

## CHAPTER 7

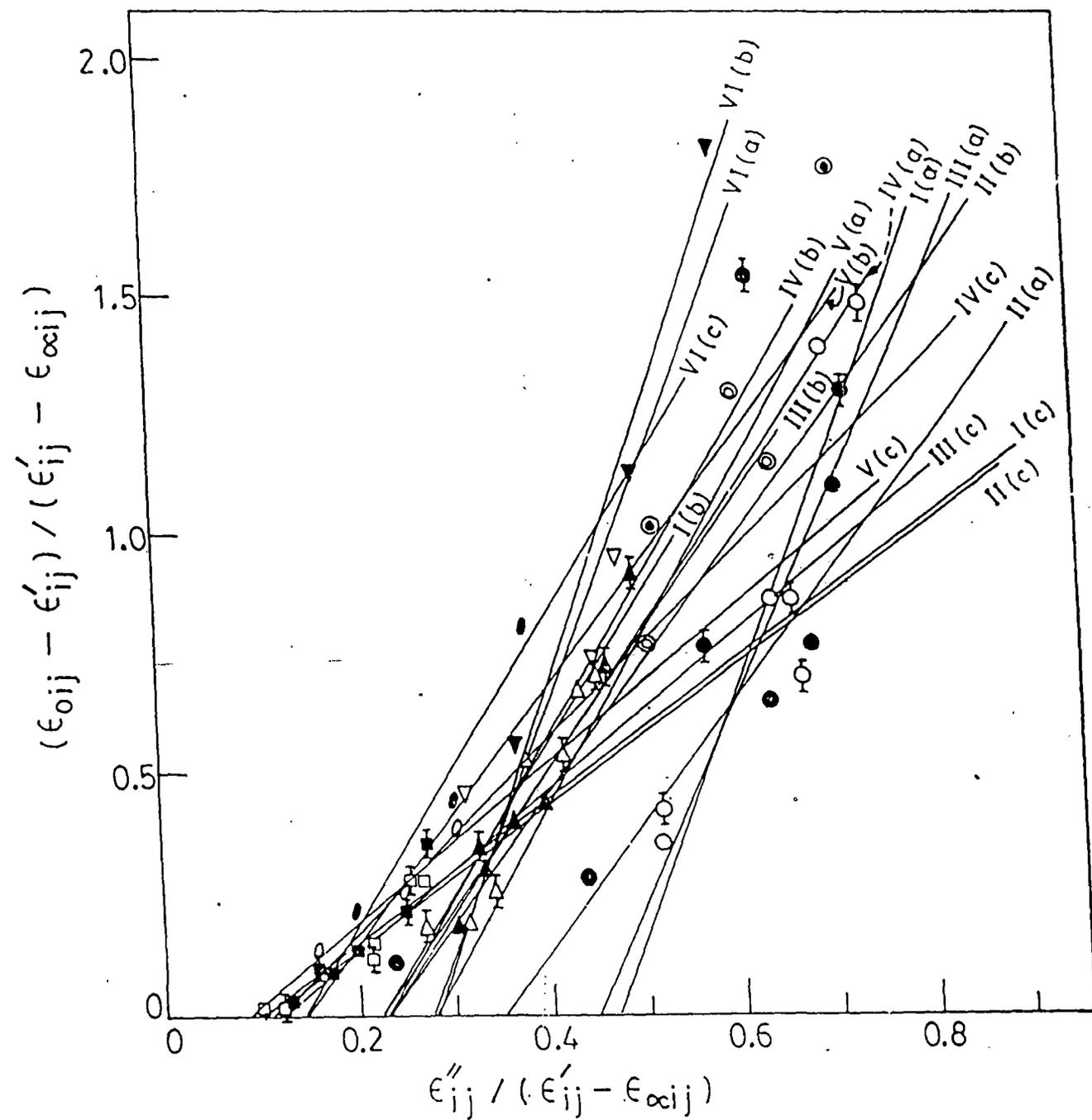
# DOUBLE RELAXATIONS OF SOME ISOMERIC OCTYL ALCOHOLS BY HIGH FREQUENCY ABSORPTION IN NONPOLAR SOLVENT

## 7.1 Introduction

The dielectric relaxation mechanism of a polar-nonpolar liquid mixture is a very convenient and useful tool in ascertaining the shape, size and structure of a polar molecule [1]. The process is generally involved with the estimation of dipole moment  $\mu$  in terms of the relaxation time  $\tau$  for a polar molecule in a nonpolar solvent under different high frequency (hf) electric field of Giga hertz (GHz) range at a fixed or different temperatures. There exist several methods to estimate  $\tau$  [2] of a polar liquid in a nonpolar solvent. They offer a deep insight into the intrinsic properties of a polar molecule because of the absence of dipole-dipole interactions in polar-nonpolar liquid mixtures.

Highly nonspherical polar molecules, on the other hand, possess more than one  $\tau$  in the electric field of GHz range for the rotations of different substituent groups attached to the parent molecule and the whole molecule itself. Budo[3], however, proposed that complex dielectric constant  $\epsilon^*$  of a polar liquid may be represented as the sum of a number of noninteracting Debye type dispersions each with a characteristic  $\tau$ . The method was then made simpler by Bergmann *et al* [4] by assuming that the dielectric relaxation is the sum of two Debye type dispersions characterised by the intramolecular and molecular  $\tau_1$  and  $\tau_2$  respectively. The corresponding relative contributions  $c_1$  and  $c_2$  towards dielectric relaxations could then be estimated. They used a graphical analysis which consists of plotting normalised values of  $(\epsilon' - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)$  against  $\epsilon''/(\epsilon_0 - \epsilon_\infty)$  on a complex plane in terms of the measured real  $\epsilon'$ , imaginary  $\epsilon''$  parts of  $\epsilon^*$ , static dielectric constant  $\epsilon_0$  and high frequency dielectric constant  $\epsilon_\infty$  of a polar liquid for different frequencies of the electric field. A number of chords were then drawn through the points on the curve until a set of parameters was found out in consistency with all the experimental points. Bhattacharyya *et al* [5] subsequently modified the above procedure to get  $\tau_1$ ,  $\tau_2$ ,  $c_1$  and  $c_2$  for a polar liquid from relaxation data measured at least at two different frequencies of the electric field.

We, [6] however, devised earlier a procedure to get  $\tau_1$  and  $\tau_2$  from the slope and intercept of a derived straight line equation involved with the single frequency measurements of the dielectric relaxation parameters like  $\epsilon_{0ij}$ ,  $\epsilon_{\infty ij}$ ,  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$  for different



**Figure 7.1** Plot of  $(\epsilon_{0ij} - \epsilon'_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})$  against  $\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$  of some isomeric octyl alcohols

System-I(a) (-O-), I(b) (-Δ-), I(c) (-□-) for 2-methyl-3-heptanol

System-II(a) (-●-), II(b) (-▲-), II(c) (-■-) for 3-methyl-3-heptanol

System-III(a) (-○-), III(b) (-△-), III(c) (-□-) for 4-methyl-3-heptanol

System-IV(a) (-●-), IV(b) (-▲-), IV(c) (-■-) for 5-methyl-3-heptanol

System-V(a) (-○-), V(b) (-▽-), V(c) (-○-) for 4-octanol

System-VI(a) (-●-), VI(b) (-▼-), VI(c) (-●-) for 2-octanol

under 24.33, 9.25 and 3.00 GHz respectively

weight fractions  $\omega_j$ ' of a polar solute (j) in a nonpolar solvent (i) at a given temperature. The technique had already been applied on disubstituted benzenes and anilines [6] at 9.945 GHz electric field as well as monosubstituted anilines at 22.06, 3.86, 2.02 GHz [7] electric fields respectively. All these investigations reveal that they often showed the double relaxation behaviours at certain frequency of the electric field.

The aliphatic alcohols, on the other hand, are long straight chain, hydrogen bonded polymer type molecules having possibility of their bending, twisting and rotation under hf electric field each with a characteristic  $\tau$ , besides the average macroscopic distribution of  $\tau$ . These alcohols have high dipole moments owing to their strong intermolecular forces exerted by them like polymers in solution. Onsager's equation may be a better choice for such associative liquids, but it is not so simple like Debye's equation because of the presence of quadratic term  $\epsilon^*_{ij}$ . The relaxation behaviour of aliphatic alcohols are very interesting because they show more than two  $\tau$ 's in pure state, but for a polar-nonpolar liquid mixture hf process becomes increasingly important on dilution [8,9]. An extensive study to detect the frequency dependence of double relaxation behaviours of four long chain normal aliphatic alcohols like 1-butanol, 1-hexanol, 1-heptanol, 1-decanol in solvent n-heptane [10] including methanol and ethanol at 9.84 GHz in benzene [11,12] at 25°C was already made [13]. All the alcohols showed  $\tau_1$  and  $\tau_2$  at all frequencies of the electric field except methanol which is a simple molecule to possess expected  $\tau_2$  only.

We, therefore, thought to apply the method as developed earlier [6] on six isomeric octyl alcohols like 2-methyl-3-heptanol, 3-methyl-3-heptanol, 4-methyl-3-heptanol, 5-methyl-3-heptanol, 4-octanol and 2-octanol at 24.33, 9.25 and 3.00 GHz electric fields, as reported in Tables 7.1- 7.4 respectively, because of the availability of  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  measured by Crossley et al [14] in n-heptane at 25°C. The straight line equations between  $(\epsilon_{0ij} - \epsilon'_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})$  and  $\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$  for all the octyl alcohols at different  $\omega_j$ 's are linear as illustrated graphically in Fig. 7.1 only to establish the applicability of Debye model in such isomeric alcohols like normal alcohols once again [13]. Moreover, all the long chain octyl alcohols are structural isomers with the molecular formula  $C_8H_{18}O$  having greater number of C-atoms in their structures. They are, therefore,

expected to possess two relaxation processes at audio and radio frequencies of electric field at low temperature in pure state [14].

The purpose of the present paper is to observe the frequency dependence of  $\tau_1$  and  $\tau_2$  at all frequencies of 24.33, 9.25 and 3.00 GHz electric field for all the octyl alcohols like normal alcohols from the measured relaxation data as shown in Table 7.1. The measured  $\tau_s$  from the slope of the linear equation of imaginary  $K''_{ij}$  and real  $K'_{ij}$  parts of the total complex hf conductivity  $K^*_{ij}$  and the most probable relaxation time  $\tau_0$  from  $\tau_0 = \sqrt{\tau_1\tau_2}$  are placed in Table 7.2 together with the estimated  $\tau_1$  and  $\tau_2$  in order to see their trends with frequency of the applied electric field.

The relative contributions  $c_1$  and  $c_2$  towards dielectric relaxations in terms of  $\tau_1$  and  $\tau_2$ , are estimated from Fröhlich's equations [15] as well as the graphical method of Figs. 7.2 and 7.3 adopted here. The estimated  $c_1$  and  $c_2$  are, however, placed in Table 7.3

The dipole moments  $\mu_1$  and  $\mu_2$  due to flexible parts as well as the whole molecules in terms of the estimated  $\tau_1$  and  $\tau_2$  (Table 7.2) and the slopes  $\beta$  of the linear variation of hf conductivity  $K_{ij}$  with  $\omega_j$  are shown in Table 7.4. The slopes  $\beta$  and the intercepts  $\alpha$  of the linear variation of  $K_{ij}$  with  $\omega_j$ , as placed in Table 7.4 at each frequency for all the isomers in n-heptane are almost the same probably due to their same polarity [16]. This fact is also supported by their conformations as sketched in Fig. 7.4. It was, therefore, very difficult to plot  $K_{ij}$  against  $\omega_j$ . The computed  $\mu_2$  for most of the isomeric alcohols show larger values at 24.33 GHz and gradually decrease with lower frequencies unlike  $\mu_1$ . In order to compare  $\mu_2$  and  $\mu_1$  with theoretical dipole moments  $\mu_{theo}$  a special attention is to be paid on the conformational structure of each isomer from the available bond angles and bond moments point of view and they are shown in Fig. 7.4. Using the usual C-C bond moment of 0.09 D from methanol and ethanol [13]  $\mu_{theo}$  for four methyl substituted octanols are found to show slightly larger values (see Fig 7.4 and Table 7.4) than 1-heptanol [13] except the desired values for 2-octanol and 4-octanol perhaps due to bond moments of C  $\leftarrow$  H<sub>3</sub> and O  $\rightarrow$  H groups in their structures. The calculated  $\mu_1$  from  $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$  assuming two relaxation processes are equally probable are also placed in the last column of Table 7.4 with all the estimated  $\mu$ 's for comparison.

**Table 7.1** Dielectric relaxation parameters like  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{0ij}$ ,  $\epsilon_{\infty ij}$  and of some isomeric octyl alcohols in n-heptane at 25°C from high frequency absorption measurements.

Weight fraction ( $\omega_j$ ) of solute	frequency f in GHz	$\epsilon'_{ij}$	$\epsilon''_{ij}$	$\epsilon_{0ij}$	$\epsilon_{\infty ij}$
System I :- 2-methyl-3-heptanol in n-heptane					
0.04337	24.33	1.960	0.0156		
	9.25	1.967	0.0088	1.971	1.930
	3.00	1.970	0.0040		
0.1299	24.33	2.022	0.0361	2.059	1.966
	9.25	2.044	0.0244		
	3.00	2.052	0.0137		
0.2522	24.33	2.095	0.0565		
	9.25	2.115	0.0412	2.172	2.007
	3.00	2.150	0.0309		
0.4081	24.33	2.169	0.0809		
	9.25	2.218	0.0710	2.330	2.054
	3.00	2.269	0.0583		
System II :- 3-methyl-3-heptanol in n-heptane					
0.0450	24.33	1.965	0.0137		
	9.25	1.968	0.0103	1.9740	1.934
	3.00	1.974	0.0043		
0.1334	24.33	2.028	0.0393		
	9.25	2.045	0.0263	2.069	1.966
	3.00	2.065	0.0131		
0.2538	24.33	2.103	0.0674		
	9.25	2.130	0.0458	2.180	2.004
	3.00	2.166	0.0272		
0.4084	24.33	2.188	0.0928		
	9.25	2.249	0.0766	2.334	2.057
	3.00	2.299	0.0489		
System III :- 4 methyl-3-heptanol in n-heptane					
0.0466	24.33	1.964	0.0146		
	9.25	1.970	0.0091	1.976	1.936
	3.00	1.975	0.0046		
0.1326	24.33	2.025	0.0375		
	9.25	2.045	0.0262	2.065	1.969
	3.00	2.059	0.0147		

0.2590	24.33	2.104	0.0616	2.185	2.011
	9.25	2.123	0.0472		
	3.00	2.167	0.0333		
0.4124	24.33	2.180	0.0849	2.352	2.065
	9.25	2.233	0.0766		
	3.00	2.289	0.0572		
System IV : - 5-methyl-3-heptanol in n-heptane					
0.1228	24.33	2.008	0.0296	2.048	1.956
	9.25	2.024	0.0225		
	3.00	2.040	0.0133		
0.2489	24.33	2.075	0.0511	2.168	2.004
	9.25	2.099	0.0441		
	3.00	2.138	0.0337		
0.3898	24.33	2.148	0.0676	2.315	2.040
	9.25	2.183	0.0706		
	3.00	2.242	0.0554		
System V : - 4-octanol in n-heptane					
0.1201	24.33	2.000	0.0265	2.040	1.948
	9.25	2.011	0.0198		
	3.00	2.029	0.0129		
0.2444	24.33	2.067	0.0449	2.148	1.997
	9.25	2.084	0.0397		
	3.00	2.117	0.0302		
0.3838	24.33	2.140	0.0659	2.282	2.031
	9.25	2.159	0.0616		
	3.00	2.212	0.0549		
System VI : - 2-octanol in n-heptane					
0.1236	24.33	2.001	0.0245	2.049	1.954
	9.25	2.015	0.0227		
	3.00	2.032	0.0156		
0.2479	24.33	2.068	0.0513	2.195	1.996
	9.25	2.089	0.0467		
	3.00	2.133	0.0419		
0.3844	24.33	2.141	0.0680	2.410	2.036
	9.25	2.169	0.0786		
	3.00	2.243	0.0791		

## 7.2 Theoretical Formulations to Estimate Relaxation Parameters

The complex dielectric constant  $\epsilon^*_{ij}$  of a polar-nonpolar liquid mixture can be represented as the sum of a number of non-interacting Debye type dispersions in accordance with Budo's [3] relation.

$$\frac{\epsilon^*_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \sum_k \frac{c_k}{1 + j\omega\tau_k}, \quad \dots\dots(7.1)$$

where  $j = \sqrt{-1}$  is a complex number and  $\sum c_k = 1$ . The term  $c_k$  is the relative contribution for the  $k$ th type of relaxation process. When the complex dielectric constant  $\epsilon^*_{ij}$  consists of two Debye type dispersions, Budo's relation reduces to Bergmann's equations [4]:

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{c_1}{1 + \omega^2\tau_1^2} + \frac{c_2}{1 + \omega^2\tau_2^2}, \quad \dots\dots(7.2)$$

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2}, \quad \dots\dots(7.3)$$

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

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = x, \quad \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = y,$$

$$\omega\tau = \alpha \text{ and using } a = \frac{1}{1 + \alpha^2} \text{ and } b = \frac{\alpha}{1 + \alpha^2}$$

the above Eqs (7.2) and (7.3) can be written as,

$$x = c_1 a_1 + c_2 a_2 \quad \dots\dots(7.4)$$

$$y = c_1 b_1 + c_2 b_2 \quad \dots\dots(7.5)$$

where suffices 1 and 2 with  $a$  and  $b$  are related to  $\tau_1$  and  $\tau_2$  respectively. From Eqs (7.4) and (7.5), since  $\alpha_2 - \alpha_1 \neq 0$  and  $\alpha_2 > \alpha_1$  we have

$$c_1 = \frac{(x \alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots\dots (7.6)$$

$$c_2 = \frac{(y - x \alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots\dots(7.7)$$

Since  $c_1 + c_2 = 1$ , we get the following equation with the help of Eqs (7.6) and (7.7) :

$\frac{1-x}{y} = (\alpha_1 + \alpha_2) - \frac{x}{y} \alpha_1 \alpha_2$  which on substitution of the values  $x$ ,  $y$  and  $\alpha$  yields

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega (\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2, \quad \dots\dots(7.8)$$

Equation (7.8) is thus a straight line equation 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. With the measured dielectric relaxation data of  $\epsilon'_{ij}$ ,  $\epsilon''_{ij}$ ,  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  and for different weight fractions  $\omega_j$ 's of each octyl alcohol in n-heptane at 25°C under 24.33, 9.25 and 3.00 GHz electric fields [14] we get slope and intercept of Eq. (7.8) to yield  $\tau_1$  and  $\tau_2$  as shown in Table 7.2

The relative contributions  $c_1$  and  $c_2$  towards the dielectric relaxations in terms of  $x$ ,  $y$  and  $\tau_1$ ,  $\tau_2$  for each octyl alcohol are found out and placed in Table 7.3. The theoretical values of  $x$  and  $y$  are, however, calculated from Fröhlich's equations [15] :

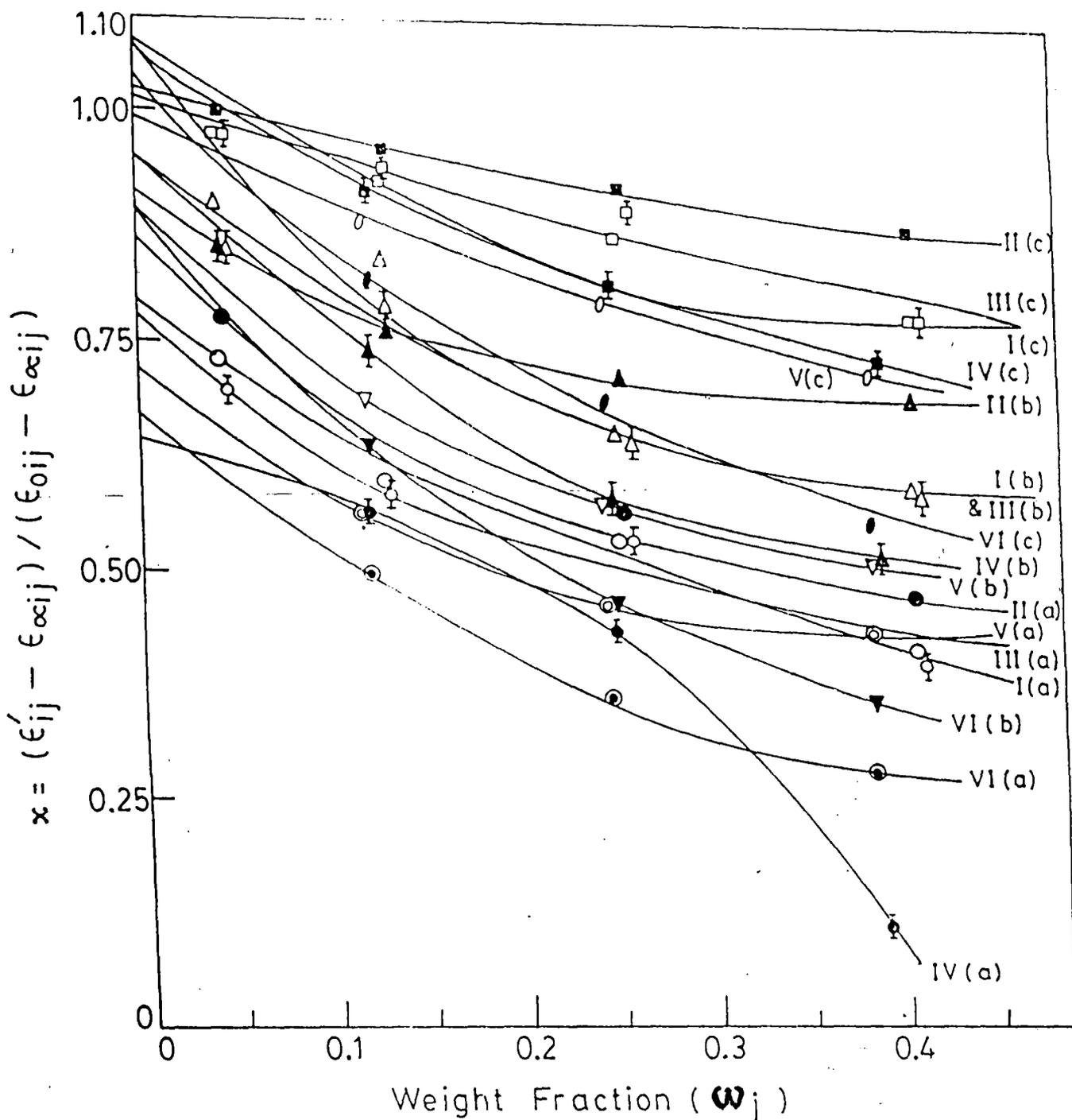
$$x = \frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left( \frac{1 + e^{2A} \omega^2 \tau_s^2}{1 + \omega^2 \tau_s^2} \right) \quad \dots\dots(7.9)$$

$$y = \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} \left[ \tan^{-1} (e^A \omega \tau_s) - \tan^{-1} (\omega \tau_s) \right] \quad \dots\dots(7.10)$$

where  $A$  = Fröhlich parameter =  $\ln (\tau_2/\tau_1)$  and  $\tau_s$  is called the small limiting relaxation time as obtained from the double relaxation method. A simple graphical extrapolation technique, on the other hand, was considered to get the values of  $x$  and  $y$  at  $\omega_j \rightarrow 0$  from the graphical plots of Figs.7.2 and 7.3 respectively. This is really in accord with

**Table 7.2** The estimated relaxation times  $\tau_2$  and  $\tau_1$  from the slopes and the intercept of straight line Eq (7.8) with errors and correlation coefficients  $r$  together with measured  $\tau_s$  from  $K_{ij}'' - K_{ij}'$  curve and most probable relaxation time  $\tau_0 = \sqrt{\tau_1 \tau_2}$  for six isomeric octyl alcohols at 25°C under different frequencies of electric fields.

System with Sl. No. & Mole wt. $M_j$	Frequency in GHz	Intercept & slope of Eq. (7.8)		Correlation coefficient ( $r$ )	% error in regression technique	Estimated values of $\tau_2$ & $\tau_1$ in pSec.		Measured $\tau_s$ in pSec.	Most probable relaxation time $\tau_0 = \sqrt{\tau_1 \tau_2}$
I. 2-methyl-3- heptanol in n- heptane $M_j = 130$ gm.	a) 24.33	2.3718	5.0952	0.9011	6.34	29.96	3.39	1.84	10.08
	b) 9.25	0.6871	3.1205	0.9700	1.99	49.61	4.10	3.58	14.26
	c) 3.00	0.1408	1.4830	0.9771	1.50	73.31	5.41	6.74	19.91
II 3-methyl-3- heptanol in n- heptane $M_j = 130$ gm	a) 24.33	0.9087	2.6282	0.9294	4.59	14.52	2.68	2.19	6.24
	b) 9.25	0.6389	2.7714	0.9709	1.93	43.34	4.37	3.70	13.76
	c) 3.00	0.1611	1.5018	0.9985	0.10	73.55	6.17	5.58	21.30
III. 4-methyl- 3-heptanol in n-heptane $M_j = 130$ gm	a) 24.33	1.9653	4.3873	0.8851	7.30	25.40	3.31	1.90	9.17
	b) 9.25	0.6411	2.8636	0.9682	2.11	45.08	4.21	4.13	13.78
	c) 3.00	0.2008	1.7153	0.9206	5.14	84.34	6.71	11.98	23.79
IV. 5-methyl- 3-heptanol in n-heptane $M_j = 130$ gm	a) 24.33	0.6929	2.9788	0.5684	26.36	17.83	1.66	1.71	5.44
	b) 9.25	0.7445	3.2866	0.9846	1.19	52.36	4.21	5.39	14.85
	c) 3.00	0.2362	2.0308	0.9371	4.74	101.22	6.58	13.11	25.81
V. 4-octanol in n-heptane $M_j = 130$ gm	a) 24.33	0.9572	3.4750	0.8569	10.34	20.77	1.97	1.83	6.40
	b) 9.25	0.3810	2.6361	0.9470	4.02	42.74	2.64	5.46	10.62
	c) 3.00	0.1428	1.6929	0.9846	1.18	85.13	4.72	12.76	20.05
VI. 2-octanol in n-heptane $M_j = 130$ gm	a) 24.33	1.3664	5.0208	0.6336	23.30	30.97	1.89	1.83	7.65
	b) 9.25	1.5853	5.6407	0.9888	0.86	92.00	5.11	6.26	21.68
	c) 3.00	0.4458	3.1697	0.9780	1.69	160.41	7.83	18.70	35.44



**Figure 7.2** Plot of  $(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$  against weight fraction  $\omega_j$  of some isomeric octyl alcohols in n-heptane at 25°C

System-I(a) (-O-), I(b) (-Δ-), I(c) (-□-) for 2-methyl-3-heptanol

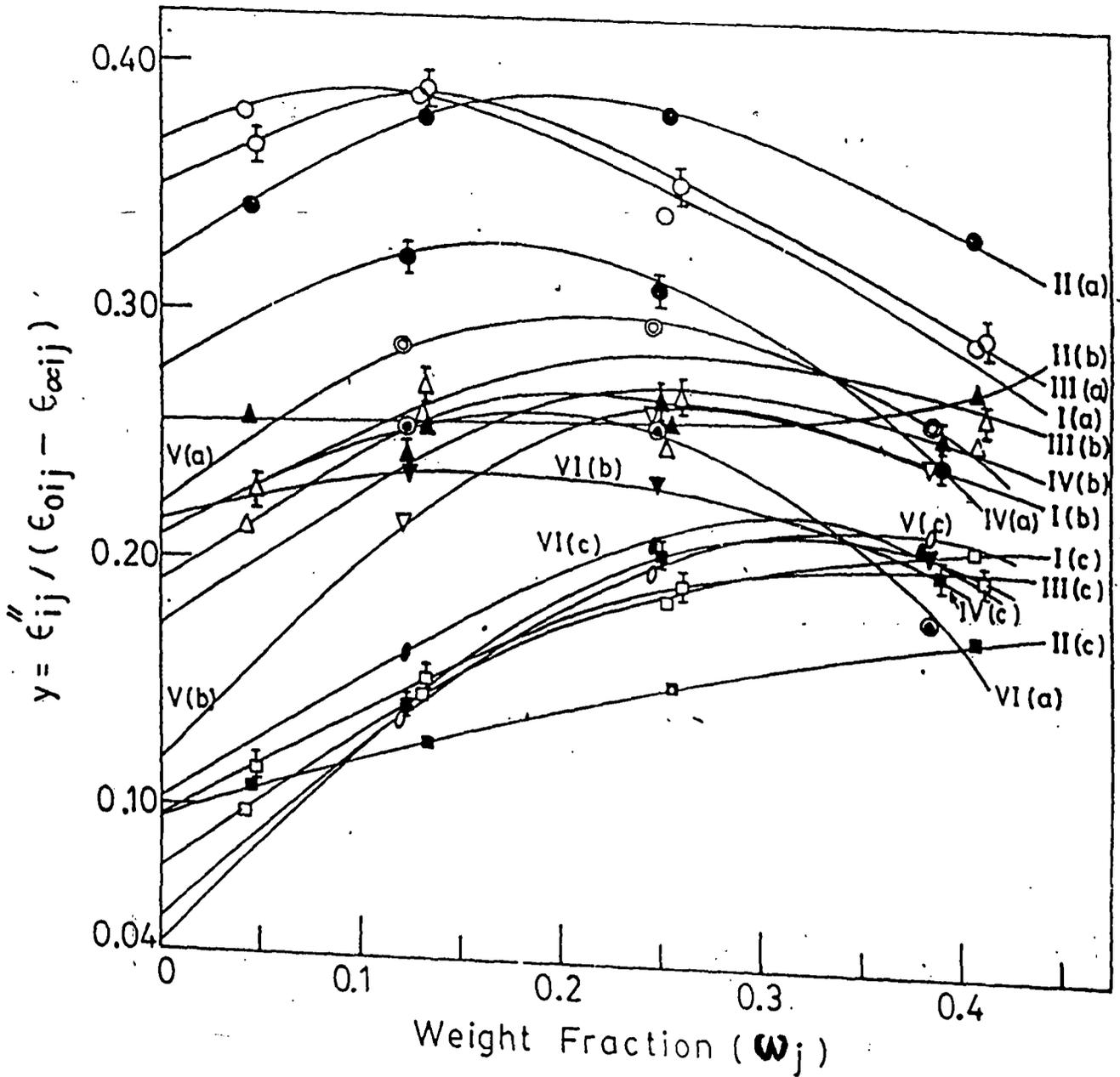
System-II(a) (-●-), II(b) (-▲-), II(c) (-■-) for 3-methyl-3-heptanol

System-III(a) (-○-), III(b) (-△-), III(c) (-□-) for 4-methyl-3-heptanol

System-IV(a) (-⊙-), IV(b) (-▲-), IV(c) (-■-) for 5-methyl-3-heptanol

System-V(a) (-⊙-), V(b) (-▽-), V(c) (-⊙-) for 4-octanol

System-VI(a) (-⊙-), VI(b) (-▼-), VI(c) (-●-) for 2-octanol



**Figure 7.3** Plot of  $\epsilon''_{ij} / (\epsilon_{0ij} - \epsilon_{\infty ij})$  against weight fraction  $\omega_j$  of some isomeric octyl alcohols in n-heptane at 25°C

System-I(a) (-O-), I(b) (-Δ-), I(c) (-□-) for 2-methyl-3-heptanol

System-II(a) (-●-), II(b) (-▲-), II(c) (-■-) for 3-methyl-3-heptanol

System-III(a) (-⊙-), III(b) (-⊘-), III(c) (-⊚-) for 4-methyl-3-heptanol

System-IV(a) (-⊖-), IV(b) (-⊗-), IV(c) (-⊕-) for 5-methyl-3-heptanol

System-V(a) (-⊗-), V(b) (-∇-), V(c) (-⊘-) for 4-octanol

System-VI(a) (-⊙-), VI(b) (-∇-), VI(c) (-●-) for 2-octanol

Bergmann's Eqs. (7.2) and (7.3) when the once estimated  $\tau_1$  and  $\tau_2$  from Eq. (7.8) are substituted in the right hand sides of the above Eqs (7.2) and (7.3)

The dipole moments  $\mu_1$  and  $\mu_2$  of octyl alcohols in terms of  $\tau_1$  and  $\tau_2$  and slope  $\beta$  of the concentration variation of the experimental hf conductivity  $K_{ij}$  were then estimated. The hf conductivity  $K_{ij}$  is, however, given by Murphy and Morgan [17]:

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon''_{ij} + \epsilon'_{ij})^2 \quad \dots\dots(7.11)$$

as a function of  $\omega_j$  of polar solute. Since  $\epsilon''_{ij} \ll \epsilon'_{ij}$  in the hf electric field, the term  $\epsilon''_{ij}$  offers resistance to polarisation. Thus the real part  $K'_{ij}$  of the hf  $K^*_{ij}$  of a polar-nonpolar liquid mixture at T K can be written according to Smyth [18] as :

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j k T} \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \omega_j \quad \dots\dots(7.12)$$

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

$$\left( \frac{d K'_{ij}}{d \omega_j} \right)_{\omega_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3 M_j k T} \left( \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad \dots\dots(7.13)$$

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 hf conductivity  $K_{ij} = \frac{\omega}{4\pi} \epsilon'_{ij}$  can be written as

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

$$\text{or. } \left( \frac{d K'_{ij}}{d \omega_j} \right)_{\omega_j \rightarrow 0} = \omega \tau \left( \frac{d K_{ij}}{d \omega_j} \right)_{\omega_j \rightarrow 0} = \omega \tau \beta \quad \dots\dots(7.14)$$

where  $\beta$  is the slope of  $K_{ij} - \omega_j$  curve at infinite dilution. From Eqs (7.13) and (7.14) we get

$$\mu_j = \left( \frac{27 M_j k T}{N \rho_i (\epsilon_i + 2)^2 \omega} \frac{\beta}{b} \right)^{1/2} \quad \dots\dots(7.15)$$

as the dipole moment of each octyl alcohol in terms of b, where b is a dimensionless parameter given by

$$b = \frac{1}{1 + \omega^2 \tau^2} \quad \dots\dots(7.16)$$

The computed  $\mu_1$  and  $\mu_2$  together with  $b_1$ ,  $b_2$  and  $\beta$  of  $K_{ij} - \omega_j$  equations for all the octyl alcohols are placed in Table 7.4

### 7.3 Results and Discussion

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 six isomeric octyl alcohols like 2-methyl-3-heptanol, 3-methyl-3-heptanol, 4-methyl-3-heptanol, 5-methyl-3-heptanol, 4-octanol and 2-octanol in solvent n-heptane at 25°C under 24.33, 9.25 and 3.00 GHz electric field at different  $\omega_j$ 's of polar solutes in terms of measured data (Table 7.1) are shown in Fig 7.1 together with the experimental points on them.  $\omega_j$ 's are however, calculated from the mole fractions  $x_i$  and  $x_j$  of solvent and solute with molecular weights  $M_i$  and  $M_j$  respectively according to the relation [19]:

$$\omega_j = \frac{x_j M_j}{x_i M_i + x_j M_j}$$

All the straight line equations are almost perfectly linear as evident from the correlation coefficients r lying in the range 0.9985 to 0.5684. The corresponding % of errors in terms of r in getting the slopes and intercepts of all the straight lines are placed in the 6th and 5th columns of Table 7.2. The errors are, however, large at 24.33 GHz indicating departure from the linear behaviour by low values of r perhaps due to inherent uncertainty in measured data for such higher frequency [13].

The estimated  $\tau_2$  and  $\tau_1$  for all the isomeric octyl alcohols from the slope and the intercept of straight line equations are of smaller magnitude at 24.33 GHz and increase gradually to attain maximum value at 3.00 GHz under the present investigation. This may be due to the fact that at higher frequency the rate of hydrogen bond rupture in long chain alcohols is maximum thereby reducing  $\tau$  for each rotating unit [13].  $\tau_2$  and  $\tau_1$  are then compared with the measured  $\tau_s$  from the relation:

$$K_{ij}'' = K_{\infty ij} + \frac{1}{\omega \tau_s} K_{ij}'$$

and  $\tau_0$  where  $\tau_0 = \sqrt{\tau_1 \tau_2}$ . As evident from Table 7.2 although  $\tau_0 > \tau_s$ ;  $\tau_s$  agrees well with  $\tau_1$  for most of the solutes except slight disagreement at 3.00 GHz for 4-methyl-3-heptanol, 5-methyl-3-heptanol, 4-octanol and 2-octanol. This is explained on the basis of the fact that conductivity measurement may be applicable in higher frequency in yielding microscopic  $\tau$  only whereas the double relaxation method offers a better understanding of molecular relaxation phenomena showing microscopic as well as macroscopic  $\tau$  as observed earlier [13]. Unlike normal aliphatic alcohols, — OH groups are screened by the substituted — CH<sub>3</sub> group, broad dispersion characterised by relatively short relaxation times were thus observed. The respective positions of — CH<sub>3</sub> and — OH groups also greatly influence the static dielectric constant, correlation factor, their temperature dependence and type of hydrogen bonding in them.

The relative contributions  $c_1$  and  $c_2$  toward dielectric relaxations are also estimated

in terms of  $\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}}$ ,  $\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}}$  with the estimated  $\tau_1$ ,  $\tau_2$  as shown in Table 7.3 by

Fröhlich and graphical methods.  $x = (\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$  and  $y = \epsilon''_{ij} / (\epsilon_{0ij} - \epsilon_{\infty ij})$  were, however, evaluated from Fröhlich's Eqs. (7.9) and (7.10) in the first case. The usual variations of  $(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$  and  $\epsilon''_{ij} / (\epsilon_{0ij} - \epsilon_{\infty ij})$  with  $\omega_j$  are concave and convex as found in Figs 7.2, and 7.3 in accordance with Bergmann equations (7.2) and (7.3) except 5-methyl-3-heptanol at 24.33 GHz whose  $[(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})] - \omega_j$  curve is convex in nature perhaps due to its nonaccurate  $\epsilon_{0ij}$  and  $\epsilon_{\infty ij}$  values like ethanol

as observed earlier [13].  $x$  and  $y$  were also obtained graphically from Figs 7.2, and (7.3) in the limit  $\omega_j = 0$ .

In Fröhlich-method  $c_1$  and  $c_2$  are all + ve as evident from 6th and 7th columns of Table 7.3 with  $c_2 > c_1$ . In graphical method  $c_1 > c_2$  with - ve  $c_2$  for most of the systems probably due to inertia of the flexible parts under hf electric field, as shown in 10th and 11th columns of same Table 7.3.  $c_2$  are, however, + ve for the systems 5-methyl-3-heptanol, 4-octanol and 2-octanol at 24.33 GHz as well as 3-methyl-3-heptanol at 9.25 GHz. Both the methods in most cases yield  $|c_1 + c_2| \geq 1$  : signifying thus the possibility of occurrence of more than two relaxation processes in them [13].

The dipole moments  $\mu_1$  and  $\mu_2$  of all the isomeric alcohols due to their flexible parts and the whole molecules are estimated in terms of dimensionless parameters  $b_1$ ,  $b_2$  and slope  $\beta$  of  $K_{ij}-\omega_j$  curves by using Eq. (7.15). The variation of  $K_{ij}$  with  $\omega_j$  are all linear having almost same intercepts  $\alpha$  and slopes  $\beta$  at each frequency of electric field. It was, therefore, difficult to plot them as they almost coincide. The values of  $\alpha$  and  $\beta$  of  $K_{ij}$ 's are little different and comparatively large at 24.33 GHz (Table 7.4). This sort of behaviour is perhaps due to same dipole moments [16] possessed by the polar molecules under investigation as evident from  $\mu_2$  and  $\mu_1$  placed in 7th and 8th columns of Table 7.4.  $\mu_2$  for most of the polar molecules shows high values at 24.33 GHz and decrease gradually with lower frequencies except 3-methyl-3-heptanol, 5-methyl-3-heptanol and 2-octanol whose  $\mu_2$ 's are found greater at 9.25 GHz electric field. This type of behaviour may be explained on the basis of the fact that such alcohols behaving almost like polymer molecules have long chain of C-atoms and tend to break up in a nonpolar solvent in order to reduce or even eliminate the absorption under hf electric field. The proportion of smaller molecular species having comparatively small number of C-atoms and their corresponding absorption will increase thereby [10]. The values of  $\mu_1$ 's, on the other hand, are almost constant exhibiting a trend to increase a little towards low frequency. They are finally compared with bond moments of 1.5 D of  $\text{—O—H}$  group making an angle  $105^\circ$  with the C—O bond axis according to the preferred conformations of all the isomers as sketched in Fig 7.4. This confirms that  $\mu_1$  arises due to the rotation of  $\text{—OH}$  group around C-O bond in the

**Table 7.3** Fröhlich parameter A, relative contributions  $c_1$  and  $c_2$  due to  $\tau_1$  and  $\tau_2$ , theoretical values of x and y from Fröhlich's equations (7.9) and (7.10) and from graphical extrapolation technique at  $\omega_j \rightarrow 0$

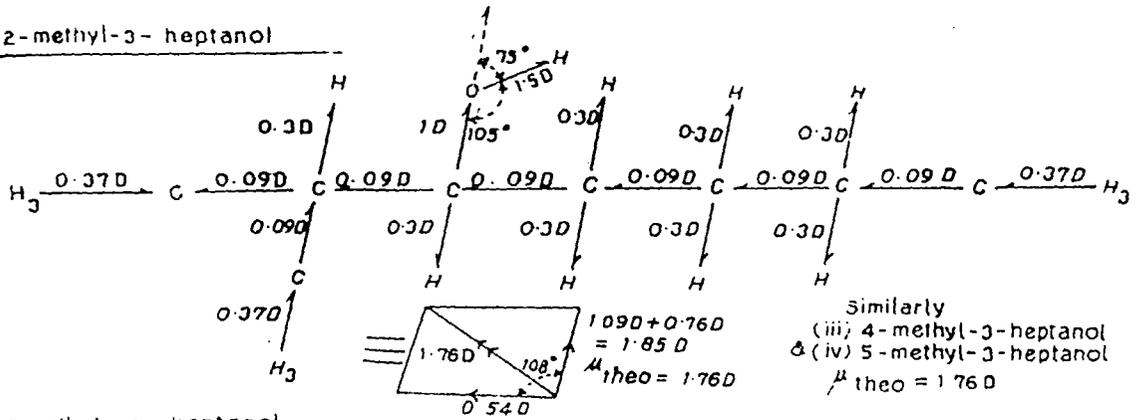
System with Sl. No.	Frequency in GHz	Fröhlich parameter A = $\ln(\tau_2/\tau_1)$	Theoretical values of x & y from eqs (7.9) and (7.10)		Theoretical values of $c_1$ and $c_2$		Estimated values of x and y at $\omega_j \rightarrow 0$		Estimated values of $c_1$ and $c_2$	
I. 2-methyl-3-heptanol in n-heptane	a) 24.33	2.1790	0.3457	0.4028	0.3686	1.2101	0.795	0.366	1.0226	-0.2476
	b) 9.25	2.4932	0.5637	0.4023	0.4886	0.9434	1.075	0.19	1.1624	-0.2324
	c) 3.00	2.6063	0.7973	0.3232	0.6144	0.5500	1.075	0.074	1.1143	-0.0808
II. 3-methyl-3-heptanol in n-heptane	a) 24.33	1.6897	0.5195	0.4490	0.4542	0.7733	0.865	0.32	1.0321	-0.1120
	b) 9.25	2.2943	0.5792	0.4115	0.4922	0.8573	0.91	0.256	0.9569	0.0810
	c) 3.00	2.4781	0.7865	0.3349	0.6028	0.5600	1.025	0.094	1.0589	-0.0579
III. 4-methyl-3-heptanol in n-heptane	a) 24.33	2.0378	0.3747	0.4173	0.3857	1.0842	0.78	0.35	0.9961	-0.2117
	b) 9.25	2.3710	0.5775	0.4075	0.4932	0.8812	0.95	0.208	1.0177	-0.0805
	c) 3.00	2.5313	0.7543	0.3490	0.5902	0.6112	1.015	0.094	1.0551	-0.0827
IV. 5-methyl-3-heptanol in n-heptane	a) 24.33	2.3741	0.5644	0.4088	0.4862	0.9057	0.645	0.274	0.6389	0.3763
	b) 9.25	2.5207	0.5499	0.4020	0.4814	0.9805	0.95	0.172	1.0297	-0.2211
	c) 3.00	2.7332	0.7222	0.3529	0.5833	0.6848	1.065	0.042	1.1326	-0.2341
V. 4-octanol in n-heptane	a) 24.33	2.3555	0.5080	0.4131	0.4553	1.0030	0.72	0.22	0.7840	0.0126
	b) 9.25	2.7844	0.6506	0.3720	0.5463	0.8372	0.895	0.116	0.9254	-0.0654
	c) 3.00	2.8924	0.7813	0.3197	0.6210	0.5900	0.99	0.052	1.0218	-0.0850
VI. 2-octanol in n-heptane	a) 24.33	2.7964	0.4507	0.3867	0.4257	1.3507	0.67	0.208	0.7223	0.0764
	b) 9.25	2.8925	0.4292	0.3795	0.4124	1.4780	0.895	0.214	0.9850	-0.3026
	c) 3.00	3.0198	0.6201	0.3658	0.5361	0.9672	1.04	0.102	1.0810	-0.1813

Table 7.4

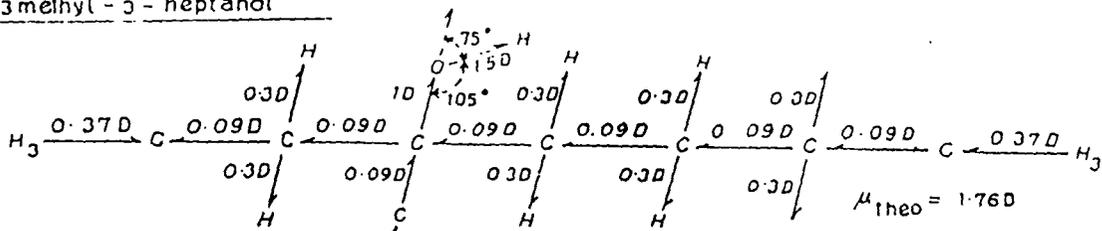
Estimated intercept and slope of  $K_{ij} - \omega_j$  equation, dimensionless parameters  $b_2, b_1$  (Eq. (7.16)), estimated dipole moments  $\mu_2, \mu_1$  (eq. (7.15)),  $\mu_{theo}$  from bond angles and bond moments together with  $\mu_1$  from  $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$  in Debye.

System with Sl. No. & Mol. wt.	Frequency in GHz	Intercept & slope of $K_{ij} - \omega_j$ equation $\alpha \times 10^{-10}$ $\beta \times 10^{-10}$		Dimensionless parameters $b_2$ $b_1$		Estimated dipole moments (in Debye) $\mu_2$ $\mu_1$		$\mu_{theo}$ in D	Estimated $\mu_1$ in D from $\mu_1 =$ $\mu_2 \left( \frac{c_1}{c_2} \right)^{1/2}$
		$\alpha \times 10^{-10}$	$\beta \times 10^{-10}$	$b_2$	$b_1$	$\mu_2$	$\mu_1$		
I. 2-methyl-3- heptanol in n- heptane $M_j = 130\text{gm}$	a) 24.33	2.3632	0.6974	0.0455	0.7885	4.80	1.15	1.76	2.65
	b) 9.25	0.8998	0.3126	0.1075	0.9463	3.39	1.14		2.44
	c) 3.00	0.2911	0.1224	0.3439	0.9897	2.08	1.23		2.20
II. 3-methyl- 3-heptanol in n-heptane $M_j = 130\text{gm}$	a) 24.33	2.3630	0.7490	0.1689	0.8564	2.58	1.15	1.76	1.98
	b) 9.25	0.8959	0.3554	0.1363	0.9395	3.21	1.22		2.43
	c) 3.00	0.2910	0.1330	0.3425	0.9867	2.18	1.28		2.26
III. 4-methyl -3- heptanol in n-heptane $M_j = 130\text{gm}$	a) 24.33	2.3635	0.7213	0.0623	0.7963	4.17	1.17	1.76	2.49
	b) 9.25	0.8984	0.3278	0.1273	0.9436	3.19	1.17		2.39
	c) 3.00	0.2911	0.1283	0.2837	0.9843	2.35	1.26		2.31
IV. 5-methyl - 3-heptanol in n-heptane $M_j = 130\text{gm}$	a) 24.33	2.3646	0.6415	0.1187	0.9396	2.85	1.01	1.76	2.09
	b) 9.25	0.9021	0.2771	0.0975	0.9436	3.35	1.08		2.35
	c) 3.00	0.2922	0.1138	0.2157	0.9849	2.54	1.19		2.34
V. 4-octanol in n-heptane $M_j = 130\text{gm}$	a) 24.33	2.3561	0.6492	0.0903	0.9169	3.29	1.03	1.08	2.22
	b) 9.25	0.8965	0.2618	0.1396	0.9770	2.72	1.03		2.20
	c) 3.00	0.2919	0.1044	0.2799	0.9922	2.13	1.13		2.19
VI. 2-octanol in n-heptane $M_j = 130\text{gm}$	a) 24.33	2.3533	0.6572	0.0428	0.9230	4.80	1.03	1.08	2.69
	b) 9.25	0.8980	0.2753	0.0338	0.9190	5.67	1.09		3.00
	c) 3.00	0.2897	0.1221	0.0987	0.9787	3.88	1.23		2.89

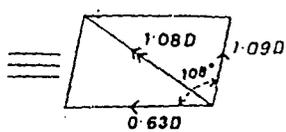
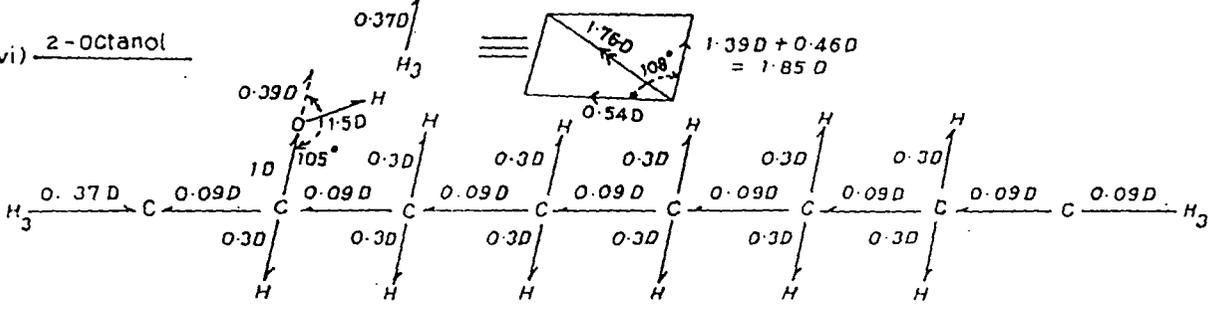
(i) 2-methyl-3-heptanol



(ii) 3-methyl-3-heptanol



(vi) 2-octanol



$\mu_{theo} = 1.08D$  and similarly for (v) 4-octanol

$\mu_{theo} = 1.08D$

Figure 7.4. Conformations of some isomeric octyl alcohols

long chain alcohols studied so far [13]. The slight difference is due to difference in steric hindrances as a result of structural configurations at different frequencies.  $\mu_1$ 's also estimated from  $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$  assuming two relaxation processes are equally probable as shown in the last column of Table 7.4. The other bond moments 0.37, 0.3, 1 and 0.09 D for  $C \leftarrow H_3$ ,  $C \rightarrow H$ ,  $C \rightarrow O$  and  $C \leftarrow C$  bonds are also involved to justify their conformations. The resultant of all these bonds by vector addition method yields  $\mu_{theo}$  of 1.76 D and 1.08 D for four methyl substituted heptanols and two octanols respectively. The derived result should decrease with increase in the number of C-atoms and  $\mu_{theo}$  for them should be less than that for 1-heptanol [13]. But  $\mu_{theo}$  in Fig 7.4 for three isomers are only displayed due to typical positions of their  $—CH_3$  and  $—OH$  groups. This may probably be the reason of having slightly larger values of  $\mu_{theo}$  from 1-heptanol as observed earlier [13].

#### 4. Conclusion

The methodology so far advanced for the double broad dispersions of the polar-nonpolar liquid mixtures based on Debye's model seems to be much simpler, straight forward and significant one to detect the very existence of double relaxation times  $\tau_1$  and  $\tau_2$  of polar liquid in a nonpolar solvent. The correlation coefficients between the desired dielectric relaxation parameters involved in the desired equation (7.8) could, however, be estimated to find out % of errors entered in the estimated  $\tau_1$  and  $\tau_2$  of a polar liquid, because  $\tau$  is claimed to be accurate within  $\pm 10\%$ . The isomeric octyl alcohols like normal aliphatic alcohols are found to yield both  $\tau_1$  and  $\tau_2$  at all frequencies of the electric field of GHz range. The corresponding dipole moments  $\mu_1$  and  $\mu_2$  can then be estimated from Eq. (7.15) in terms of  $b_1$  and  $b_2$  which are, however, involved with  $\tau_1$  and  $\tau_2$  as estimated, to arrive at their preferred conformations sketched in Fig 7.4

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