.034	0.0103	0.040
	0.1299	0.078	0.0244	0.093	0.1334	0.079	0.0263	0.103
	0.2522	0.108	0.0412	0.165	0.2538	0.126	0.0458	0.176
	0.4081	0.164	0.0710	0.276	0.4085	0.192	0.0766	0.277
24.33	0.0437	0.030	0.0156	0.041	0.0450	0.031	0.0187	0.040
	0.1299	0.056	0.0362	0.093	0.1334	0.061	0.0394	0.103
	0.2522	0.088	0.0565	0.165	0.2538	0.099	0.0674	0.176
	0.4081	0.115	0.0809	0.276	0.4085	0.131	0.0928	0.277

Frequency $f$ in GHz	Weight fraction $w_j$	$\chi_{ij}'$	$\chi_{ij}''$	$\chi_{oij}$	Weight fraction $w_j$	$\chi_{ij}'$	$\chi_{ij}''$	$\chi_{oij}$
	VII. 4-methyl 3-heptanol				VIII. 5-methyl 3-heptanol			
3.00	0.0466	0.039	0.0046	0.040	0.1228	0.084	0.0143	0.092
	0.1326	0.090	0.0147	0.096	0.2489	0.134	0.0337	0.164
	0.2590	0.156	0.0338	0.174	0.3898	0.202	0.0554	0.275
	0.4124	0.224	0.0572	0.287				
9.25	0.0466	0.034	0.0091	0.040	0.1228	0.068	0.0225	0.092
	0.1326	0.076	0.0262	0.096	0.2489	0.095	0.0441	0.164
	0.2590	0.112	0.0472	0.174	0.3898	0.143	0.0706	0.275
	0.4124	0.168	0.0766	0.287				
24.33	0.0466	0.028	0.0146	0.040	0.1228	0.051	0.0297	0.092
	0.1326	0.055	0.0376	0.096	0.2489	0.071	0.0511	0.164
	0.2590	0.093	0.0616	0.174	0.3898	0.107	0.0675	0.275
	0.4124	0.115	0.0849	0.287				
	IX. 2-octanol				X. 4-octanol			
3.00	0.1236	0.078	0.0156	0.065	0.1201	0.081	0.0129	0.092
	0.2479	0.137	0.0419	0.199	0.2445	0.120	0.0302	0.151
	0.3844	0.207	0.0791	0.374	0.3838	0.181	0.0549	0.251
9.25	0.1236	0.061	0.0227	0.065	0.1201	0.063	0.0198	0.092
	0.2479	0.093	0.0467	0.199	0.2445	0.087	0.0397	0.151
	0.3844	0.133	0.0786	0.374	0.3838	0.128	0.0616	0.251
24.33	0.1236	0.047	0.0285	0.065	0.1201	0.052	0.0266	0.092
	0.2479	0.072	0.0513	0.199	0.2445	0.070	0.0449	0.151
	0.3844	0.105	0.0680	0.374	0.3838	0.109	0.0659	0.251

susceptibility  $\chi_{oij}$  which is real. The data set for alcohols and octanols are presented in Table 10.1. Several values of  $\ln\omega_1$  and  $\ln\omega_2$  ( $\omega_1 > \omega_2$ ) are chosen for same  $f(\omega_k)$  plotted against  $\ln\omega_k$  in Fig.10.1 at constant  $\omega$ .  $\tau_1$  and  $\tau_2$  are estimated from the intersection points of  $\ln\omega_1$  vs  $\ln\omega_2$  curve of Fig.10.2. They are placed in Table 10.2.  $\tau_1$  and  $\tau_2$  are also estimated from the linear plot of  $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$  against  $\chi_{ij}''/\chi_{ij}'$  at different  $w_j$ 's as shown in Fig.10.3 and are presented in Table 10.2.  $\mu_1$  and  $\mu_2$  are calculated in terms of slope  $\beta$  of  $\chi_{ij}'-w_j$  curve (Fig.10.4). All the  $\mu$ 's along with theoretical  $\mu_{theo}$ 's from Fig.10.5 are placed in Table 10.3 for comparison.

## 10.2. Theoretical Formulations for $\tau_1$ and $\tau_2$ :

Debye equation for a polar-nonpolar liquid mixture in terms of the complex  $hf \chi_{ij}^*$  for a distribution of  $\tau$  is :

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \int_0^{\infty} \frac{f(\tau)d\tau}{1 + j\omega\tau} \quad \dots (10.1)$$

where  $f(\tau)$  is the Fröhlich distribution function for the relaxation time such that:

$$f(\tau) = \frac{1}{A\tau} \quad \tau_1 < \tau < \tau_2 \quad \dots (10.2)$$

$$= 0 \quad \tau_1 > \tau, \tau_2 < \tau$$

and  $A = \text{Fröhlich parameter} = \ln \frac{\tau_2}{\tau_1}$

Table 10.2: Intercepts of  $\chi_{ij}''/\chi_{ij}'$  against  $w_j$  curve at  $w_j \rightarrow 0$ , values of  $\ln \omega_2$  and  $\ln \omega_1$  from Fig.10.2 and their average  $\tau_2$  and  $\tau_1$ ,  $\tau_2$  and  $\tau_1$  from single frequency measurement of Eq.(10.8) under 3.00, 9.25 and 24.33 GHz electric fields of some normal and isomeric octyl alcohols in *n*-heptane at 25°C.

System with sl. no	Frequency $f$ in GHz	Intercept of $\chi_{ij}''/\chi_{ij}' - w_j$ at $w_j \rightarrow 0$	Values of $\ln \omega_2$ and $\ln \omega_1$ from the Fig.10.2		Average $\tau_2$ and $\tau_1$ in psec		$\tau_2$ and $\tau_1$ from single frequency measurement		Average $\tau_2$ and $\tau_1$ in psec	
I. 1-Butanol	a) 3.00	0.1262	ab)	23.5015 30.8189			211.41	9.10		
	b) 9.25	0.2120	bc)	24.2051 29.8712	48.41	0.08	101.87	3.73	122.63	4.96
	c) 24.33	0.3231	ca)	23.6737 30.1101			54.60	2.04		
II. 1-Hexanol	a) 3.00	0.1246	ab)	23.2412 31.8059			204.26	9.17		
	b) 9.25	0.1933	bc)	24.1343 30.4314	57.03	0.04	85.24	3.76	110.44	5.01
	c) 24.33	0.2928	ca)	23.5801 30.6780			41.81	2.10		
III. 1-Heptanol	a) 3.00	0.0711	ab)	23.8767 33.6138			208.81	9.20		
	b) 9.25	0.1306	bc)	26.4479 27.0234	18.80	0.91	83.03	3.30	113.91	4.98
	c) 24.33	0.4503	ca)	25.2871 27.7518			49.89	2.43		
IV. 1-Decanol	a) 3.00	0.0438	ab)	25.5281 27.9946			135.66	6.89		
	b) 9.25	0.1620	bc)	24.5801 30.5149	13.12	0.29	83.14	5.61	83.68	5.27
	c) 24.33	0.2631	ca)	25.3244 29.7019			32.25	3.30		
V. 2-methyl 3-heptanol	a) 3.00	0.0700	ab)	24.9650 28.6944			73.31	5.41		
	b) 9.25	0.1974	bc)	25.6712 27.3056	11.19	0.90	49.61	4.10	50.96	4.3
	c) 24.33	0.4952	ca)	25.1384 27.6667			29.96	3.39		
VI. 3-methyl 3-heptanol	a) 3.00	0.0921					73.55	6.17		
	b) 9.25	0.2882		25.0098 27.4128	13.75	1.24	43.34	4.37	43.80	4.41
	c) 24.33	0.5807					14.52	2.68		
VII. 4-methyl 3-heptanol	a) 3.00	0.0892					84.34	6.71		
	b) 9.25	0.2174		25.8707 26.9313	5.81	2.01	45.08	4.21	51.61	4.74
	c) 24.33	0.4932					25.40	3.31		
VIII. 5-methyl 3-heptanol	a) 3.00	0.0358					101.22	6.58		
	b) 9.25	0.1040		26.4103 27.3200	3.39	1.36	52.36	4.21	57.13	4.15
	c) 24.33	0.3276					17.83	1.66		
IX. 2-octanol	a) 3.00	0.0604					160.41	7.83		
	b) 9.25	0.1964		24.8271 29.2251	16.51	0.20	92.00	5.11	94.46	4.94
	c) 24.33	0.3447					30.97	1.89		
X. 4-octanol	a) 3.00	0.0286					85.13	4.72		
	b) 9.25	0.0699		26.4780 28.0264	3.17	0.67	42.74	2.64	49.55	3.11
	c) 24.33	0.2409					20.77	1.97		

Separating the real and imaginary parts of both sides of Eq.(10.1), the following equations are obtained.

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{1}{A} \int_0^{\tau_2} \frac{d\tau}{\tau(1+\omega^2\tau^2)} \quad \dots (10.3)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \int_0^{\tau_2} \frac{\omega d\tau}{\tau(1+\omega^2\tau^2)} \quad \dots (10.4)$$

where  $\chi'_{ij} = (\epsilon'_{ij} - \epsilon_{oij})$ ,  $\chi''_{ij} = \epsilon''_{ij}$  and  $\chi_{oij} = (\epsilon_{oij} - \epsilon_{oij})$ , are the real, imaginary and low frequency dielectric susceptibilities  $\chi'_{ij}$ 's expressed in terms of relative permittivities  $\epsilon'_{ij}$ 's.

Dividing Eq.(10.4) by (10.3) and evaluating the integral one gets:

$$\frac{\chi''_{ij}}{\chi'_{ij}} = \frac{2[\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)]}{\ln \frac{\tau_2^2(1+\omega^2\tau_1^2)}{\tau_1^2(1+\omega^2\tau_2^2)}} \quad \dots (10.5)$$

Assuming smaller relaxation time  $\tau_1 = 1/\omega_1$ , larger relaxation time  $\tau_2 = 1/\omega_2$  and on rearrangement of Eq.(10.5) becomes [10.16]:

$$\frac{\chi''_{ij}}{\chi'_{ij}} \ln(\omega_1^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_1} = \frac{\chi''_{ij}}{\chi'_{ij}} \ln(\omega_2^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_2}$$

or,  $f(\omega_1) = f(\omega_2) = f(\omega_k)$

where,

$$f(\omega_k) = \left[ \left( \frac{\chi''_{ij}}{\chi'_{ij}} \right) \ln(\omega_k^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_k} \right] \quad \dots (10.6)$$

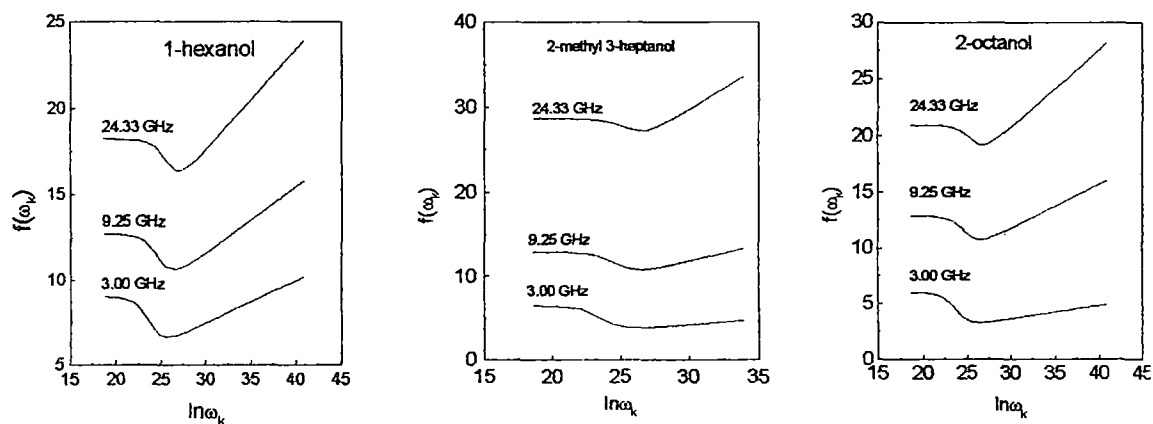


Figure 10.1: Variation of  $f(\omega_k)$  with  $\ln \omega_k$  for 1-hexanol, 2-methyl 3-heptanol and 2-octanol in *n*-heptane under 3.00, 9.25 and 24.33 GHz electric field at 25°C.

The term  $\chi_{ij}''/\chi_{ij}'$  of Eq.(10.6) is a function of weight fraction  $w_j$  of polar solute at a temperature  $T$  and angular frequency  $\omega$  of the electric field. The factor  $f(\omega_k)$  is, however, made constant for a fixed  $\tau_1$  and  $\tau_2$  at a given angular frequency  $\omega$  by introducing the following term in the Eq.(10.6).

$$f(\omega_k) = \left( \frac{\chi_{ij}''}{\chi_{ij}'} \right)_{w_j \rightarrow 0} \ln(\omega_k^2 + \omega^2) + 2 \tan^{-1} \frac{\omega}{\omega_k} \quad \dots (10.7)$$

Table 10.3: Slope  $\beta$  of  $\chi_{ij}'-w_j$  curve at  $w_j \rightarrow 0$ , dipole moment from Eq.(10.13), dipole moment from single frequency measurement and theoretical dipole moment  $\mu_{theo}$  from the available bond angles and bond moments in Coulomb.metre (C.m).

System with sl. no & mol. wt	Frequency $f$ in GHz	Slope $\beta$ of $\chi_{ij}'-w_j$ at $w_j \rightarrow 0$	$\mu \times 10^{30}$ (C.m) from average $\tau_2$ and $\tau_1$ of Fig.10.2		$\mu \times 10^{30}$ (C.m) from single frequency measurement		Theoretical dipole moment $\mu_{theo} \times 10^{30}$ in C.m
			$\mu_2$	$\mu_1$	$\mu_2$	$\mu_1$	
I. 1-Butanol $M_j = 0.074$ Kg	a) 3.00	1.028	4.67	3.45	17.44	4.30	4.95
	b) 9.25	0.627	8.04	2.69	22.07	3.77	
	c) 24.33	0.796	22.69	3.04	29.17	3.63	
II. 1-Hexanol $M_j = 0.102$ Kg	a) 3.00	0.608	4.57	3.11	16.87	4.30	4.35
	b) 9.25	0.330	7.95	2.29	18.77	3.80	
	c) 24.33	-0.089	-	-	21.20	3.43	
III. 1-Heptanol $M_j = 0.116$ Kg	a) 3.00	0.447	3.02	2.85	17.40	4.33	4.05
	b) 9.25	0.213	2.91	1.97	18.40	3.80	
	c) 24.33	0.588	9.94	3.30	27.01	3.73	
IV. 1-Decanol $M_j = 0.158$ Kg	a) 3.00	0.383	3.17	3.08	11.94	4.40	3.15
	b) 9.25	0.192	2.74	2.18	18.40	3.93	
	c) 24.33	0.133	4.06	1.81	17.24	3.83	
V. 2-methyl 3-heptanol $M_j = 0.130$ Kg	a) 3.00	0.530	3.36	3.28	6.93	4.10	5.85
	b) 9.25	0.376	3.30	2.77	11.30	3.80	
	c) 24.33	0.359	5.35	2.73	16.00	3.83	
VI. 3-methyl 3-heptanol $M_j = 0.130$ Kg	a) 3.00	0.663	3.79	3.67	7.27	4.30	5.85
	b) 9.25	0.477	3.99	3.12	10.70	4.07	
	c) 24.33	0.414	6.75	2.95	8.60	30.83	
VII. 4-methyl 3-heptanol $M_j = 0.130$ Kg	a) 3.00	0.643	3.64	3.62	7.83	4.20	5.85
	b) 9.25	0.413	3.06	2.92	10.64	3.90	
	c) 24.33	0.424	3.93	3.07	13.90	3.90	
VIII. 5-methyl 3-heptanol $M_j = 0.130$ Kg	a) 3.00	0.277	2.38	2.37	8.47	3.97	5.85
	b) 9.25	0.038	0.90	0.88	11.17	3.60	
	c) 24.33	0.024	0.79	0.71	9.50	3.37	
IX. 2-octanol $M_j = 0.130$ Kg	a) 3.00	0.420	3.06	2.92	12.94	4.10	3.58
	b) 9.25	0.207	2.84	2.05	18.90	3.63	
	c) 24.33	0.143	4.63	1.71	16.00	3.43	
X. 4-octanol $M_j = 0.130$ Kg	a) 3.00	0.142	1.70	1.70	7.10	3.77	3.58
	b) 9.25	0.053	1.06	1.04	9.07	3.43	
	c) 24.33	-0.041	-	-	10.97	3.43	

where  $(\chi_{ij}''/\chi_{ij}')_{w_j \rightarrow 0}$  is the intercept of  $\chi_{ij}''/\chi_{ij}'$  against  $w_j$  curve at  $w_j \rightarrow 0$ . The graphs are drawn by adopting least squares fitting technique of the experimental data at different  $w_j$ 's of solute of Table 10.1. The values of  $(\chi_{ij}''/\chi_{ij}')_{w_j \rightarrow 0}$  are placed in Table 10.2. Curves of  $f(\omega_k)$  against  $\ln \omega_k$  [10.16] for 1-hexanol, 2-methyl 3-heptanol and 2-octanol are drawn in Fig.10.1 by varying  $\omega_k$  independently for a constant angular frequency  $\omega$  to get two values of  $\ln \omega_2$  and  $\ln \omega_1$  ( $\omega_2 < \omega_1$ ) for same  $f(\omega_k)$ . Finally graphs of  $\ln \omega_1$  vs  $\ln \omega_2$  are plotted in Fig.10.2 for three different values of  $\omega (=2\pi f)$ ,  $f$  being the frequency of the electric field of 3.00, 9.25 and 24.33 GHz respectively. The points of intersection of the curves yield the values of  $\tau_2$  and  $\tau_1$  of the polar molecules. They are placed in Table 10.2 along with those from double relaxation method by single frequency measurement technique [10.7-10.8].

$\tau$ 's are also estimated from the following equation [10.11]:

$$\frac{\chi_{oij} - \chi_{ij}'}{\chi_{ij}'} = \omega(\tau_2 + \tau_1) \frac{\chi_{ij}''}{\chi_{ij}'} - \omega^2 \tau_1 \tau_2 \quad \dots (10.8)$$

The term  $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$  vs  $\chi_{ij}''/\chi_{ij}'$  on both sides of Eq.(10.8) are functions of  $w_j$ 's of polar solute at a constant angular frequency  $\omega$  and fixed  $\tau_1$  and  $\tau_2$ . Graphs of  $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$  with  $\chi_{ij}''/\chi_{ij}'$  are drawn against different  $w_j$ 's at 3.00, 9.25 and 24.33 GHz electric fields to get fixed intercepts and slopes from which  $\tau_1$ 's and  $\tau_2$ 's were obtained. They are placed in Table 10.2. Three sets of  $\tau_1$  and  $\tau_2$  are obtained for alcohols at 3.00, 9.25 and 24.33 GHz electric fields respectively. The average  $\tau_1$  and  $\tau_2$  are placed in Table 10.2 for comparison with the graphical method.

### 10.3. Estimation of $\mu_1$ and $\mu_2$ from $\tau_1$ and $\tau_2$ :

The Debye equation [10.17] for a polar-nonpolar liquid mixture under  $hf$  electric field in terms of  $\chi_{ij}$ 's is written as:

$$\frac{d\chi_{ij}''}{d\chi_{ij}'} = \omega\tau \quad \dots (10.9)$$

$$\frac{(d\chi_{ij}''/dw_j)_{w_j \rightarrow 0}}{(d\chi_{ij}'/dw_j)_{w_j \rightarrow 0}} = \omega\tau \quad \dots (10.10)$$

Again, the imaginary part  $\chi_{ij}''$  of the complex  $hf$  susceptibility  $\chi_{ij}^*$  as a function of  $w_j$  of a solute can be written as [10.17]

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



which on differentiation with respect to  $w_j$  and at  $w_j \rightarrow 0$  yields:

$$\left( \frac{d\chi_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_o k_B T M_j} \frac{\omega\tau}{1 + \omega^2\tau^2} (\varepsilon_i + 2)^2 \quad \dots (10.11)$$

where the density of the solution  $\rho_{ij}$  becomes  $\rho_i$  = density of solvent,  $(\varepsilon_{ij}+2)^2$  becomes  $(\varepsilon_i+2)^2$  at  $w_j \rightarrow 0$ ,  $k_B$ =Boltzmann constant,  $N$ = Avogadro's number,  $\varepsilon_i$ = relative permittivity of solvent and  $\varepsilon_o$ = permittivity of free space =  $8.854 \times 10^{-12}$  Farad. metre<sup>-1</sup>. All are expressed in SI units.

Comparing Eqs.(10.10) and (10.11) one gets:

$$\left( \frac{d\chi_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_o k_B T M_j} \frac{1}{1 + \omega^2\tau^2} (\varepsilon_i + 2)^2 = \beta \quad \dots (10.12)$$

where  $\beta$  is the slope of  $\chi_{ij}'$ - $w_j$  curves of Fig.10.4 at  $w_j \rightarrow 0$ . Here no approximation in determination of  $\mu_j$  is made like the conductivity measurement technique[10.9]. After simplification, the  $hf$  dipole moment  $\mu_j$  is given by:

$$\mu_j = \left( \frac{27\varepsilon_o k_B T M_j \beta}{N\rho_i (\varepsilon_i + 2)^2 b} \right)^{\frac{1}{2}} \quad \dots (10.13)$$

The dimensionless parameter  $b$  in terms of  $\tau$  of Eq.(10.13) is given by:

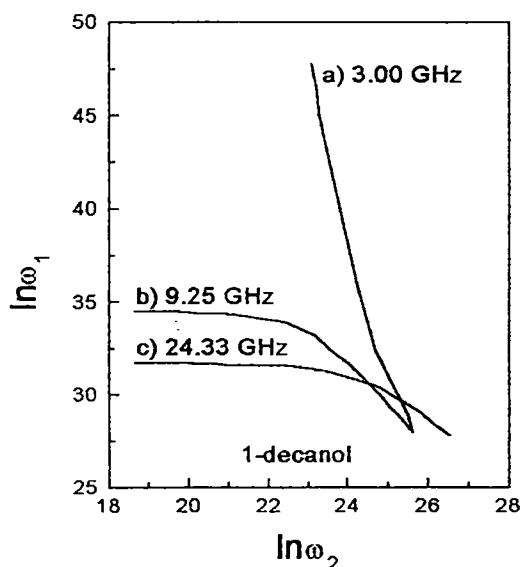
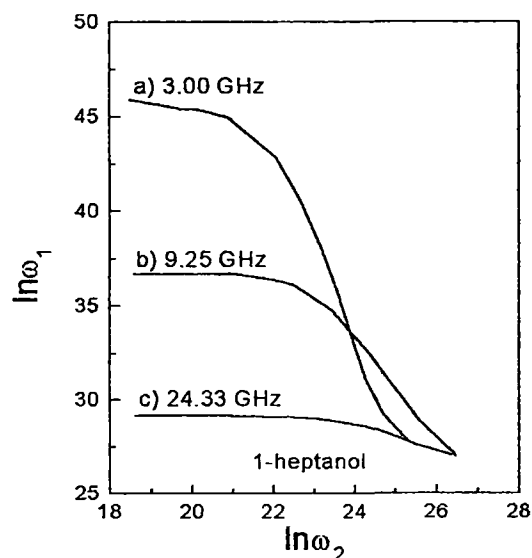
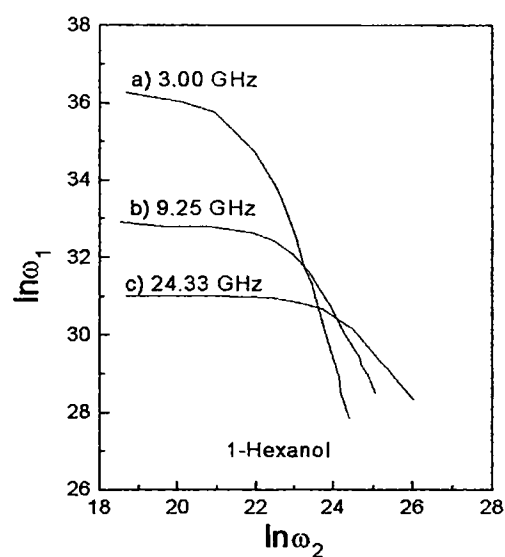
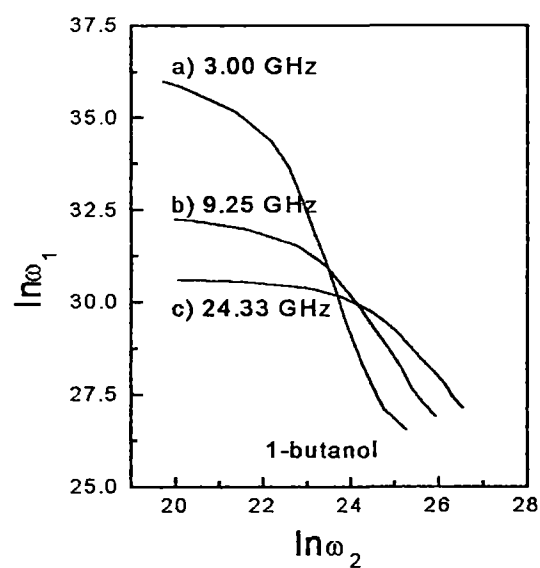
$$b = 1/(1 + \omega^2\tau^2) \quad \dots (10.14)$$

where  $\tau$  is estimated from the graphical plots of  $\ln\omega_1$  vs  $\ln\omega_2$  of Fig.10.2. All the  $\tau$ 's are placed in Table 10.2.

#### 10.4. Results and Discussions :

The data of  $\chi_{ij}'$ ,  $\chi_{ij}''$  and  $\chi_{oij}$  at different  $w_j$ 's of dipolar alcohols in *n*-heptane at 25°C under 3.00, 9.25 and 24.33 GHz electric fields are extracted from the measured permittivities  $\varepsilon_{ij}$ 's of Crossley *et al* [10.5] and Glasser *et al* [10.6] as presented in Table 10.1. The terms  $\chi_{ij}''/\chi_{ij}'$  for each alcohol are plotted against different  $w_j$ 's for 3.00, 9.25 and 24.33 GHz electric fields. Eventually, the least squares fitted curves are found to be parabolic in nature. The values of intercepts of  $(\chi_{ij}''/\chi_{ij}')$ - $w_j$  curves at  $w_j \rightarrow 0$  are placed in column 3 of Table 10.2. For several arbitrary values of angular frequency  $\omega_k$ , three graphs of  $f(\omega_k)$  against  $\ln\omega_k$  of Eq.(10.6) for each alcohol are drawn for 3.00, 9.25 and 24.33 GHz electric fields. The variations of  $f(\omega_k)$  against  $\ln\omega_k$  are shown for three peculiar dipolar alcohols like 1-hexanol, 2-methyl 3-heptanol and 2-octanol at 3.00, 9.25 and 24.33 GHz electric fields. They are sketched in Fig.10.1. The graphs are drawn by using a PC which show the

gradual decrease of  $f(\omega_k)$  with the increase of  $\ln\omega_k$  to exhibit minimum at a certain frequency  $\omega_k$  and then increase afterwards [10.16]. A large number of arbitrary values of  $\ln\omega_2$  and  $\ln\omega_1$  ( $\ln\omega_2 < \ln\omega_1$ ) are selected for a fixed  $f(\omega_k)$  in order to draw the graphs of  $\ln\omega_1$  vs  $\ln\omega_2$  at 3.00, 9.25 and 24.33 GHz electric fields. All the graphs as shown in Fig.10.2 are similar in nature. They show larger values initially and decrease gradually in order to cut at a point for all most all the dipolar liquids to yield significant values of  $\tau_2$  and  $\tau_1$  respectively. Unlike other systems, 1-butanol, 1-hexanol, 1-heptanol, 1-decanol and 2-methyl 3-heptanol, the curves meet at three points to exhibit three values of  $\tau_2$  and  $\tau_1$ . This type of behaviour may be due to some uncertainty in measurements



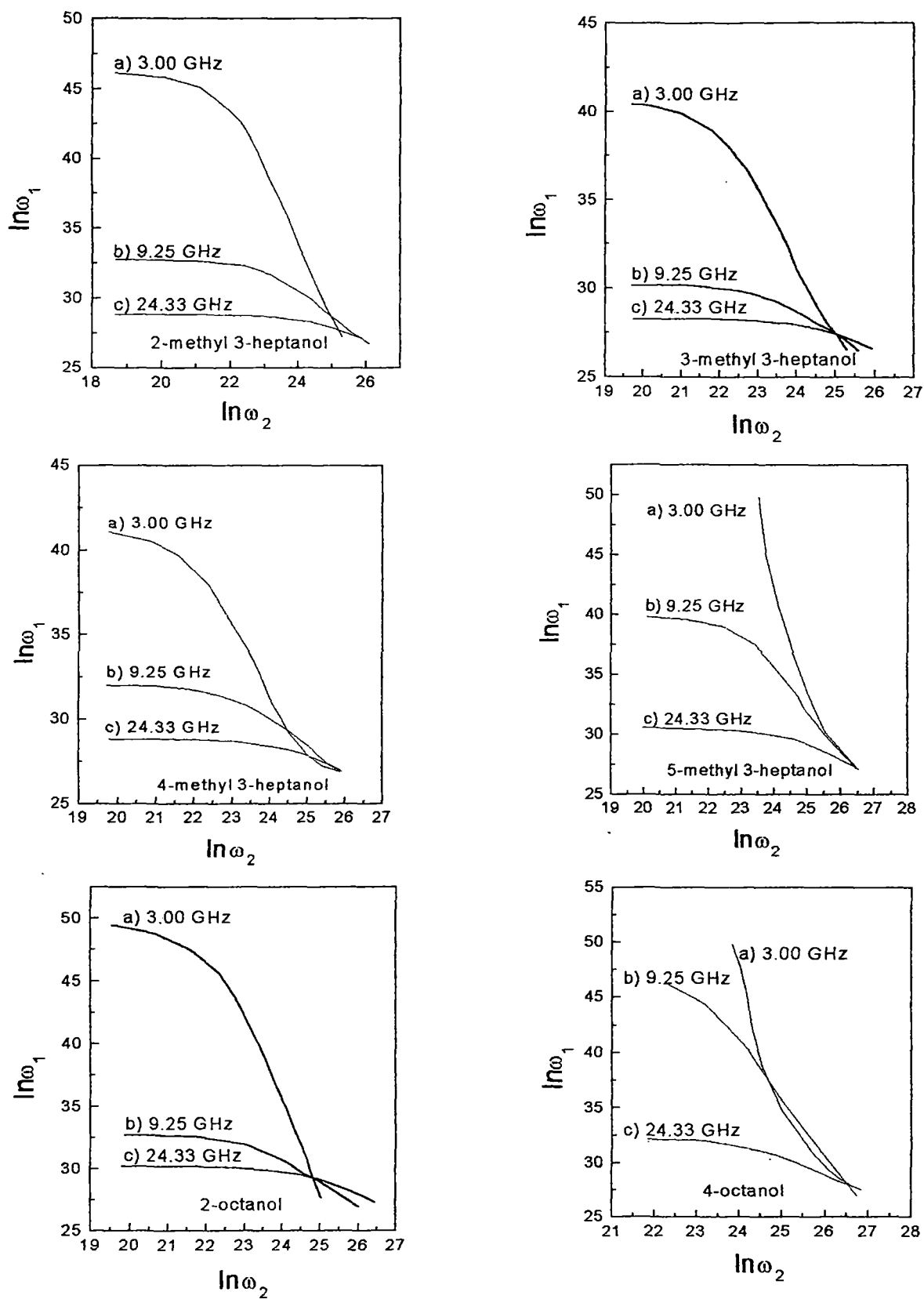


Figure 10.2: Plot of  $\ln \omega_1$  against  $\ln \omega_2$  for some normal alcohols and isomeric octyl alcohols in *n*-heptane under 3.00, 9.25 and 24.33 GHz electric fields at 25°C.

of experimental data (Table 10.1) of polar-nonpolar liquid mixtures at different  $hf$  electric fields. The average of the three  $\tau$ 's along with single  $\tau_2$  and  $\tau_1$  for the rest five systems are placed in Table 10.2.

$\tau_2$  and  $\tau_1$  are also calculated from the slopes and intercepts of straight line Eq.(10.8) from single frequency measurement technique [10.11]. The plots of  $(\chi_{oij}-\chi_{ij}')/\chi_{ij}'$  against  $\chi_{ij}''/\chi_{ij}'$  at different  $w_j$ 's of alcohols for 24.33 GHz electric field are shown in Fig.10.3 only to see the soundness of the theory. The alcohols usually show peak at 24.33 GHz electric field when dielectric loss ( $\chi_{ij}''=\epsilon_{ij}''$ ) is plotted against angular frequency  $\omega (=2\pi f)$ ,  $f$  being the frequency of the electric field at a fixed weight fraction  $w_j$ 's of solute [10.9]. The estimated  $\tau_2$  and  $\tau_1$  are placed in ninth and tenth column of Table 10.2. They are found to be dependent on frequency of the applied electric field. The alcohols under investigation are in the same environment and are expected to show fixed  $\tau_2$  and  $\tau_1$  at all the three frequencies in order to exhibit the material property of the systems. The  $\tau_2$  and  $\tau_1$  thus obtained from the straight line Eq.(10.8) are made average and placed in the 11th column of Table 10.2. They are compared with those of graphical technique adopted here. The values from single relaxation technique are greater than the graphical method.  $\tau_2$  from graphical method agree well with  $\tau_1$  of Eq.(10.8) for almost all the octyl alcohols except 2-methyl 3-heptanol and 2-octanol. This type of behaviour may reveal the applicability of both the methods for the systems under study. Moreover, the graphical technique based on Debye-Fröhlich model provides better understanding to reflect the material property of the systems.

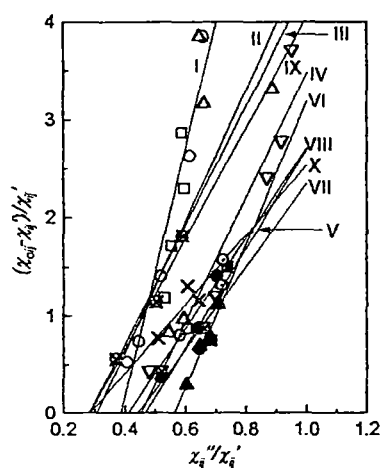


Figure 10.3: Plot of  $(\chi_{oij}-\chi_{ij}')/\chi_{ij}'$  against  $\chi_{ij}''/\chi_{ij}'$  for different  $w_j$ 's under 24.33 GHz electric field at 25°C.

I. 1-butanol (○), II. 1-hexanol (△), III. 1-heptanol (□), IV. 1-decanol (▽), V. 2-methyl 3-heptanol (●), VI. 3 methyl 3-heptanol (▲), VII. 4-methyl 3-heptanol (⊠), VIII. 5-methyl 3-heptanol (⊙), IX. 2-octanol (⊗) and X. 4-octanol (\*) in *n*-heptane.

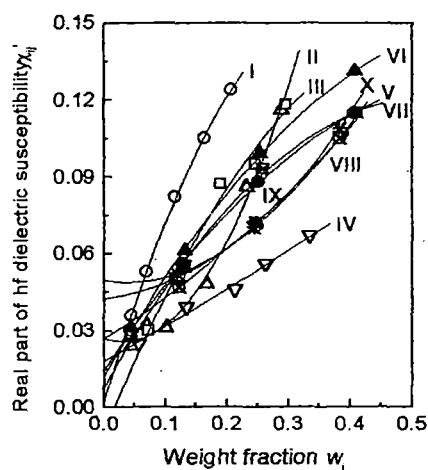


Figure 10.4: Variation of real part of complex dielectric orientation susceptibility  $\chi_{ij}'$  with  $w_j$ 's under 24.33 GHz electric field at 25°C.

I. 1-butanol (○), II. 1-hexanol (△), III. 1-heptanol (□), IV. 1-decanol (▽), V. 2-methyl 3-heptanol (●), VI. 3 methyl 3-heptanol (▲), VII. 4-methyl 3-heptanol (⊠), VIII. 5-methyl 3-heptanol (⊙), IX. 2-octanol (⊗) and X. 4-octanol (\*) in *n*-heptane.

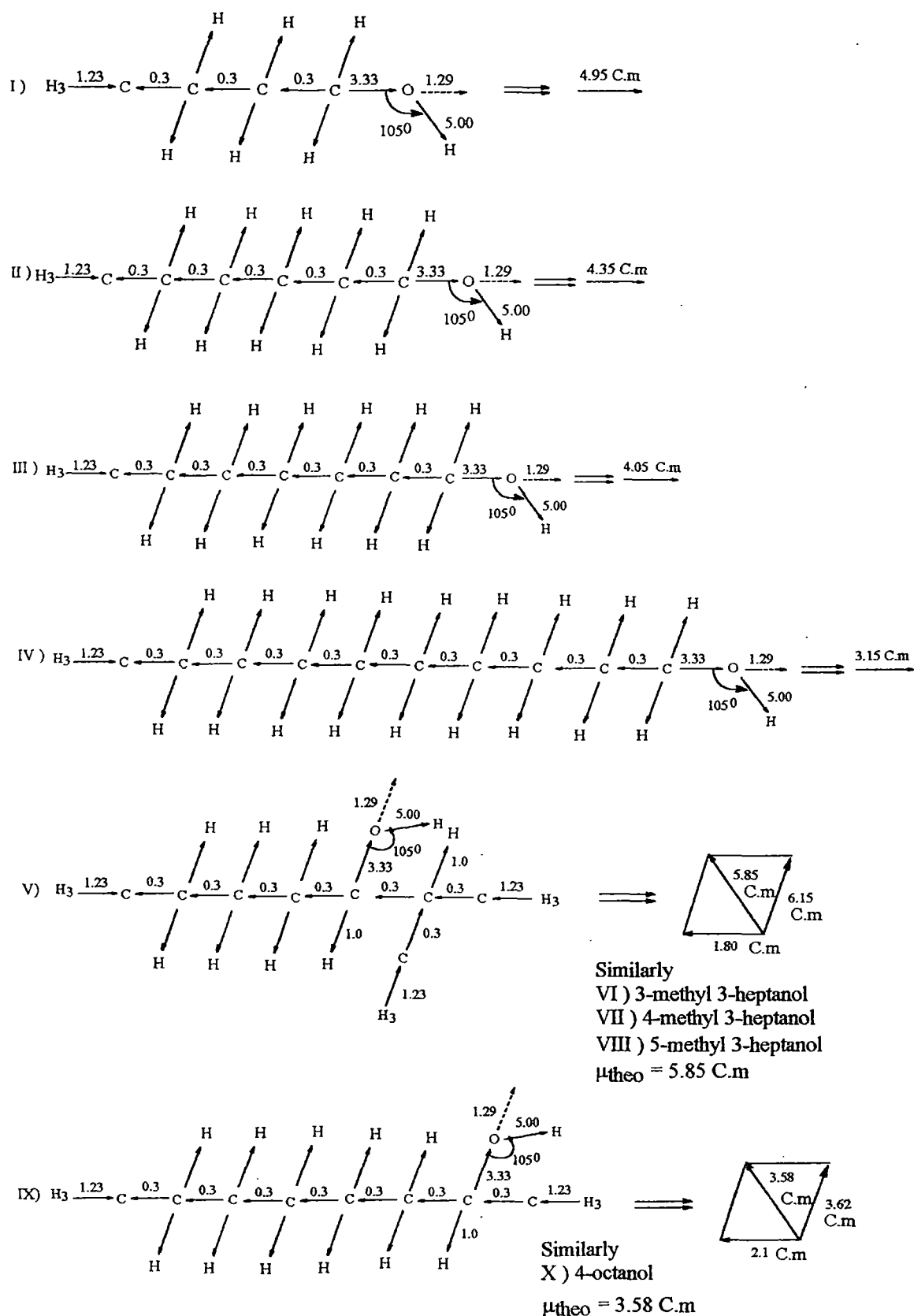


Figure 10.5: Conformational structures of polar molecules in terms of bond angles and bond moments ( $\times 10^{-30}$  Coulomb. metre) of the substituents groups: I.) 1-Butanol, II.) 1-Hexanol, III.) 1-Heptanol, IV.) 1-Decanol, V.) 2-methyl 3-heptanol and IX.) 2-octanol.

The alcohols show effective dispersive region nearly 24.33 GHz electric field as observed elsewhere [10.9]. The dipole moments  $\mu_2$  and  $\mu_1$  of the whole and flexible parts of the dipolar alcohols in terms of  $\tau_2$  and  $\tau_1$  of Eq.(10.13) and slope  $\beta$  of  $\chi_{ij}'-w_j$  curves are calculated at 3.00, 9.25 and 24.33 GHz electric fields. They are shown in Table 10.3. Plot of  $\chi_{ij}'$  against  $w_j$  for all the alcohols at 24.33 GHz electric field are made in Fig.10.4. The variations are parabolic in nature. The graphs are almost same for the systems 5-methyl 3-heptanol (VIII), 2-octanol (IX) and 4-octanol (X) respectively. This may be due to almost same polarity of the molecules [10.18]. The convex or concave nature of all the curves may perhaps reveal the solute-solute molecular association in the higher concentration region due to hydrogen bonding. Besides 24.33 GHz electric field dipole moments are almost constant for all the systems at 3.00 and 9.25 GHz electric fields. Difference in  $\mu_2$  and  $\mu_1$  are, however, observed in case of 1-butanol (I), 1-hexanol (II) and 1-heptanol (III). This may indicate that the accurate measurement of  $\epsilon_{\omega_{ij}}$  is needed [10.7] to get a sharp cutting of plot of  $\ln\omega_1$  against  $\ln\omega_2$  instead of little spread in Fig.10.2 for such molecules.  $\mu_2$  and  $\mu_1$  are in agreement with the single frequency measurement technique. Little disagreement among  $\mu$ 's may be due to steric hindrances and various effects like inductive, mesomeric and electromeric effects present in the substituent polar groups. The theoretical dipole moment  $\mu_{theo}$ 's are sketched in Fig.10.5 considering planar structure of the alcohols. The available bond moments of  $H_3 \rightarrow C$ ,  $C \leftarrow C$ ,  $C \rightarrow O \rightarrow$  and  $O \rightarrow H$  (making an angle  $105^\circ$ ) substituted polar groups are 1.23 C.m, 0.3 C.m, 3.33 C.m and 5.00 C.m respectively. In these polar molecules inductive and mesomeric effects among substituted groups play vital role to yield conformational structure. They can be taken into account by taking the ratio of  $\mu_1/\mu_{theo}$  which may be multiplied to the bond moment value to get  $\mu_{theo}$ 's in exact agreement with calculated  $\mu_1$ 's.

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