

CHAPTER -4

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

DOUBLE RELAXATIONS OF SOME ISOMERIC OCTYL ALCOHOLS BY HIGH FREQUENCY ABSORPTION IN NON-POLAR SOLVENT

4.1. 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 μ in terms of the relaxation time τ for a polar molecule in a nonpolar solvent under different high frequency (*hf*) electric field of gigahertz (GHz) range at a fixed or different temperatures. There exist several methods[2] to estimate τ 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 non-spherical polar molecules, on the other hand, possess more than one τ 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 ϵ^* , of a polar liquid may be represented as the sum of a number of non-interacting Debye type dispersions each with a characteristic τ . 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 τ_1 and τ_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 ϵ' , imaginary ϵ'' parts of ϵ^* , static dielectric constant ϵ_0 and high frequency dielectric constant ϵ_∞ 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 τ_1 , τ_2 and c_2, c_2 for a polar liquid from the relaxation data measured at least at two different frequencies of the electric fields.

A procedure was devised [6] to get τ_1 and τ_2 from the slope and intercept of a derived straight line equation involved with the single frequency measurements of the dielectric relaxation parameters like ϵ_{oij} , $\epsilon_{\infty ij}$, ϵ'_{ij} and ϵ''_{ij} for different weight fractions w_j 's 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[7] at 22.06, 3.86, 2.02 GHz electric fields respectively. All these investigations reveal that they often showed the double relaxation behaviour at certain frequency of the electric field.

The aliphatic alcohols 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 τ , besides the average macroscopic distribution of τ . The 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 ϵ^*_{ij} . The relaxation behaviour of aliphatic alcohols is very interesting because they show more than two τ '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 behaviour 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 τ_1 and τ_2 at all frequencies of the electric field except methanol which is a simple molecule to possess the expected τ_2 only.

The method [6] was applied 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 1-3 respectively, because of the availability of ϵ'_{ij} , ϵ''_{ij} , ϵ_{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 w_j 's are linear as shown in Figure 4.1 only to establish the applicability of Debye model in such isomeric alcohols like normal alcohols [13] once again. 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].

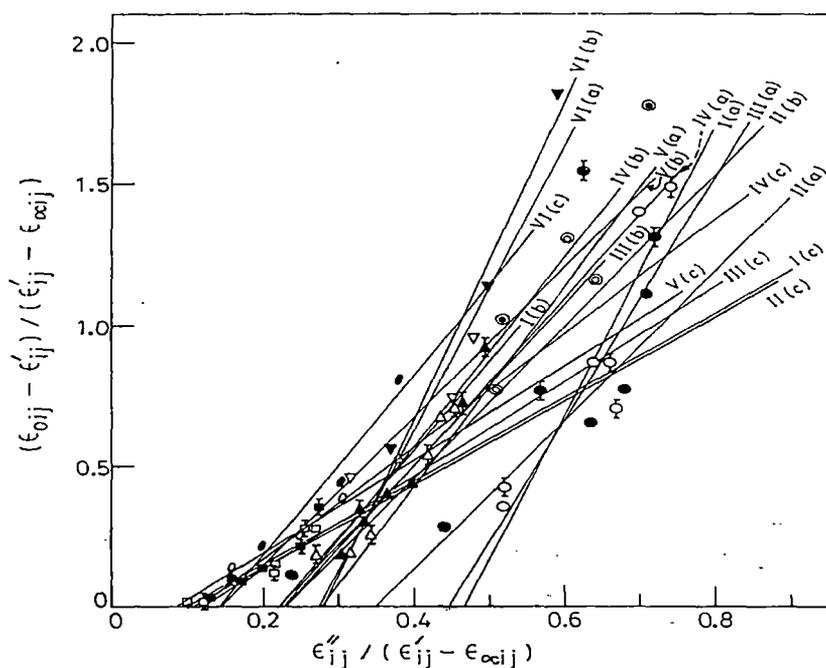


Figure 4.1 : Plot of $(\epsilon_{0ij} - \epsilon'_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})$ against $\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$ of some isomeric octyl alcohols in n-heptane at 25°C.

Ia, Ib, Ic for 2 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (O, Δ , \square)
 IIa, IIb, IIc for 3 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (\bullet , \blacktriangle , \blacksquare)
 IIIa, IIIb, IIIc for 4 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (\odot , \triangleleft , \square)
 IVa, IVb, IVc for 5 methyl 3 heptanol at 24.33, 9.25, and 3.00 GHz (\oplus , \blacktriangle , \blacksquare)
 Va, Vb, Vc for 4 octanol at 24.33, 9.25 and 3.00 GHz (\ominus , ∇ , \circ)
 VIa, VIb, VIc for 2 octanol at 24.33, 9.25 and 3.00 GHz (\odot , \blacktriangledown , \bullet)

Table 4.1 : The estimated relaxation times τ_2 and τ_1 from the slopes and the intercepts of straight line Eq. (4.8) with % of errors and correlation coefficients (r) together with measured τ_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.&Mol.wt.M _i	Frequency in GHz	Intercept & slope of Eq.(4.8)		Correlation coefficient (r)	% Error in regression technique	Estimated value of τ_2 & τ_1 in p. Sec.		Measured τ_s in p. Sec.	Most probable relaxation time $\tau_0 = \sqrt{\tau_1\tau_2}$
I 2-methyl-3-heptanol(a) in n-heptane M _i =130gm	24.33	2.3718	5.0952	0.9011	6.34	29.96	3.39	1.84	10.08
	9.25	0.6871	3.1205	0.9700	1.90	49.61	4.10	3.58	14.26
	3.00	0.1408	1.4830	0.9771	1.50	73.31	5.41	6.74	19.91
II 3-methyl-3-heptanol(a) in n-heptane M _i =130gm	24.33	0.9087	2.6282	0.9294	4.59	14.52	2.68	2.19	6.24
	9.25	0.6389	2.7714	0.9709	1.93	43.34	4.37	3.70	13.76
	3.00	0.1611	1.5018	0.9985	0.10	73.55	6.17	5.58	21.30
III 4-methyl-3-heptanol(a) in n-heptane M _i =130gm	24.33	1.9653	4.3873	0.8851	7.30	25.40	3.31	1.90	9.17
	9.25	0.6411	2.8636	0.9682	2.11	45.08	4.21	4.13	13.78
	3.00	0.2008	1.7153	0.9206	5.14	84.34	6.71	11.98	23.79
IV 5-methyl-3-heptanol(a) in n-heptane M _i =130gm	24.33	0.6929	2.9788	0.5684	26.36	17.83	1.66	1.71	5.44
	9.25	0.7445	3.2866	0.9846	1.19	52.36	4.21	5.39	14.85
	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 _i =130gm	24.33	0.9572	3.4750	0.8569	10.34	20.77	1.97	1.83	5.40
	9.25	0.3810	2.6361	0.9470	4.02	42.74	2.64	5.46	10.62
	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 _i =130 gm.	24.33	1.3664	5.0208	0.6336	23.30	30.97	1.89	1.83	7.65
	9.25	1.5853	5.6407	0.9888	0.86	92.00	5.11	6.26	21.68
	3.00	0.4458	3.1697	0.9780	1.69	160.41	7.83	18.70	35.44

Table 4.2 : Fröhlich parameter A, relative contributions c_1 and c_2 due to τ_1 and τ_2 , theoretical values of x and y from Fröhlich's Eqs(4.9) and (4.10) and from graphical extrapolation technique at $\omega_j \rightarrow 0$.

System with Sl. No.	Frequency, GHz	Fröhlich parameter A = ln(τ_1/τ_2)	Theoretical values of x & y from Eqs. (4.9) and (4.10)		Theoretical values of c_1 & c_2		Estimated values of x & 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(a) in n-heptane	(a) 24.33	1.6997	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(a) 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(a) 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	7.5207	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	2.7833	0.6506	0.8720	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	2.3925	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

The paper presents the frequency dependence of τ_1 and τ_2 at all frequencies of 24.33, 9.25 and 3.00 GHz electric field for all the octyl alcohols like normal alcohols too. The measured τ_s from the slope of the linear equation of imaginary

K''_{ij} and real K'_{ij} part of the total complex hf conductivity K^*_{ij} and the most probable relaxation time τ_0 from $\tau_0 = \sqrt{\tau_1\tau_2}$ are placed in Table 4.1 together with the estimated τ_1 and τ_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 intramolecular relaxation time τ_1 and molecular relaxation time τ_2 are then estimated from Fröhlich's equations [15] as well as the graphical method of Figures 4.2 and 4.3. The estimated c_1 and c_2 are placed in Table 4.2.

The dipole moments μ_1 and μ_2 due to flexible parts as well as the whole molecules in terms of the estimated τ_1 and τ_2 and the slopes β of the linear variation of hf conductivity K_{ij} with w_j are shown in Table 4.3.

Table 4.3 : Estimated intercept and slope of $K_{ij}-w_j$ equation, dimensionless parameters b_1, b_2 Eq.(4.16), estimated dipole moments μ_2, μ_1 Eq.(4.15), μ_{theo} from bond angles and bond moments together with μ_1 from $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$ in Debye.

System with Sl. No. & Mol wt.	Frequency GHz	Intercept & slope of of $K_{ij}-w_j$ equation		Dimensionless parameter		Estimated dipole moments (In Debye)		μ_{theo} in D	Estimated μ_1 in D from $\mu_1 = \mu_2(c_1/c_2)^{1/2}$
		$\alpha \times 10^{-18}$	$\beta \times 10^{-10}$	b_1	b_2	μ_2	μ_1		
I 2-methyl-3-heptanol(a) in n-heptane $M_1 = 130\text{gm}$	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(a) in n-heptane $M_1 = 130\text{gm}$	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	0.2867	2.18	1.29		2.26
III 4-methyl-3-heptanol(a) in n-heptane $M_1 = 130\text{gm}$	24.33	2.3635	0.7213	0.6230	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(a) in n-heptane $M_1 = 130\text{gm}$	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 $M_1 = 130\text{gm}$	(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 $M_1 = 130\text{ gm.}$	(a) 24.33	2.3533	0.6572	0.9428	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	0.0887	0.9787	3.88	1.23		2.89

The slopes β and the intercepts α of the linear variation of K_{ij} with w_j , as placed in Table 4.3, at each frequency for all isomers in n-heptane are almost the same probably due to their same polarity [16]. This fact is also supported by their conformations as shown in Figure 4.4. It was, therefore, very difficult to plot K_{ij} against w_j . The computed μ_2 's for most of the isomeric alcohols show larger

values at 24.33 GHz and gradually decrease with lower frequencies unlike μ_1 . In order to compare μ_2 and μ_1 with theoretical dipole moments μ_{theo} , a special attention is to be paid on the conformational structure of each isomer from the available bond angles and bond moment. They are shown in Figure 4.4. Using the usual C—C bond moment of 0.09 D from methanol and ethanol [13] μ_{theo} for four methyl substituted octanols are found to show slightly larger values (see Figure 4.4 and Table 4.3) than 1-heptanol [13] except the desired values for 2-octanol and 4-octanol perhaps due to bond moments of C—H₃ and —O—H groups in their structures. The calculated value of μ_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 4.3 with all the estimated μ 's for comparison.

4.2. Theoretical Formulations to Estimate Relaxation Parameters

The complex dielectric constant ϵ_{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.

$$\frac{\epsilon_{ij}^* - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \sum \frac{c_k}{1 + j\omega\tau_k} \quad (4.1)$$

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

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{c_1}{1 + \omega^2\tau_1^2} + \frac{c_2}{1 + \omega^2\tau_2^2} \quad (4.2)$$

and

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (4.3)$$

such that $c_1 + c_2 = 1$. Now with

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

$\omega\tau = \alpha$ and using $a = (1/1+\alpha^2)$ $b = \alpha/(1+\alpha^2)$ the Eqs (4.2) and (4.3) can be written as;

$$x = c_1 a_1 + c_2 a_2 \quad (4.4)$$

$$y = c_1 b_1 + c_2 b_2 \quad (4.5)$$

where suffixes 1 and 2 with a and b are related to τ_1 and τ_2 respectively. From Eqs (4.4) and (4.5), since $\alpha_2 - \alpha_1 \neq 0$ and $\alpha_2 > \alpha_1$ we have

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad (4.6)$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad (4.7)$$

Since $c_1 + c_2 = 1$, we get the following equation with the help of Eqs (4.6) and (4.7):

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

which on substitution of the values x , y and α yields :

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2 \quad (4.8)$$

Eq. (4.8) is thus a straight line equation between $(\epsilon_{0ij} - \epsilon'_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})$ and $\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$ with slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2 \tau_1 \tau_2$ respectively, where ω is the angular frequency of the applied electric field of frequency f in GHz. With the measured dielectric relaxation data of ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ for different weight fractions w_j 's of each octyl alcohol in n-heptane at 25°C under 24.33, 9.25 and 3.00 GHz electric field [14] we get slope and intercept of Eq. (4.8) to yield τ_1 and τ_2 as shown in Table 4.1.

The relative contributions, c_1 and c_2 towards the dielectric relaxations in terms of x , y and τ_1 , τ_2 for each octyl alcohol are found out and placed in Table 4.2. The theoretical values [15] of x and y are, however, calculated from Fröhlich's Eqs:

$$x = \frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left(\frac{e^{2A} \omega^2 \tau_1^2 + 1}{1 + \omega^2 \tau_1^2} \right) \quad (4.9)$$

$$y = \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} [\tan^{-1}(e^A \omega \tau_1) - \tan^{-1}(\omega \tau_1)] \quad (4.10)$$

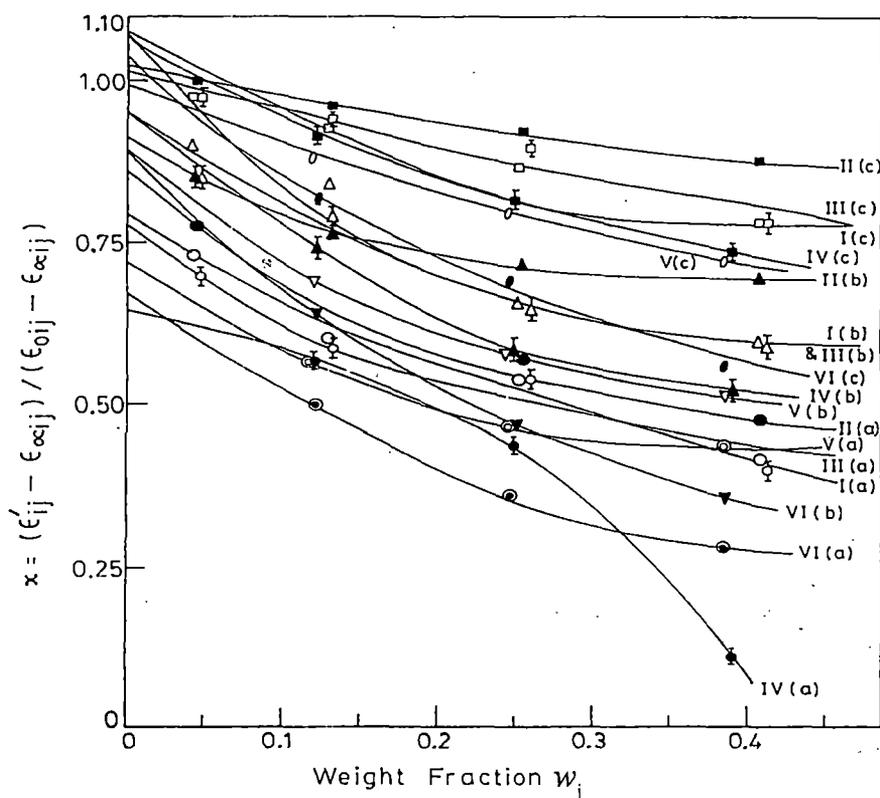


Figure 4.2 : Plot of $(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction w_j of some isomeric octyl alcohols in n-heptane at 25°C.

Ia, Ib, Ic for 2 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (O, Δ , \square)

Ila, Ilb, Ilc for 3 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (\bullet , \blacktriangle , \blacksquare)

IIIa, IIIb, IIIc for 4 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (\circ , Δ , \square)

IVa, IVb, IVc for 5 methyl 3 heptanol at 24.33, 9.25, and 3.00 GHz (\odot , \blacktriangle , \blacksquare)

Va, Vb, Vc for 4 octanol at 24.33, 9.25 and 3.00 GHz (\ominus , ∇ , \circ)

VIa, VIb, VIc for 2 octanol at 24.33, 9.25 and 3.00 GHz (\odot , \blacktriangledown , \bullet)

where $A = \text{Fröhlich parameter} = \ln(\tau_2/\tau_1)$ and τ_1 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 $w_j \rightarrow 0$ from Figures 4.2 and 4.3 respectively. This is really in accordance with Bergmann's Eqs (4.2) and (4.3) when the once estimated τ_1 and τ_2 from Eq. (4.8) are substituted in the right hand sides of above Eqs (4.2) and (4.3).

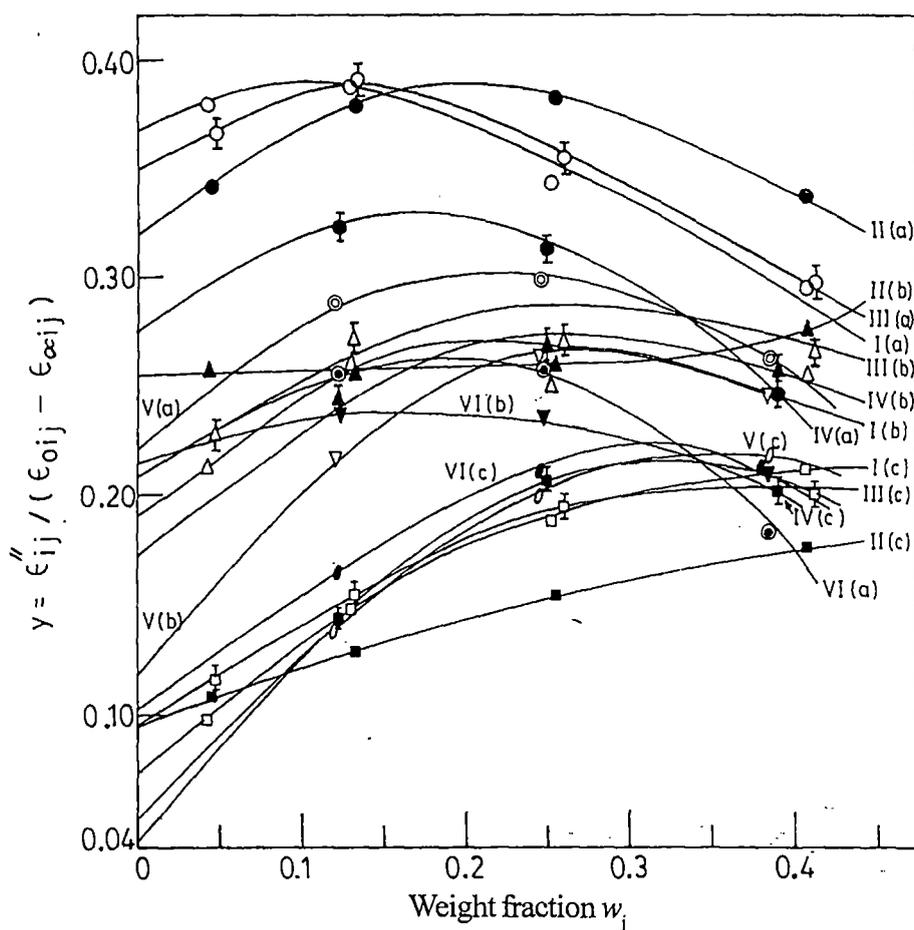


Figure 4.3 : Plot of $\epsilon''_{ij}/(\epsilon_{0ij}-\epsilon_{\infty ij})$ against weight fraction w_j of some isomeric octyl alcohols in n-heptane at 25°C.

Ia, Ib, Ic for 2 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (O, Δ , \square)

Ila, IIb, IIc for 3 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (\bullet , \blacktriangle , \blacksquare)

IIIa, IIIb, IIIc for 4 methyl 3 heptanol at 24.33, 9.25 and 3.00 GHz (\odot , \triangleleft , \square)

IVa, IVb, IVc for 5 methyl 3 heptanol at 24.33, 9.25, and 3.00 GHz (\odot , \blacktriangle , \blacksquare)

Va, Vb, Vc for 4 octanol at 24.33, 9.25 and 3.00 GHz (\odot , ∇ , \circ)

VIa, VIb, VIc for 2 octanol at 24.33, 9.25 and 3.00 GHz (\odot , \blacktriangledown , \bullet)

The values of μ_1 and μ_2 of octyl alcohols in terms of τ_1 , τ_2 and slope β 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]:

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon''_{ij}{}^2 + \epsilon'_{ij}{}^2)^{1/2} \quad (4.11)$$

as a function w_j of polar solute. Since $\epsilon''_{ij} \ll \epsilon'_{ij}$ in the *hf* electric field, the term ϵ''_{ij} offers resistance of polarisation. Thus the real K'_{ij} of the *hf* K^*_{ij} of a polar-nonpolar liquid mixture at TK can be written according to Smyth [18] as :

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) w_j \quad (4.12)$$

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

$$\left(\frac{dK'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad (4.13)$$

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

Again, the total *hf* conductivity $K_{ij} = (\omega/4\pi)\epsilon_{ij}$ can be written as :

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

or

$$\left(\frac{dK'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega\tau \left(\frac{dK_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega\tau\beta \quad (4.14)$$

where β is the slope of $K_{ij} - w_j$ curve at infinite dilution. From Eqs. (4.13) and (4.14) we get :

$$\mu_j = \left[\frac{27M_j kT}{N\rho_j (\epsilon_j + 2)^2} \cdot \frac{\beta}{\omega b} \right]^{1/2} \quad (4.15)$$

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

$$b = \frac{1}{1 + \omega^2 \tau^2} \quad (4.16)$$

The computed μ_1 and μ_2 together with b_1 , b_2 and β of $k_{ij}-w_j$ equations for all the octyl alcohols are placed in Table 4.3.

4.3. 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 w_j 's of polar solutes are shown in Figure 4.1 together with the experimental points on them. w_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].

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

All the straight line equations are almost perfectly linear as evident from the correlation coefficients r lying in the range 0.9985-0.5684. 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 4.1. The errors are, however, large at 24.33 GHz indicating departure from the linear behaviour as evident from low values of r perhaps due to inherent uncertainty in measured data for such higher frequency [13].

The estimated values of τ_2 and τ_1 for all the isomeric octyl alcohols from the slopes and the intercepts 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 the maximum thereby reducing τ for each rotating unit [13]. τ_2 and τ_1 are then compared with the measured τ_s from the relation :

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

and τ_0 where $\tau_0 = \sqrt{\tau_1\tau_2}$. As evident from Table 4.1 although $\tau_0 > \tau_1$; τ_s agrees well with τ_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 τ only whereas the double relaxation method offers a better understanding of molecular relaxation phenomena showing microscopic as well as macroscopic τ as observed elsewhere [13]. Unlike normal aliphatic alcohols, -OH groups are screened by the substituted -CH₃ group, broad dispersion characterised by relatively short relaxation times were thus observed [14]. The respective positions of -CH₃ and -OH groups also greatly affect the static dielectric constant, correlation factor, their temperature dependence and type of hydrogen bonding in them.

The relative contributions c_1 and c_2 towards dielectric relaxations are also estimated in terms of $(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$, $\epsilon''_{ij} / (\epsilon_{0ij} - \epsilon_{\infty ij})$ with the estimated, τ_1, τ_2 as shown in Table 4.2 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.(4.9) and (4.10) 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 ω_j are concave and convex as found in Figures 4.2 and

4.3 in accordance with Bergmann Eqs. (4.2) and (4.3), except 5-methyl-3-heptanol at 24.33 GHz whose $[(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})]$ curves is convex in nature due to its non-accurate ϵ_{0ij} and $\epsilon_{\infty ij}$ values like ethanol as observed elsewhere [13]. x and y were also obtained graphically from Figures 4.2 and 4.3 in the limit $w_j = 0$.

In Fröhlich method c_1 and c_2 are all positive as evident from 6th columns of Table 4.2 with $c_2 > c_1$. In graphical method $c_1 > c_2$ with negative 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 4.2. c_2 are, however, positive 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 $|c_2 + c_1| \geq 1$, signifying thus the possibility of occurrence of more than two relaxation processes in them [13].

The dipole moments μ_1 and μ_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 β of $K_{ij} - w_j$ curves by using Eq. (4.15). The variations of K_{ij} with w_j are all linear having almost the same intercepts α and slopes β at each frequency of electric field. It was, therefore, difficult to plot them as they almost coincide. The values of α and β of K_{ij} 's are little different and comparatively large at 24.33 GHz (Table 4.3). This sort of behaviour is perhaps due to same dipole moments [16] possessed by the polar molecules under investigation as evident from μ_2 and μ_1 placed in 7th and 8th columns of Table 4.3. μ_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 μ_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 the polymer molecules have long chain of C-atoms and tend to break up in 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 μ_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 O-H group making an angle 105° with the -C-O- bond axis according to the preferred conformations of all the isomers as sketched in Figure 4.4.

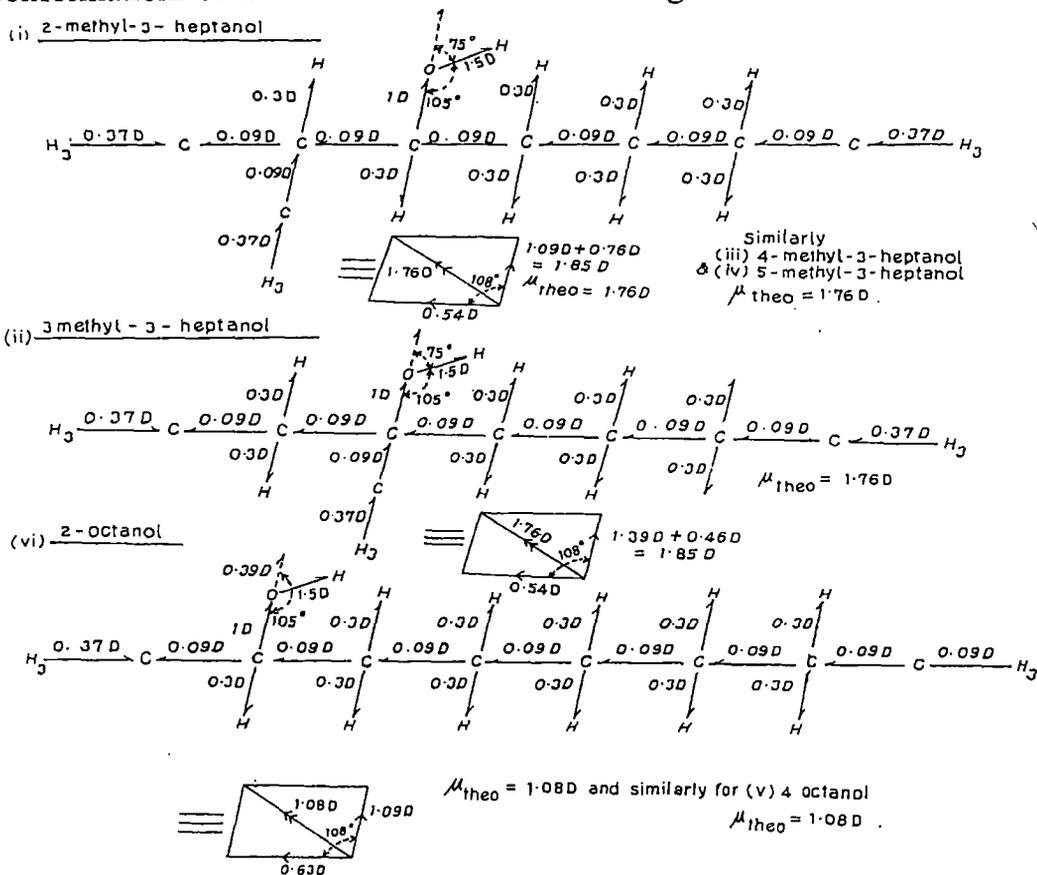


Figure 4.4: Conformations of some isomeric octyl alcohols

This confirms that μ_1 arises due to the rotation of -OH group around C-O bond in the 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. μ_1 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 4.3. The other bond moments 0.47, 0.3, 1.0 and 0.09 D for C-H₃, C-H, C-O

and C–C bonds are also involved to justify their conformations. The resultant of all these bonds by vector addition method yields μ_{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 μ_{theo} for them should be less than that for 1-heptanol [13]. But for μ_{theo} in Figure 4.4 three isomers are only displayed due to typical positions of $-\text{CH}_3$ and $-\text{OH}$ groups. This may probably be the reason of having slightly larger values of μ_{theo} from 1-heptanol as observed elsewhere [13].

4.4 Conclusions

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, straightforward and significant one to detect the very existence of τ_1 and τ_2 of a polar liquid in a nonpolar solvent. The correlation coefficients between the desired dielectric relaxation parameters involved in the derived equations of Eq. (4.8) could, however, be estimated to find out % of errors entered in the estimated τ_1 and τ_2 of a polar liquid, because τ is claimed to be accurate within $\pm 10\%$. The isomeric octyl alcohols like normal aliphatic alcohols are found to yield both τ_1 and τ_2 at all frequencies of the electric field of GHz range. The corresponding μ_1 and μ_2 can then be estimated from Eq. (4.15) in terms of b_1 and b_2 which are, however, involved with τ_1 and τ_2 as estimated, to arrive at their preferred conformations as shown in Figure 4.4.

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