

**LIST OF PUBLISHED AND COMMUNICATED
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The subject matter of this thesis has been published in different Indian and foreign journals of international repute

- 1) **"Double relaxation times of nonspherical polar liquids in nonpolar solvent: A new approach based on single frequency measurement"** U Saha, S K Sit, R C Basak and S Acharyya; J. Phys D: Appl. Phys. (London) 27 (1994) 596-603.
- 2) **"Single frequency measurement of double relaxation times of monosubstituted anilines in benzene"** S K Sit, R C Basak, U Saha and S Acharyya; J. Phys D: Appl. Phys. (London) 27 (1994) 2194-2202.
- 3) **"Double relaxations of monosubstituted anilines in benzene under effective dispersive region"** S K Sit and S Acharyya; Indian J. Pure & Appl. Phys 34 (1996) 255-262.
- 4) **"Double relaxation of straight chain alcohols under high frequency electric field"** S K Sit and S Acharyya; Indian J. Phys 70B (1996) 19-36.
- 5) **"Double relaxation of some isomeric octyl alcohols by high frequency absorption in nonpolar solvent"** S K Sit, N Ghosh and S Acharyya; Indian J. Pure & Appl. Phys. 35 (1997) press.
- 6) **"Structural and associational aspects of binary and single polar liquids in nonpolar solvent under high frequency electric field"** S K Sit, N Ghosh, U Saha and S Acharyya; Indian J. Phys 71B (1997) to be published in August issue of the Journal.
- 7) **"Double relaxation times, dipole moments and molecular structures of some non-spherical aprotic polar liquids in benzene from high frequency absorption measurement"** S K Sit, S Acharyya, T Palmajumder and S Roy; J Phys. D: Appl. Phys (London) 1997 Communicated.
- 8) **"Dipole moment of isotopomer molecule"** S K Sit and S Acharyya; J Phys B: Atom. Mole. Phys (London) 1997 communicated.

Double relaxation times of non-spherical polar liquids in non-polar solvent: a new approach based on single frequency measurement

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Abstract. A new approach based on single frequency measurement is suggested to estimate the double relaxation times, τ_1 and τ_2 of some highly non-spherical polar liquids in solvents benzene and carbon tetrachloride. The smaller relaxation time τ_1 refers to the smallest flexible part attached to the parent molecule while the larger one τ_2 is due to end-over-end rotation of the polar molecule. The weighted contributions c_1 and c_2 towards relaxations are calculated from Fröhlich's equations as well as by a new technique adopted here. The dipole moments μ_1 and μ_2 are also computed from the slope β of the ultra-high-frequency conductivity K_{ij} against the weight fraction ω_j for the compounds in terms of τ_1 and τ_2 . The close agreement of μ_2 values thus computed with those of existing methods immediately indicates that the approach suggested is correct.

1. Introduction

The dielectric relaxation of polar liquids in non-polar solvents is much simpler in comparison to the case in pure polar liquids because, in dilute polar liquid solutions, the effects of the macroscopic viscosity, dipole-dipole interaction, internal field etc. are minimized. The dielectric relaxation parameters, namely the relaxation times τ_1 and τ_2 , the dipole moments μ_1 and μ_2 etc. are the effective tools to investigate the molecular and intramolecular rotations, sizes, shapes and structures of polar molecules. Careful investigation of the phenomenon of dielectric relaxation in binary (Acharyya and Chatterjee 1985) and ternary (Chatterjee *et al* 1992, Saha and Acharyya 1993) solute-solvent mixtures is therefore necessary to throw much light on the structures of the polar liquids.

Khameshara and Sisodia (1980), Gupta *et al* (1978) and Arrawatia *et al* (1977) measured the static dielectric constant ϵ_{0ij} , the square of the refractive indices n_{Dij}^2 , the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of the complex dielectric constant ϵ^*_{ij} of five and seven disubstituted anilines and benzenes respectively in solvents benzene and carbon tetrachloride at 35 °C under a single high-frequency 9.945 GHz electric field. Aniline as well as benzene derivatives are expected to absorb very strongly in the microwave electric field due to the presence of

their flexible parts such as methyl or other groups. They are, therefore, expected to have more than one relaxation time because of the existence of internal rotation of these groups. Although one should not make strong conclusions based on single frequency measurements, provided that the experimental values of ϵ_{0ij} and $\epsilon_{\infty ij}$ are not accurately known. Non-spherical molecular liquids on the other hand, are known to have non-Debye relaxation behaviour.

The existing method of Bergmann *et al* (1960) was involved in measurements of ϵ'_{ij} , ϵ''_{ij} , $\epsilon_{\infty ij}$ and ϵ_{0ij} of a non-spherical polar liquid (j) in solvent (i) for various frequencies at a given experimental temperature in degrees Celsius to yield τ_1 and τ_2 . They actually used the Cole-Cole plot to make τ_1 and τ_2 represent the relaxation times of the smallest flexible unit attached to the parent ring and the molecule itself. Kastha *et al* (1969) subsequently simplified the procedure of Bergmann *et al* (1960) by measuring the experimental parameters at two given frequencies of the electric field in the microwave region.

We, in this context, therefore thought to suggest an alternative method in which single frequency measurements of dielectric relaxation parameters like ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ (Khameshara and Sisodia 1980, Gupta *et al* 1978 and Arrawatia *et al* 1977) for some highly non-spherical polar liquids like anilines and

Table 1. The double relaxation times τ_1 (smaller) and τ_2 (larger) estimated from intercepts and slopes of equation (7) with errors and correlation coefficients together with reported τ of polar liquids.

System with slope number and molecular weight M_f (g)	Intercept and slope of equation (7)		Correlation coefficient	Percentage error in regression technique	Estimated values of τ_1 and τ_2 (ps)		Reported τ (ps)
(i) 4-chloro-2-methyl aniline in benzene $M_f = 141.52$	-1.4276	3.2169	0.9964	1.33	8.51	42.97	18.5
(ii) 3-chloro-4-methyl aniline in benzene $M_f = 141.52$	-0.5605	1.8913	0.9982	0.76	5.89	24.38	13.6
(iii) 5-chloro-2-methyl aniline in benzene $M_f = 141.52$	-0.8107	2.0749	0.9727	3.67	8.36	24.85	16.6
(iv) 3-chloro-2-methyl aniline in benzene $M_f = 141.52$	-0.3862	1.5960	0.9918	1.09	4.76	20.78	9.9
(v) 2-chloro-6-methyl aniline in benzene $M_f = 141.52$	-0.3132	1.3711	0.9250	2.77	4.63	17.31	7.8
(vi) o-chloronitrobenzene in benzene $M_f = 157.5$	-0.3033	1.3129	0.8170	3.77	4.79	16.22	13.5
(vii) 4-chloro-3-nitrotoluene in benzene $M_f = 171.5$	-0.3863	1.8623	0.8776	11.90	3.81	25.99	20.9
(viii) m-nitrobenzotrifluoride in benzene $M_f = 191.0$	-0.6003	1.9038	0.9929	2.44	6.38	24.09	19.7
(ix) 4-chloro-3-nitrobenzotrifluoride in carbon tetrachloride $M_f = 225.5$	-0.0587	1.6634	0.9524	5.33	0.58	26.04	21.1
(x) o-nitrobenzotrifluoride in benzene $M_f = 191.039$	-0.0620	1.0560	0.6992	4.17	0.99	15.90	13.7
(xi) 4-chloro-3-nitrotoluene in carbon tetrachloride $M_f = 171.5$	-0.1335	2.2819	0.9771	7.51	0.96	35.56	35.0
(xii) 4-chloro-3-nitrobenzotrifluoride in benzene $M_f = 225.5$	2.5194	-3.0302	-0.8599	13.07	—	10.87	10.2
(xiii) m-aminobenzotrifluoride in benzene $M_f = 161.05$	0.8445	0.0452	0.0088	11.38	—	15.07	14.5
(xiv) o-chloronitrobenzene in carbon tetrachloride $M_f = 157.5$	0.0194	1.2973	0.9277	5.57	—	21.00	15.8
(xv) o-chlorobenzotrifluoride in benzene $M_f = 180.5$	0.2856	0.5696	0.1405	19.10	—	14.25	12.3

benzene derivatives in solvents benzene and carbon tetrachloride respectively are enough to estimate τ_1 and τ_2 within the framework of the Debye model (Bergmann *et al* 1960). The systems of polar-non-polar liquid mixtures under investigation are placed in the first columns of tables 1-3. Moreover, such rigorous studies on various types of di- or even mono-substituted polar compounds in non-polar solvents could be made in order to detect the existence of double relaxation phenomena from available data measured under a single-frequency electric field in the gigahertz region. Finally, τ_1 and τ_2 thus estimated (table 1) from our method on the basis of single frequency measurement, which appears to be much simpler, can be used to obtain μ_1 and μ_2 (see table 3 later) of the polar molecules from the slope β of the concentration variation of ultra-high-frequency conductivity K_{ij} of the solution (see figure 4 and table 3 later) in order to explore their conformations (see figure 5 later).

2. Theoretical formulations to estimate τ_1 , τ_2 and c_1 and c_2

The relative contributions c_1 and c_2 towards the dielectric relaxation by the two extreme values τ_1 and τ_2 (Higasi *et al* 1960) can be given by (Bergmann *et al* 1960)

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

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

provided that $c_1 + c_2 = 1$. The symbols used in equations (1) and (2) have their usual meanings. Let

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

and $\omega\tau = \alpha$. Equations (1) and (2) can be written as

$$x = c_1 a_1 + c_2 a_2 \quad (3)$$

$$y = c_1 b_1 + c_2 b_2 \quad (4)$$

where $a = 1/(1 + \alpha^2)$ and $b = \alpha/(1 + \alpha^2)$. The suffixes 1 and 2 are related to τ_1 and τ_2 respectively. Solving equations (3) and (4) for c_1 and c_2 , one gets

$$c_1 = \frac{(x a_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad (5)$$

$$c_2 = \frac{(y - x \alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad (6)$$

provided that $\alpha_2 > \alpha_1$. Now adding equations (5) and (6) we get, since $c_1 + c_2 = 1$,

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

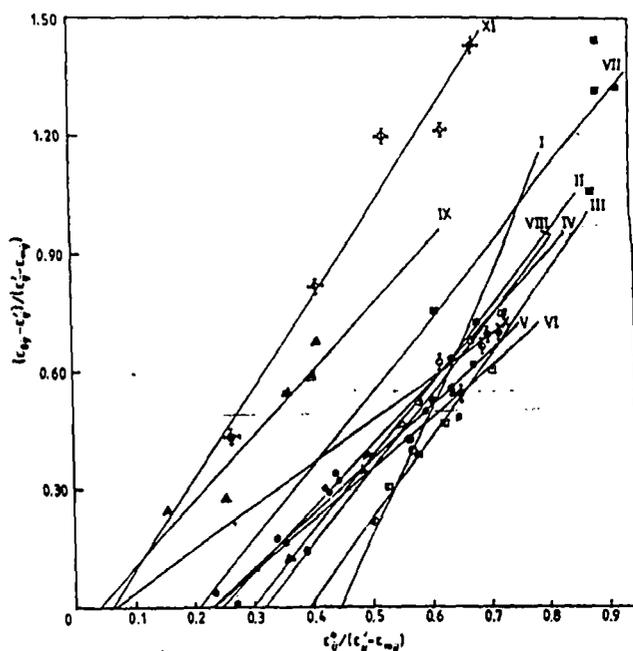


Figure 1. Straight line plots of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ against $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ for the polar-non-polar liquid mixtures: (I), (II), (III), (IV), (V), of disubstituted anilines, (VI), (VII), (VIII), (IX), (X) and (XI) of disubstituted benzenes respectively at 35°C (table 1).

or

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2 \quad (7)$$

which is simply a straight line between $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ and $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ having intercept $-\omega^2 \tau_1 \tau_2$ and slope $\omega(\tau_1 + \tau_2)$ where $\omega = 2\pi f$, f being the frequency of the applied electric field in the gigahertz region. When equation (7) is fitted to the experimental data ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ for different concentrations ω_j of each of the polar molecules at 35°C, we get the intercept and slope and the corresponding values of τ_1 and τ_2 found as shown in table 1 together with the reported τ . The error as well as correlation coefficient were also found for each curve of equation (7) and placed in table 1, only to see how far they are linear as shown in figure 1.

The Fröhlich parameters A , where $A = \ln(\tau_2/\tau_1)$ shown in table 2 for all the polar compounds, are used to evaluate both x and y of equations (3) and (4) in terms of ω and small limiting relaxation time τ_s , where $\tau_s = \tau_1$ by the following equations (Fröhlich 1949):

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + e^{2A} \omega^2 \tau_s^2}{1 + \omega^2 \tau_s^2} \right) \quad (8)$$

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} [\tan^{-1}(e^A \omega \tau_s) - \tan^{-1}(\omega \tau_s)] \quad (9)$$

The computed values of x and y from the above equations and the corresponding c_1 and c_2 from equations (1) and (2) are presented in table 2. Again the left-hand sides of equations (1) and (2) are obviously

Table 2. Reported Fröhlich parameter A , relative contributions c_1 and c_2 towards dielectric relaxations with estimated values x and y due to Fröhlich equations (8) and (9) and those by our method.

System with slope number and molecular weight M_j (g)	Fröhlich parameter $A = \ln(\tau_2/\tau_1)$	Theoretical values of x and y using equations (8) and (9)		Theoretical values of c_1 and c_2		Estimated values of $x = \left(\frac{\epsilon' - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}}\right)_{\omega_j \rightarrow 0}$ and $y = \left(\frac{\epsilon''}{\epsilon_0 - \epsilon_{\infty}}\right)_{\omega_j \rightarrow 0}$		Estimated values of c_1 and c_2	
(i) 4-chloro-2-methyl aniline in benzene $M_j = 141.52$	1.6193	0.4269	0.4478	0.4159	0.8418	1.14	0.4455	1.5577	-0.6112
(ii) 3-chloro-4-methyl aniline in benzene $M_j = 141.52$	1.4205	0.8448	0.4483	0.8239	0.3953	1.32	0.2745	1.7061	-0.6065
(iii) 5-chloro-2-methyl aniline in benzene $M_j = 141.52$	1.0894	0.5478	0.4745	0.4642	0.6239	1.08	0.3758	1.6069	-0.6227
(iv) 3-chloro-2-methyl aniline in benzene $M_j = 141.52$	1.4737	0.6937	0.4241	0.5180	0.5845	0.99	0.2385	1.1382	-0.1497
(v) 2-chloro-6-methyl aniline in benzene $M_j = 141.52$	1.3187	0.7369	0.4114	0.5272	0.5430	1.17	0.1440	1.5339	-0.5334
(vi) <i>o</i> -chloro nitrobenzene in benzene $M_j = 157.5$	1.2197	0.7456	0.4107	0.5259	0.5326	0.82	0.3803	0.6874	0.3832
(vii) 4-chloro-3-nitrotoluene in benzene $M_j = 171.5$	1.9201	0.6783	0.4086	0.5282	0.6486	0.64	0.3173	0.5504	0.4328
(viii) <i>m</i> -nitrobenzotrifluoride in benzene $M_j = 191.0$	1.3286	0.6103	0.4551	0.4852	0.6252	0.97	0.3128	1.2013	-0.2176
(ix) 4-chloro-3-nitrobenzo-trifluoride in carbon tetrachloride $M_j = 225.5$	3.8044	0.8302	0.2583	0.6876	0.5231	0.91	0.1012	0.8682	0.1565
(x) <i>o</i> -nitrobenzotrifluoride in benzene $M_j = 191.039$	2.7764	0.8771	0.2592	0.6595	0.4371	0.67	0.3487	0.3413	0.6554
(xi) 4-chloro-3-nitrotoluene in carbontetrachloride $M_j = 171.5$	3.6120	0.7540	0.3010	0.6379	0.7022	0.88	0.1642	0.8314	0.3061

the functions of ω_j of the solute in a given solvent, as is evident from the plots of x and y against ω_j in figures 2 and 3 respectively. This at once prompted us to get the fixed values of x and y when $\omega_j \rightarrow 0$ from figures 2 and 3 to estimate c_1 and c_2 , which are shown in table 2 for comparison with those of Fröhlich (1949). This is really in conformity with the fixed estimated values of τ_1 and τ_2 from the slope and intercept of equation (7) for each compound when substituted on the right-hand sides of equations (1) and (2).

3. Mathematical formulations to estimate μ_1 and μ_2

According to Murphy and Morgan (1939) the ultra-high-frequency (UHF) conductivity K_{ij} as given by

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon_{ij}''^2 + \epsilon_{ij}'^2)^{1/2} \quad (10)$$

is a function of ω_j of a polar solute. Even in the high-frequency (HF) electric field $\epsilon_{ij}'' \ll \epsilon_{ij}'$, ϵ_{ij}'' is responsible for offering resistance to polarization. Hence the real part K'_{ij} of the HF conductivity of a polar-non-polar liquid mixture at a given temperature T K is given by (Smyth 1955)

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \omega_j \quad (11)$$

where M_j is the molecular weight of a polar solute, N is Avogadro's number, k is the Boltzmann constant and $F_{ij} (= [(\epsilon_{ij} + 2)/3]^2)$ is the local field. The total HF

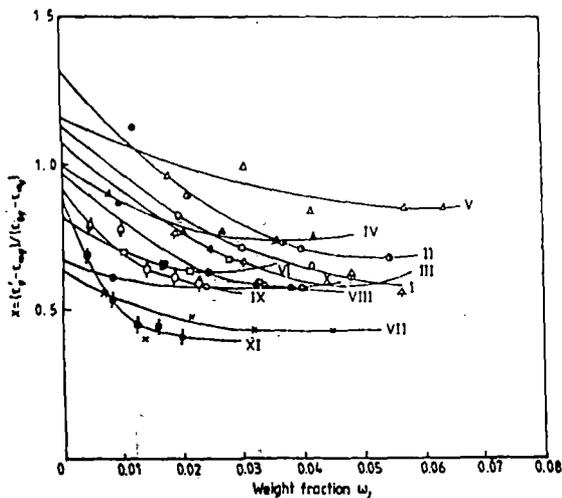


Figure 2. Variation of $(\epsilon'_{ij} - \epsilon_{\infty ij})/(\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction ω_j of polar solutes in dilute solutions at 35°C (table 2): (I), (II), (III), (IV), (V) of disubstituted anilines, (VI), (VII), (VIII), (IX), (X) and (XI) of disubstituted benzenes respectively.

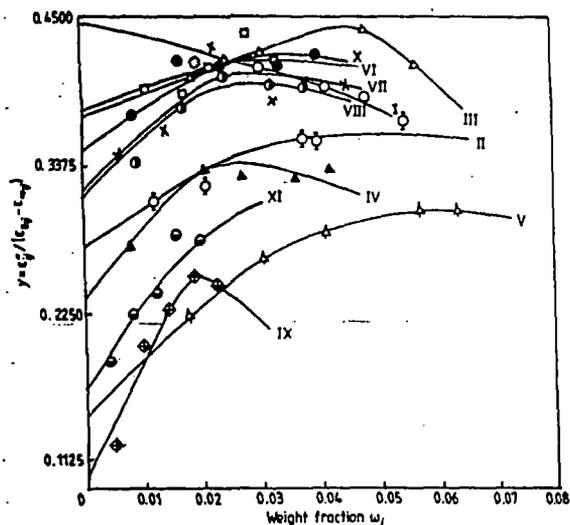


Figure 3. Variation of $\epsilon''_{ij}/(\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction ω_j of polar solutes in dilute solutions at 35°C (table 2): (I), (II), (III), (IV), (V) of disubstituted anilines, (VI), (VII), (VIII), (IX), (X) and (XI) of disubstituted benzenes respectively.

conductivity $K_{ij} = \omega \epsilon'_{ij}/4\pi$ can be represented by

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

$$\left(\frac{dK'_{ij}}{d\omega_j}\right)_{\omega_j \rightarrow 0} = \omega\tau \left(\frac{dK_{ij}}{d\omega_j}\right)_{\omega_j \rightarrow 0} = \omega\tau\beta \quad (12)$$

where β is the slope of the $K_{ij}-\omega_j$ curve at $\omega_j \rightarrow 0$.

Equation (11), on being differentiated with respect to ω_j for $\omega_j \rightarrow 0$, becomes

$$\left(\frac{dK'_{ij}}{d\omega_j}\right)_{\omega_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2}\right) \quad (13)$$

because $\rho_{ij} \rightarrow \rho_i$, the density of the solvent $F_{ij} \rightarrow F_i$ the local field of the solvent, in the limit $\omega_j = 0$. Using

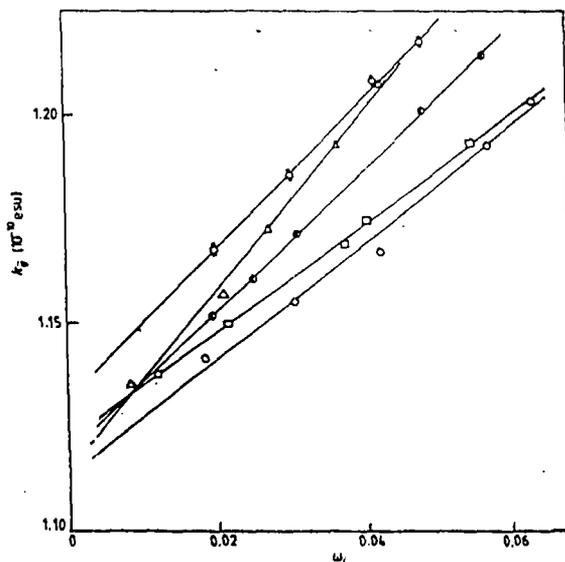


Figure 4. Concentration variation of microwave conductivity K_{ij} of five disubstituted anilines at 35°C.

equations (12) and (13) we finally get

$$\mu_j = \left(\frac{3M_j kT\beta}{N\rho_i F_i \omega b}\right)^{1/2} \quad (14)$$

to evaluate μ_1 and μ_2 in terms of b , where b is a dimensionless parameter given by

$$b = \frac{1}{1 + \omega^2 \tau^2} \quad (15)$$

for τ_1 and τ_2 respectively. The values of b as well as μ_1 and μ_2 thus computed from equations (14) and (15) are placed in table 3.

4. Results and discussion

Figure 1 represents the linear relationship of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ to $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$, satisfying equation (7) having intercepts and slopes presented in table 1 with the experimental points placed on each curve for 11 systems possessing double relaxation phenomena. The error involved in such regressions as well as the correlation coefficients for all the curves were also calculated and placed in table 1 in order to test their linearity and to assess the errors introduced in τ values; which may normally be claimed to be accurate up to $\pm 10\%$. Attempts were made to measure the double relaxation times of the molecules as mentioned in tables 1-3 in order to calculate μ_1 and μ_2 of the flexible parts as well as the whole molecules. They are shown in tables 1 and 3 respectively. In 11 systems out of 15, nevertheless, double relaxation phenomena were found by showing the lower as well as higher values of τ_1 and τ_2 respectively. As shown in table 1, eight molecules, namely all the disubstituted anilines and three benzene derivatives namely *o*-chloronitrobenzene,

Table 3. Reports of the estimated intercepts and slopes of the concentration variation of ω_{HF} conductivity, dimensionless parameter b , dipole moments μ_1 and μ_2 in Debye (D) for the flexible part and the end-over-end rotation of a polar molecule, reported μ_1 and μ_2 in D due to existing methods, the theoretical μ values from the bond length and bond moments.

Slope number and systems	Intercepts and slopes of K_j against ω_j		Dimensionless parameters b		Estimated dipole moment		Reported μ (D)	Theoretical μ (D)	Experi-mental μ_1 (D)	
	α (10^{-10} esu)	β (10^{-10} esu)	$b_1 = \frac{1}{1 + \omega^2 \tau_1^2}$	$b_2 = \frac{1}{1 + \omega^2 \tau_2^2}$	μ_1 (D)	μ_2 (D)	Guggenheim	Higasi <i>et al</i>	μ_2 from bond length and moments	Using $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$
(i) 4-chloro-2-methyl aniline in C_6H_6	1.1323	1.7863	0.7797	0.1219	2.51	6.36	3.28	3.12	3.06	4.47
(ii) 3-chloro-4-methyl aniline in C_6H_6	1.1220	1.2865	0.8808	0.3014	2.01	3.43	2.61	2.43	2.20	4.95
(iii) 5-chloro-2-methyl aniline in C_6H_6	1.1189	1.6848	0.7858	0.2934	2.43	3.98	3.10	2.92	2.83	3.43
(iv) 3-chloro-2-methyl aniline in C_6H_6	1.1144	2.1490	0.9188	0.3725	2.54	3.99	3.02	2.86	2.48	3.75
(v) 2-chloro-6-methyl aniline in C_6H_6	1.1135	1.3766	0.9228	0.4611	2.03	2.87	2.32	2.20	1.85	2.83
(vi) <i>o</i> -chloronitrobenzene in C_6H_6	1.1265	4.0539	0.9178	0.4935	3.68	5.02	4.35	4.43	5.28	4.99
(vii) 4-chloro-3-nitrotoluene in C_6H_6	1.1250	2.8594	0.9464	0.2751	3.18	5.89	4.49	4.59	5.58	5.31
(viii) <i>m</i> -nitrobenzotrifluoride in C_6H_6	1.1262	1.7747	0.8630	0.3064	2.77	4.64	3.67	3.80	3.74	4.08
(ix) 4-chloro-3-nitrobenzotrifluoride in CCl_4	1.0999	1.5781	0.9987	0.2744	1.99	3.79	3.17	3.15	3.78	4.34
(x) <i>o</i> -nitrobenzotrifluoride in C_6H_6	1.1169	4.1557	0.9962	0.5035	3.94	5.54	4.96	5.07	6.18	6.80
(xi) 4-chloro-3-nitrotoluene in CCl_4	1.1044	3.2769	0.9964	0.1686	2.50	6.07	4.68	4.63	5.58	5.78
(xii) 4-chloro-3-nitrobenzotrifluoride in C_6H_6	1.1286	1.1894	—	0.6845	—	2.76	2.97	2.98	3.78	—
(xiii) <i>m</i> -aminobenzotrifluoride in C_6H_6	1.1106	2.3536	—	0.5303	—	3.73	3.51	3.60	2.48	—
(xiv) <i>o</i> -chloronitrobenzene in CCl_4	1.0973	5.4508	—	0.3676	—	5.08	4.19	4.13	5.28	—
(xv) <i>o</i> -chlorobenzotrifluoride in C_6H_6	1.1199	2.0159	—	0.5580	—	3.57	3.38	3.49	3.98	—

4-chloro-3-nitrotoluene and *m*-nitrobenzotrifluoride, all in C_6H_6 , show considerably larger values of τ_1 in their relaxation behaviours. This is perhaps due to the fact that the flexible $-CH_3$ group in aniline, and those attached to the benzene rings mentioned above, absorb energy much more strongly in the microwave electric field and thereby yield large values of τ_1 . 4-chloro-3-nitrobenzotrifluoride in CCl_4 , *o*-nitrobenzotrifluoride in C_6H_6 and 4-chloro-3-nitrotoluene in CCl_4 have their τ_1 much smaller, presumably due to the fact that their flexible parts are comparatively rigidly fixed to the parent ones (table 1). It is, however, interesting to note that

the last four systems of table 1 show single relaxation processes, probably owing to their rigid attachment to the flexible parts. The slopes and intercepts of equation (7) yield τ_1 with negative sign for the aforesaid molecules.

Again, *o*-chloronitrobenzene shows a double relaxation phenomenon in C_6H_6 but a single relaxation process in CCl_4 . The reverse case, however, occurs in 4-chloro-3-nitrobenzotrifluoride, which shows a low value of τ_1 in CCl_4 and a single relaxation process in C_6H_6 . This may perhaps be attributed to solvent effects upon the polar molecules. So a firm conclusion on solvent effects seems to be of utmost importance if measure-

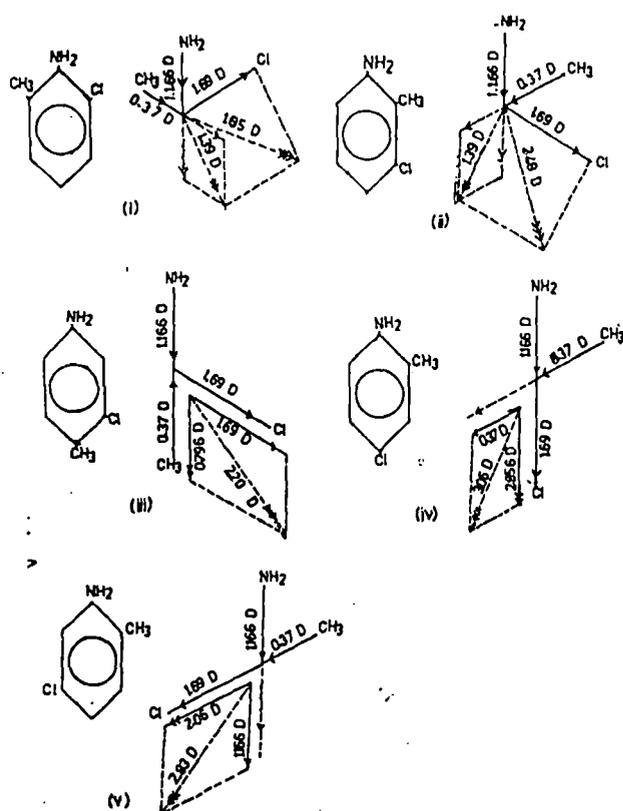


Figure 5. Conformations of five disubstituted anilines showing the orientation of the bond axes and bond moments and dipole moments.

ments are to be performed on a single polar molecule in different non-polar solvents.

Table 2 reports the relative contributions c_1 and c_2 due to τ_1 and τ_2 (table 1) towards relaxation as computed from Fröhlich's equations (8) and (9) for x and y as well as by our graphical technique (figures 2 and 3). In total, c_2 values calculated for six polar molecules are negative although they fulfil the condition $c_1 + c_2 \approx 1$. The disagreements in c_1 and c_2 with those of Fröhlich (1949) indicate that their flexible parts are loosely bound. In HF electric field the contribution by the rest of the molecule towards relaxation could not be in accord with the flexible one, due to inertia.

The variation of HF conductivities K_{ij} of five disubstituted anilines with respect to ω_j of polar solutes is shown in figure 4. The intercept α and slope β are placed in table 3 to compute μ_1 and μ_2 using relaxation times τ_1 and τ_2 of table 1 from equations (14) and (15). The values of b_1 and b_2 are also placed in the fourth and fifth columns of table 3. The corresponding μ_1 and μ_2 from equation (14) are shown in table 3. They are compared with μ values of Guggenheim (1949) and Higasi *et al* (1952). The disubstituted benzenes had already been studied by Acharyya and Chatterjee (1985) by the conductivity method. The theoretical μ_j from bond lengths and bond angles had also previously been studied. The same data, with those of disubstituted anilines, are shown again in table 3 for comparison only.

In figure 5 the bond moments of $\text{CH}_3 \rightarrow \text{C}$ and $\text{C} \rightarrow \text{Cl}$ are 0.37 D and 1.69 D respectively. The bond moment 1.48 D of $\text{C} \rightarrow \text{NH}_2$ makes an angle 142° with

the bond axis. The component along the bond axis in these molecules becomes 1.166 D. With these preferred conformational structures of the disubstituted anilines, the theoretical μ_j were computed by the vector addition method and are placed in table 3. The close agreement of these μ_j with our experimental μ_2 values suggests their correct conformational structures as shown in figure 5.

The values of μ_1 may also be obtained from $\mu_1 = \mu_2(c_1/c_2)^{1/2}$ when the two relaxation phenomena are equally probable (Fröhlich 1949). However, the present investigation finds that μ_1 values as calculated from the above relation are larger for c_1 and c_2 due to Fröhlich's equations. The τ values gradually decrease due to various conformations of the disubstituted anilines (figure 5 and table 1), probably due to decrease in the effective radii of the rotating units under HF electric field. Although the molecules are in the same environment and their molecular weights are the same, the most probable relaxation time due to Higasi (1966) and Guggenheim (1957) also show a trend similar to ours as shown in table 1.

5. Conclusions

The close agreement of μ_2 values with literature values at once suggests that our new approach can justifiably be claimed to be a simple, straightforward and useful one. The method of single frequency measurements of dielectric relaxation data at a given temperature is comparatively easy to perform. It requires only easy and time-saving calculations, unlike other existing methods, to detect the very existence of double relaxation phenomena in polar-non-polar liquid mixtures. Thus the present procedure offers a significant improvement for derivation of τ_1 and τ_2 and μ_1 and μ_2 because it allows one to find not only an estimate of the errors, but also the correlation coefficients between the desired values generated from the dielectric relaxation.

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Single-frequency measurement of double-relaxation times of mono-substituted anilines in benzene

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Abstract. Single-frequency measurements of dielectric relaxation parameters at different concentrations are used to estimate the double-relaxation times τ_1 (smaller) and τ_2 (larger) of some mono-substituted anilines in benzene at 35°C for 2.02, 3.86 and 22.06 GHz electric fields respectively. The *o*- and *m*-anisidines like *p*-toluidines exhibit double-relaxation phenomena at 3.86 and 22.06 GHz whereas *o*- and *m*-toluidines show the same effect at 2.02 and 3.86 GHz respectively. Only *p*-anisidine, however, shows the mono-relaxation behaviour at all frequencies. The relative contributions c_1 and c_2 towards dielectric relaxation for τ_1 and τ_2 are computed from Fröhlich's equations only for comparison with those of the graphical techniques adopted here. The dipole moments μ_1 and μ_2 in terms of τ_1 and τ_2 are then determined from the slope β of concentration variation of the ultra-high-frequency conductivity K_{ij} for those compounds to establish their conformations.

List of symbols used

$\epsilon'_{ij}, \epsilon''_{ij}$	real and imaginary parts of the dielectric constant of a solution
$\epsilon^*_{ij} = \epsilon'_{ij} - j\epsilon''_{ij}$	where $j = \sqrt{-1}$ is a complex number
$\epsilon_{0ij}, \epsilon_{\infty ij}$	static and optical dielectric constants of the solution
$\omega = 2\pi f$	angular frequency of the applied electric field, f being the frequency in hertz
K'_{ij}, K''_{ij}	real and imaginary parts of the complex electrical conductivity K^*_{ij} of a solution
$K^*_{ij} = K'_{ij} + jK''_{ij}$	where $j = \sqrt{-1}$ is a complex number
$K_{\infty ij}$	constant conductivity of the solution at $\omega_j \rightarrow 0$
μ_j	dipole moment of the j th type of solute
μ_1, μ_2	dipole moments of the flexible part and the parent molecule
τ_s	relaxation time of the solute
τ_1, τ_2	relaxation times of the flexible part and the parent molecule
τ_0	most probable relaxation time of the solute
$A = \ln(\tau_2/\tau_1)$	the Fröhlich parameter
w_j	weight fraction of the solute
c_1, c_2	relative contributions due to τ_1 and τ_2 respectively
M_j	molecular weight of the j th type of solute
β	slope of $K_{ij} - w_j$ curve.

1. Introduction

In recent years the dielectric relaxation phenomena of polar–non-polar liquid mixtures under ultra-high-frequency (UHF) electric fields have gradually gained the attention of a large number of workers [1–3] as they reveal significant information on various types of molecular associations. There exist several methods [4–6] of estimating the relaxation time τ_s as well as the dipole moment μ_j of a polar liquid within the framework of the Debye and Smyth model. We [7], however, observe that the imaginary K''_{ij} and real K'_{ij} of the complex UHF conductivity K^*_{ij} of a polar–non-polar liquid mixture vary linearly and independently in the low-concentration region. The relaxation time, which is the lag in response to the alternation of the electric field, could, however, be estimated from their slopes.

Bergmann *et al* [8] devised a graphical technique in order to obtain τ_1 and τ_2 to represent relaxation times of the flexible part attached to the parent molecule and the molecule itself respectively. The corresponding contributions c_1 and c_2 towards dielectric relaxations in terms of τ_1 and τ_2 were also found for some complex molecules. The method is based on plotting the normalized experimental points involved with the measured data of the real ϵ' , the imaginary ϵ'' of the complex dielectric constant ϵ^* , the static dielectric constant ϵ_0 and the optical dielectric constant ϵ_∞ at various frequencies ω on a semicircle in a complex plane. A point was then selected on the chord through

the two fixed points on the semicircle in consistency with all the experimental points. Bhattacharyya *et al* [9] subsequently modified the above procedure to get τ_1 , τ_2 , c_1 and c_2 with the experimental values measured at two different frequencies.

Under such conditions, an alternative procedure [10] has recently been suggested to determine τ_1 and τ_2 based on a single-frequency measurement of dielectric relaxation parameters like ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ of a polar molecule (j) for different weight fractions w_j in a non-polar solvent (i) at a given temperature in degrees Celsius. They are, however, estimated from the slope and intercept of the straight line equation between $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ and $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$. This is derived from the dielectric relaxation data for different w_j of a polar solute measured under a single-frequency electric field in the GHz region. The correlation coefficient, r , could also be calculated because of the linear behaviour of the derived parameters. This helps one find out the percentage error introduced in the obtained results, too.

The corresponding contributions c_1 and c_2 towards dielectric relaxation in terms of the estimated τ_1 and τ_2 can, however, be calculated from x and y where

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

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

in Fröhlich's equations [11]. The variations of x and y with w_j of a polar solute in a system of a polar-non-polar liquid mixture are found to obey the equations of Bergmann *et al* [8] almost exactly. c_1 and c_2 can also be calculated by the graphical technique suggested by Saha *et al* [10], which consists of plotting those experimental values at different w_j with a view to getting x and y at infinite dilution. The UHF electrical conductivity K_{ij} of a polar-non-polar liquid mixture, on the other hand, is thought to be a sensitive tool in ascertaining the dipole moment μ_j of a polar liquid in terms of τ_s .

Some of the disubstituted aniline and benzene derivatives had already been studied in detail by the new approach suggested by Saha *et al* [10]. Ten out of 12 highly non-spherical disubstituted anilines and benzenes were found to exhibit the double-relaxation phenomena as their flexible parts are not rigidly fixed in relation to the parent ones.

We, therefore, thought to study the available solution data of ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ of mono-substituted anilines like anisidines and toluidines in their *ortho*, *meta* and *para* forms for their various concentrations as measured by Srivastava and Suresh Chandra [12] at different frequencies of 2.02, 3.86 and 22.06 GHz electric fields at 35°C to obtain τ_1 and τ_2 based on the new approach of Saha *et al* [10]. Highly non-spherical molecules like mono-substituted anilines are also expected to possess the double-relaxation phenomena by showing τ_1 and τ_2 . Although they are strongly of non-Debye type in their relaxation behaviour, it is found, in the present

investigation, that they do not exhibit the effect of double-relaxation phenomena at all frequencies of the electric field. When the available data [12] were extended to 9.945 GHz (about 3 cm wavelength), which is supposed to be the most effective dispersive region for such polar molecules, all of them, on the other hand, showed the double-relaxation phenomena of reasonable τ_1 and τ_2 [13]. However, out of 18 systems, as shown in tables and figures, eight systems like *o*- and *m*-anisidine and *p*-toluidine at 3.86 and 22.06 GHz together with *o*- and *m*-toluidine at 2.02 and 3.86 GHz are found to show τ_1 and τ_2 . Only *p*-anisidine is an exception. It shows mono-relaxation behaviour at all frequencies. This sort of mono-relaxation behaviour may equally well be explained by considering a distribution of relaxation times, namely a single broad dispersion. Only τ_2 values of the compounds showing mono-relaxation are, however, obtained from the slopes of the straight line equations (such as (15), see later) of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ with $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ having zero intercepts.

The relaxation times τ , since accurate values for mono-substituted anilines are not available, are also estimated from the slopes of K''_{ij} versus K'_{ij} . They may be called the most probable relaxation time τ_0 of the three isomers of anisidine and toluidine. τ_0 is often given by $\tau_0 = (\tau_1 \tau_2)^{1/2}$ where τ_1 and τ_2 convey their usual meanings. c_1 and c_2 in terms of τ_1 and τ_2 are also calculated from Fröhlich's equations [11] as well as by our graphical technique. The dipole moments μ_1 and μ_2 of these three isomers of anisidine and toluidine are finally estimated from the slope β of their concentration variation of UHF conductivities K_{ij} at $w_j \rightarrow 0$ and in terms of the estimated τ_1 and τ_2 in order to establish the conformational structures of those compounds under investigation.

2. Theoretical formulations of c_1 and c_2 in terms of τ_1 and τ_2 based on the single-frequency method

When the complex dielectric constants ϵ_{ij}^* is represented as the sum of two non-interacting Debye-type dispersions; the dielectric relaxation by the two extreme values of τ , τ_1 and τ_2 ; their relative contributions c_1 and c_2 can, however, be expressed for a polar-non-polar liquid mixture [8] by

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

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

such that $c_1 + c_2 = 1$. All the symbols used are of their usual significance. Putting

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

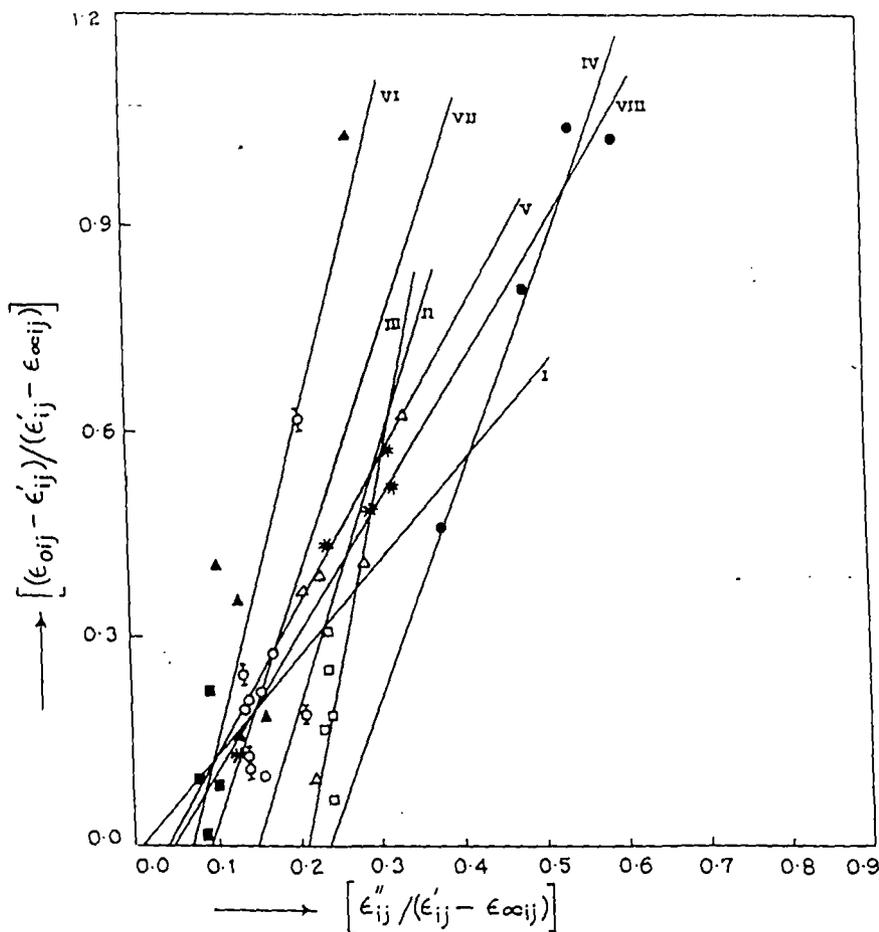


Figure 1. Variation of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ against $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ at 35°C for different weight fraction w_j (table 1): (I) *o*-anisidine at 3.86 GHz (○); (II) *o*-anisidine at 22.06 GHz (Δ); (III) *m*-anisidine at 3.86 GHz (□); (IV) *m*-anisidine at 22.06 GHz (●); (V) *o*-toluidine at 2.02 GHz (■); (VI) *m*-toluidine at 3.86 GHz (▲); (VII) *p*-toluidine at 3.86 GHz (◇); and (VIII) *p*-toluidine at 22.06 GHz (*).

with $\omega\tau = \alpha$ and using the abbreviations $a = 1/(1 + \alpha^2)$ and $b = \alpha/(1 + \alpha^2)$, the above equations (1) and (2) can be written as

$$x = c_1 a_1 + c_2 a_2 \tag{3}$$

$$y = c_1 b_1 + c_2 b_2 \tag{4}$$

where suffices 1 and 2 with a and b are related to τ_1 and τ_2 respectively.

From equations (3) and (4), since $\alpha_2 - \alpha_1 \neq 0$ and $\alpha_2 > \alpha_1$ we have

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \tag{5}$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \tag{6}$$

Now, using the relation $c_1 + c_2 = 1$; one can easily get the following equation with the help of equations (5) and (6):

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

which, on substitution of the values of x , y and α , becomes

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2 \tag{7}$$

Equation (7) is simply a straight line relation between $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ and $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ having slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2 \tau_1 \tau_2$ respectively. Here $\omega = 2\pi f$, f being the frequency of the alternating electric field in gigahertz. When equation (7) is fitted with the measured data of ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ for different weight fractions w_j of *ortho*, *meta* and *para* anisidines and toluidines in benzene at 35°C [12] we get slopes and intercepts as shown in table 1 to determine τ_1 and τ_2 for each single frequency of 2.02, 3.86 and 22.06 GHz electric fields respectively. The error as well as the correlation coefficient were also found out for each curve of equation (7) and placed in table 1, only to verify their linearity as illustrated graphically in figure 1 together with the experimental points upon them.

The Fröhlich parameter A as shown in table 2 for polar solutes exhibiting the double-relaxation

Table 1. The intercepts and the slopes of the straight line curves of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ against $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ of anisidines and toluidines at 35°C to estimate the relaxation times τ_1 (smaller) and τ_2 (larger) with respective errors and correlation coefficients involved in the calculations as well as their estimated τ_s 's.

System with molecular wt M_j in gm.	Frequency f in GHz	Intercept and slope of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ versus $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ curve		Estimated relaxation times		Correlation coefficient r	% error involved in calculation	Estimated relaxation time $\tau_0 \times 10^{12}$ s	$\tau_2 \times 10^{12}$ due to single broad dispersion
		Intercept	Slope	$\tau_1 \times 10^{12}$ s	$\tau_2 \times 10^{12}$ s				
<i>o</i> -anisidine $M_j = 123$	2.02	-0.0596	0.3759	—	39.10	0.1082	29.81	6.02	96.83
	3.86	0.0179	1.4360	0.52	58.72	0.3021	27.41	5.89	—
	22.06	0.5406	3.6741	1.11	25.41	0.8274	9.52	1.61	—
<i>m</i> -anisidine $M_j = 123$	2.02	-0.2109	-0.4703	—	22.13	-0.2588	28.14	11.87	120.9
	3.86	-1.1404	5.5485	8.82	220.07	-0.9999	0	8.46	—
	22.06	0.7318	3.1447	1.83	20.87	0.9805	1.16	3.88	—
<i>p</i> -anisidine $M_j = 123$	2.02	-0.2406	-2.1899	—	8.27	-0.7375	13.75	6.64	61.63
	3.86	-0.4927	-2.2136	—	8.41	-0.4782	23.27	6.53	34.31
	22.06	-1.2868	-1.2818	—	4.77	-0.3395	26.69	3.15	9.91
<i>o</i> -toluidine $M_j = 107$	2.02	0.0773	2.0910	2.97	161.86	0.0743	33.54	5.01	—
	3.86	-0.5925	-2.3787	—	9.38	-0.6779	16.30	6.84	35.94
	22.06	-0.4603	0.6684	—	7.87	0.3732	25.96	4.06	8.76
<i>m</i> -toluidine $M_j = 107$	2.02	-0.4062	-3.0101	—	10.20	-0.5757	20.17	8.70	258.61
	3.86	0.2938	4.5092	2.73	183.29	0.8469	8.53	6.78	—
	22.06	-1.2064	-0.6295	—	5.98	-0.3213	27.05	3.42	13.31
<i>p</i> -toluidine $M_j = 107$	2.02	-0.6655	-3.5127	—	14.21	-0.5101	22.31	4.08	167.73
	3.86	0.3149	3.4446	3.88	138.22	0.6477	17.51	5.15	—
	22.06	0.0821	1.9151	0.32	13.51	0.9408	3.47	2.91	—

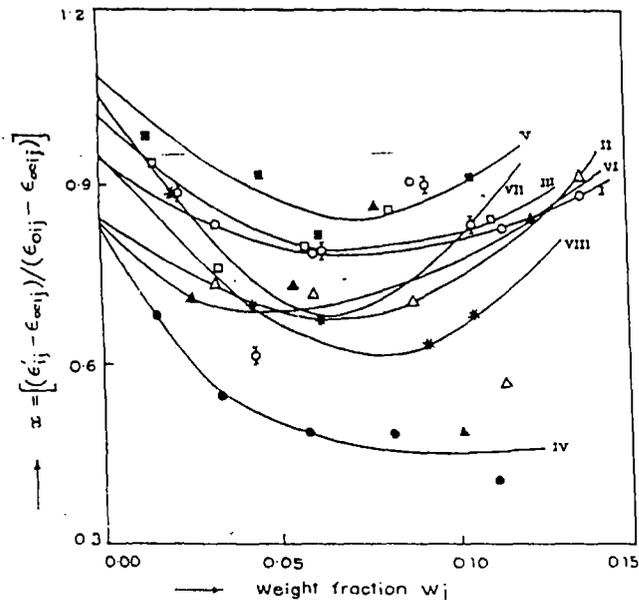


Figure 2. Plot of $(\epsilon'_{ij} - \epsilon_{\infty ij})/(\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction w_j for the polar-non-polar liquid mixture at 35°C (table 2): (I) *o*-anisidine at 3.86 GHz (\circ); (II) *o*-anisidine at 22.06 GHz (\square); (III) *m*-anisidine at 3.86 GHz (\triangle); (IV) *m*-anisidine at 22.06 GHz (\bullet); (V) *o*-toluidine at 2.02 GHz (\blacksquare); (VI) *m*-toluidine at 3.86 GHz (\blacktriangle); (VII) *p*-toluidine at 3.86 GHz (\circ); and (VIII) *p*-toluidine at 22.06 GHz ($*$).

phenomena are used to evaluate both x and y of equations (3) and (4) in terms of ω and the small limiting

relaxation time $\tau_s = \tau_1$ by the following equations [11]:

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + e^{2A} \omega^2 \tau_s^2}{1 + \omega^2 \tau_s^2} \right) \quad (8)$$

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} [\tan^{-1}(e^A \omega \tau_s) - \tan^{-1}(\omega \tau_s)] \quad (9)$$

where $A = \ln(\tau_2/\tau_1)$. The computed values of x and y are placed in table 2 to obtain c_1 and c_2 from equations (5) and (6). The latter are also shown in table 2. The left-hand sides of equations (1) and (2) are really the function of w_j of the solutes in a given solvent as shown from the plots of x and y against w_j in figures 2 and 3 respectively. The fixed values of x and y when $w_j \rightarrow 0$ for each system, as shown in table 2, can then be used to estimate c_1 and c_2 from equations (5) and (6) in order to compare them with those of Fröhlich [11]. The τ_1 and τ_2 values estimated from the slope and intercept of equation (7) for each solute, when substituted on the right-hand sides of equations (1) and (2), suggest the limiting values of x and y as obtained from figures 2 and 3 at infinite dilution.

3. Estimated μ_1 and μ_2 from UHF conductivity K_{ij} in terms of τ_1 and τ_2

The UHF conductivity K_{ij} is given by Murphy and Morgan [14] as

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon''_{ij} + \epsilon'_{ij})^2 \quad (10)$$

Table 2. The relative contributions c_1 and c_2 towards dielectric relaxations, Fröhlich parameters $A(= \ln(\tau_2/\tau_1))$ together with the estimated values of x and y due to Fröhlich equations (equations (8) and (9)) and those by our graphical techniques (figures 2 and 3).

System with SI No.	Frequency in GHz	Fröhlich parameter A (= $\ln(\tau_2/\tau_1)$)	Theoretical values of x and y using equations (8) and (9)		Estimated values					
					Theoretical values c_1 and c_2		of $x = \left(\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}\right)_{w_j \rightarrow 0}$ and $y = (\epsilon''/(\epsilon_0 - \epsilon_\infty))_{w_j \rightarrow 0}$		Estimated values of c_1 and c_2 from figures 2 and 3	
1 <i>o</i> - anisidine	3.86	4.7267	0.8829	0.1999	0.7491	0.4051	0.942	0.072	0.8995	0.1278
2 <i>o</i> - anisidine	22.06	3.1308	0.5894	0.3645	0.5200	1.0893	0.840	0.117	0.8636	-0.0484
3 <i>m</i> - anisidine	3.86	3.2169	0.4811	0.3650	0.4496	1.5081	1.017	0.132	1.081	-0.4915
4 <i>m</i> - anisidine	22.06	2.4340	0.5534	0.4063	0.4816	0.9439	0.828	0.221	0.8767	0.0393
5 <i>o</i> - toluidine	2.02	3.9982	0.7936	0.2699	0.6755	0.6212	1.086	0.066	1.0751	0.0649
6 <i>m</i> - toluidine	3.86	4.2067	0.6401	0.3049	0.5827	1.2441	0.834	0.014	0.8471	-0.1952
7 <i>p</i> - toluidine	3.86	3.5730	0.6509	0.3320	0.5727	1.0167	1.050	0.048	1.0750	-0.1905
8 <i>p</i> - toluidine	22.06	3.7428	0.7992	0.2766	0.6685	0.5943	0.948	0.036	0.9532	-0.0149

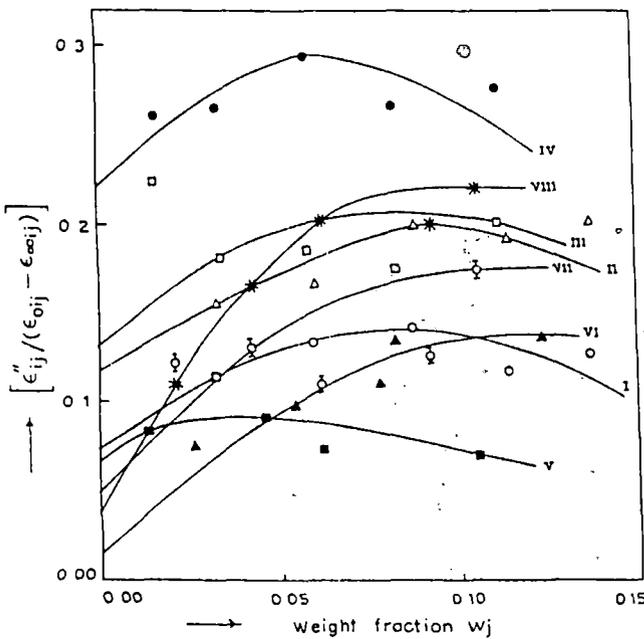


Figure 3. Plot of $\epsilon''_{ij}/(\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction w_j of polar solutes in dilute solutions at 35 °C (table 2): (I) *o*-anisidine at 3.86 GHz (○); (II) *o*-anisidine at 22.06 GHz (△); (III) *m*-anisidine at 3.86 GHz (□); (IV) *m*-anisidine at 22.06 GHz (●); (V) *o*-toluidine at 2.02 GHz (■); (VI) *m*-toluidine at 3.86 GHz (▲); (VII) *p*-toluidine at 3.86 GHz (◇); and (VIII) *p*-toluidine at 22.06 GHz (*).

namely as a function of w_j of a polar solute. In the UHF electric field, although $\epsilon''_{ij} \ll \epsilon'_{ij}$, the ϵ''_{ij} term still offers resistance to polarization. Thus the real part K'_{ij} of the UHF conductivity of a polar-non-polar liquid mixture at T K is [15]

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

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

$$\left(\frac{dK'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad (11)$$

where M_j is the molecular weight of a polar solute, N is Avogadro's number, k is the Boltzmann 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 the solvent at $w_j \rightarrow 0$.

Again the total UHF conductivity $K_{ij} = \omega \epsilon'_{ij}/(4\pi)$ can be written as

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

or

$$\left(\frac{dK'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega \tau \left(\frac{dK_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega \tau \beta \quad (12)$$

where β is the slope of the $K_{ij}-w_j$ curve at $w_j \rightarrow 0$. From equations (11) and (12) we thus get

$$\mu_j = \left(\frac{3M_j k T \beta}{N \rho_{ij} F_{ij} \omega b} \right)^{1/2} \quad (13)$$

as the dipole moments μ_1 and μ_2 in terms of b , where b is a dimensionless parameter given by

$$b = 1/(1 + \omega^2 \tau^2) \quad (14)$$

for τ_0 , τ_1 and τ_2 . The computed values of μ_0 , μ_1 and μ_2 with b are given in table 3.

Table 3. Estimated slope β of $K_{ij} - w_j$ equations with % of error involved, the dimensionless parameters b_0, b_1, b_2 in terms of most probable relaxation time τ_0 , relaxation time due to flexible part τ_1 and the same due to end-over-end rotation of the molecule τ_2 ; corresponding estimated dipole moments μ_0, μ_1 and μ_2 together with the theoretical values of μ_j from bond angles and bond moments and estimated values of μ_1 from $\mu_1 = \mu_2(C_1/C_2)^{1/2}$ respectively.

System	Frequency in GHz	Slope $\beta \times 10^{10}$ of $K_{ij} - w_j$ equations	% error involved in calculation	Dimensionless parameters			Estimated dipole moments (in Debye)			Theoretical μ_j in D from bond angle and bond moment	Estimated μ_1 in D from $\mu_1 = \mu_2(C_1/C_2)^{1/2}$
				$b_0 = \frac{1}{1+\alpha^2\tau_0^2}$	$b_1 = \frac{1}{1+\alpha^2\tau_1^2}$	$b_2 = \frac{1}{1+\alpha^2\tau_2^2}$	μ_0	μ_1	μ_2		
o-anisidine	2.02	0.1620	0.40	0.9942		0.8026	1.39	1.54			
	3.86	0.1786	0.41	0.9800	0.9998	0.3119	1.06	1.05	1.88	1.02	
	22.06	0.3870	1.01	0.9526	0.9769	0.0747	0.66	0.65	2.37	2.56	
m-anisidine	2.02	0.3347	0.18	0.9778		0.9269	2.01	2.07			
	3.86	0.2311	2.06	0.9596	0.9563	0.0339	1.22	1.22	6.49	1.65	
	22.06	2.2841	0.08	0.7758	0.9396	0.1068	1.78	1.62	4.81	3.54	
p-anisidine	2.02	0.3380	0.35	0.9930		0.9891	2.01	2.01			
	3.86	0.6473	0.09	0.9756		0.9601	2.03	2.04	1.89		
	22.06	2.8513	0.31	0.8400		0.6960	1.91	2.10			
o-toluidine	2.02	0.2097	0.26	0.9960	0.9986	0.1917	1.47	1.47	3.35	3.49	
	3.86	0.5507	0.37	0.9732		0.9508	1.74	1.76	1.39		
	22.06	1.3618	0.09	0.7597		0.4569	1.29	1.67			
m-toluidine	2.02	0.2359	0.39	0.9879		0.9835	1.56	1.57			
	3.86	0.4889	1.82	0.9737	0.9956	0.0482	1.64	1.63	7.38	1.03	
	22.06	0.9826	1.30	0.8167		0.5930	1.06	1.24		5.05	
p-toluidine	2.02	0.0906	0.21	0.9973		0.9685	0.97	0.98			
	3.86	0.1583	0.44	0.1873	0.9912	0.0818	2.13	0.93	3.23	1.54	
	22.06	1.2927	0.34	0.8602	0.9980	0.2221	1.19	1.10	2.34	2.42	

4. Results and discussion

Figure 1 represents the fitted straight line curves between $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ and $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ for different weight fractions w_j of *o*-anisidine, *m*-anisidine and *p*-toluidine for 3.86 and 22.06 GHz, and for *o*-toluidine and *m*-toluidine at 2.02 and 3.86 GHz respectively, together with their experimental points. The w_j for the compounds in benzene were, however, calculated from the experimental mole fractions x_i and x_j of solvent and solutes of molecular weights M_i and M_j respectively by using the relation [16]

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

The correlation coefficients r for each curve were also calculated to confirm their linearity. Some of the coefficients were found to be negative only due to their negative slopes, as is evidenced from table 1. The percentage of error involved in the calculation was found for each curve. The slope and intercept of equation (7) for each straight line were, however, used to determine τ_1 and τ_2 for each compound as shown in table 1. Although equation (7) is based on assumption of the existence of τ_1 and τ_2 , the mono-relaxation behaviour showing only τ_2 for some compounds at different frequencies of the electric field may be equally explained by taking into

account a single broad dispersion. The resulting equation (7) becomes, when $\tau_1 = 0$,

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega \tau_2 \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} \quad (15)$$

which may also be derived by using $c_1 = 0$ in equations (1) and (2) of section 2. Equation (15) for ten different frequencies of the electric field was then used to obtain τ_2 values, which are shown in the last column of table 1 for comparison. It is, however, interesting to note that the agreement is closer with τ_2 values obtained from the method of double-relaxation phenomena, as the frequency of the electric field increases from 2.02 to 22.06 GHz. The most probable relaxation time τ_0 , as accurate values for these mono-substituted anilines are not available, was also calculated from the slope m of the linear plot of the imaginary K''_{ij} versus the real K'_{ij} parts [7] of the complex conductivity K^*_{ij} under UHF electric field in the relation:

$$K''_{ij} = K_{ij\infty} + \frac{1}{\omega \tau_0} K'_{ij} \quad (16)$$

where $\tau_0 = 1/(2\pi f m)$. They are seen to correspond to the relation $\tau_0 = (\tau_1 \tau_2)^{1/2}$ approximately, which gives 5.53, 5.31, 44.06, 6.18, 21.93, 22.37, 23.16 and 4.32 ps respectively for the mono-substituted anilines showing the double-relaxation phenomena at different frequencies

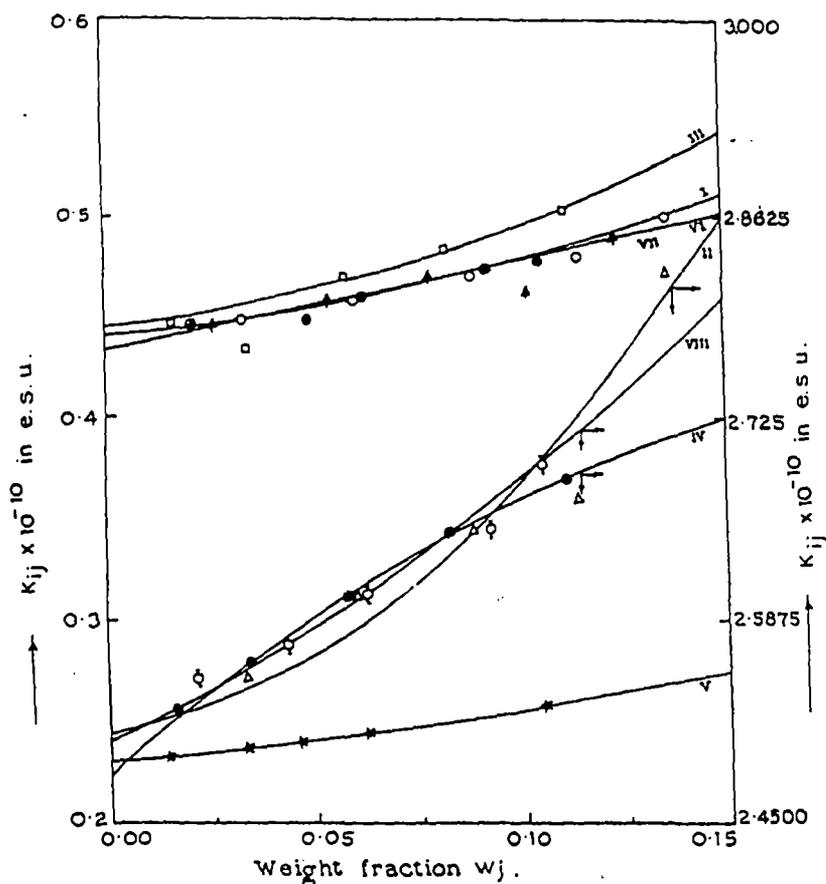


Figure 4. Concentration variation of ultra-high-frequency conductivity K_{ij} of mono-substituted anilines at 35 °C: (I) *o*-anisidine at 3.86 GHz (\circ); (II) *o*-anisidine at 22.06 GHz (Δ); (III) *m*-anisidine at 3.86 GHz (\square); (IV) *m*-anisidine at 22.06 GHz (\bullet); (V) *o*-toluidine at 2.02 GHz (\ast); (VI) *m*-toluidine at 3.86 GHz (\blacktriangle); (VII) *p*-toluidine at 3.86 GHz (\odot); and (VIII) *p*-toluidine at 22.06 GHz (\diamond).

of the applied electric field. Some of these relaxation times are reasonably good. The estimated values of τ_1 , τ_2 and τ_0 are all given in table 1.

It is found in table 1 that *m*-anisidine, *m*- and *p*-toluidines at 3.86 GHz and *o*-toluidine at 2.02 GHz show considerably high values of τ_1 in the range 9–3 ps; while their τ_2 values are comparatively much larger in the range 220–138 ps. This fact confirms that, under such frequencies of alternating electric field, the flexible parts are loosely bound to the parent molecules. They, therefore, require longer times to accommodate their flexible parts towards dielectric relaxation as shown by c_2 values in table 2 being greater than unity. The other molecules like *o*-anisidine at 3.86 and 22.06 GHz and *m*-anisidine and *p*-toluidine at 22.06 GHz show very small values of τ_1 , often less than or equal to unity, while their τ_2 values are more or less consistent with the expected values that are often observed in the literature. However, *p*-anisidine shows the mono-relaxation behaviour at all frequencies by showing only τ_2 in agreement with τ_0 . Hence *p*-anisidine unlike *p*-toluidine appears to be highly rigid at all the experimental frequencies. The *o*- and *m*-anisidines at 2.02 GHz, *o*-toluidine at 3.86

and 22.06 GHz, *m*-toluidine at 2.02 and 22.06 GHz and *p*-toluidine at 2.02 GHz exhibit the mono-relaxation behaviour in yielding τ_2 values in agreement with our τ_0 values. They indicate their rigidity at those frequencies. When the dielectric relaxation data are extended to 9.945 GHz [13] it is really interesting to note that all these mono-substituted anilines show τ_1 and τ_2 in close agreement with the expected literature values. This fact establishes that an X-band microwave electric field is actually the most effective dispersive region for highly non-spherical polar molecules like mono- or disubstituted aniline and benzene respectively [10].

The τ_1 and c_2 values were also calculated from the values of x and y in Fröhlich's equations (8) and (9) with $\tau_1 = \tau_s$ (table 1) and Fröhlich's parameter A , where $A = \ln(\tau_2/\tau_1)$. They are given in table 2 together with those values obtained from the graphical technique of determination of x and y from figures 2 and 3 at infinite dilution. The experimental x and y values on the left-hand sides of equations (1) and (2) as plotted with different w_j in figures 2 and 3 show the usual decrease in x while the latter increases with w_j in concave and convex ways respectively indicating the values of τ_1 and

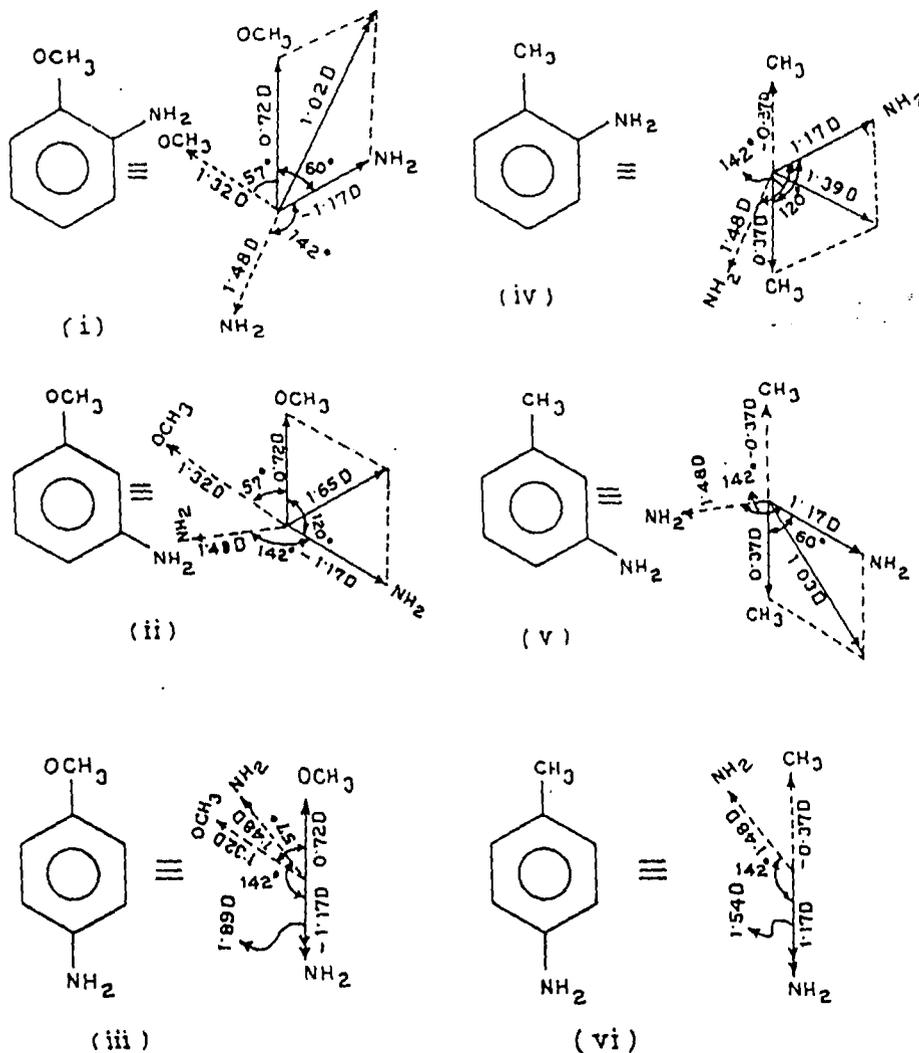


Figure 5. Conformational structures of anisidines and toluidines in *ortho*, *meta* and *para* forms: (i) *o*-anisidine, (ii) *m*-anisidine, (iii) *p*-anisidine, (iv) *o*-toluidine, (v) *m*-toluidine and (vi) *p*-toluidine.

τ_2 as a function of concentration [5]. τ_1 and τ_2 , as obtained from the slope and intercept of equation (7) for a polar-non-polar liquid mixture are, therefore, fixed for a polar compound in consistency with the right-hand sides of equations (1) and (2). The values of c_1 by Fröhlich's method are found to be less than unity while c_2 values are greater than and nearly equal to unity. The graphical technique adopted here yields the opposite results by showing $c_1 \geq 1.0$ and c_2 very small, often becoming negative (table 2), probably due to inertia [10]. The values of c_1 and c_2 in table 2 suggest that the two double-relaxation phenomena are not equally probable.

The UHF K_{ij} as a function of w_j for the following mono-substituted anilines showing τ_1 and τ_2 were, however, arrived at:

(i) *o*-anisidine at 3.86 GHz: $K_{ij} \times 10^{-10} = 0.4398 + 0.1786w_j + 1.9381w_j^2$

(ii) *o*-anisidine at 22.06 GHz: $K_{ij} \times 10^{-10} = 2.5112 + 0.3870w_j + 13.011w_j^2$

(iii) *m*-anisidine at 3.86 GHz: $K_{ij} \times 10^{-10} = 0.4438 + 0.2311w_j + 2.9354w_j^2$

(iv) *m*-anisidine at 22.06 GHz: $K_{ij} \times 10^{-10} = 2.4896 + 2.2841w_j - 4.7796w_j^2$

(v) *o*-toluidine at 2.02 GHz: $K_{ij} \times 10^{-10} = 0.2294 + 0.2097w_j + 0.5641w_j^2$

(vi) *m*-toluidine at 3.86 GHz: $K_{ij} \times 10^{-10} = 0.4326 + 0.4889w_j - 0.1380w_j^2$

(vii) *p*-toluidine at 3.86 GHz: $K_{ij} \times 10^{-10} = 0.4402 + 0.1583w_j + 2.1467w_j^2$ and

(viii) *p*-toluidine at 22.06 GHz: $K_{ij} \times 10^{-10} = 2.5063 + 1.2927w_j + 4.5909w_j^2$

which are shown graphically in figure 4 together with the experimental points upon the curves. The slopes of $K_{ij}-w_j$ curves are, however, listed in table 3 together with those of the other ten $K_{ij}-w_j$ equations showing the monorelaxation behaviour. The percentage of error in computation of $K_{ij}-w_j$ equations are also shown in table 3. The slopes β are finally used to estimate μ_1 and μ_2 from equations (13) and (14) in terms of τ_1 and τ_2 as presented in table 1. The dimensionless parameters b_0 , b_1 and b_2 in terms of τ_0 , τ_1 and τ_2 are also given in

table 3.

An attempt was made to estimate from the available bond moments and bond angles the theoretical μ values of the polar liquids, assuming the molecules to be planar. The bond moments and bond angles of $C \rightarrow OCH_3$ in anisidine and $C \leftarrow CH_3$ in toluidine are 1.32 D, 0.37 D and 57° , 180° with respect to the benzene ring while those of $C \rightarrow NH_2$ are 1.48 D and 142° respectively [17]. The conformational structures thus obtained by the vector addition method for anisidine and toluidine in their *ortho*, *meta* and *para* forms are displayed in figure 5. The estimated μ_j are given in table 3, with those of μ_1 , where $\mu_1 = \mu_2(c_1/c_2)^{1/2}$ assuming that the two relaxation phenomena are equally probable. The close agreement of μ values as shown in table 3 at once indicates that the method as suggested is a simple, straightforward and unique one.

5. Conclusion

The determination of slope and intercept of the derived linear equation (equation (7)) involved with a single UHF dielectric relaxation recording of a polar-non-polar liquid mixture at different w_j and at a given temperature in degrees Celsius is an analytical and reliable method by which to calculate τ_1 and τ_2 of the flexible part as well as of the whole molecule itself. The relative contributions c_1 and c_2 towards dielectric relaxations in terms of τ_1 and τ_2 can be calculated by using Fröhlich's equations. The graphical techniques used are also convenient tools to estimate c_1 and c_2 . The dipole moments μ_1 and μ_2 in terms of τ_1 and τ_2 , and from the slope β of the concentration variation of K_{ij} of polar-non-polar liquid mixtures, throw much light on the structural conformation of a complex polar liquid under investigation. The methodology so far advanced seems to be a significant improvement over the existing ones

in that it allows estimation of correlation coefficients between the data used and the percentage of error introduced in the obtained results. The procedure is thus simple, straightforward and requires less computational work than the existing methods, in which experimental data of a pure polar liquid at two or more electric field frequencies are usually needed.

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Double relaxations of monosubstituted anilines in benzene under effective dispersive region

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Mono- or di-substituted aniline and benzene derivatives are thought to absorb energy much more strongly in the effective dispersive region of nearly 10 GHz electric field. The dielectric relaxation data of the monosubstituted anilines measured at different frequencies (Sit *et al* 1994) showed either double or monorelaxation behaviour. When the same data are extended to 9.945 GHz (≈ 3 cm wavelength) electric field, each of them, on the other hand; exhibits the double relaxation phenomenon by showing the reasonable relaxation times τ_1 (smaller) and τ_2 (larger) for the flexible part as well as the whole molecule itself for their rotations in hf electric field. τ_1 and τ_2 are, however, obtained from the slope and intercept of a derived equation involved with dielectric relaxation data for different weight fractions ω_j 's measured under a single frequency electric field. The relative contributions c_1 and c_2 in terms of τ_1 and τ_2 towards relaxation are calculated from Fröhlich's equations and our graphical technique. The values of symmetric and asymmetric distribution parameters γ and δ are also calculated to test the rigidity of the molecules under investigation. The dipole moments μ_1 and μ_2 in terms of τ_1 and τ_2 are finally estimated from the slope β of hf conductivity K_{ij} as a function of ω_j 's in order to support their conformations.

1 Introduction

The highly nonspherical molecules like mono- or di-substituted benzenes and anilines have more than one relaxation times τ 's due to presence of their flexible parts attached to the parent molecule^{1,2}. The study of dielectric relaxation phenomena of such polar molecules in nonpolar solvent provides one with the valuable information of various types of interactions such as monomer and dimer formations³⁻⁵ in liquids. The polar nonpolar liquid mixtures instead of pure polar liquids deserve much more advantages as the polar-polar interactions, viscosity effect and the other factors become minimized. Moreover, much disputed ambiguity concerning the internal field correction can also be avoided.

Bergmann *et al.*⁶ however, devised a graphical method to obtain τ_1 and τ_2 to represent the relaxation times of the smallest flexible part as well as the whole molecule for their end-over-end rotations under an electric field of Giga hertz frequency. The respective contributions c_1 and c_2 towards dielectric relaxations were also estimated in terms of τ_1 and τ_2 . The method consists of plotting the normalised experimental points involved with the measured data of the real ϵ' , the

imaginary ϵ'' parts of the complex dielectric constant ϵ^* , the static dielectric constant ϵ_0 and the optical dielectric constant ϵ_∞ at different frequencies ω on a semicircle in a complex plane. A point was, however, then selected on the chord through the two fixed points lying on the said semicircle which contained all the experimental points in consistency with the measured data for various frequencies. Bhattacharyya *et al.*⁷ subsequently simplified the above procedure to get τ_1 , τ_2 and the weighted contributions c_1 and c_2 towards dielectric relaxations with the experimental values of ϵ' , ϵ'' , ϵ_0 and ϵ_∞ of a pure polar liquid measured at two different frequencies in GHz regions.

The highly nonspherical polar liquid molecules like mono- or di-substituted anilines and benzenes are usually thought to absorb energy much more strongly in a high frequency electric field of nearly 10 GHz. Moreover, such type of polar liquids are supposed to be non-Debye in their relaxation behaviours. From this point of view, the study of dielectric relaxation of polar-nonpolar liquid mixtures under the electric field of nearly 3 cm wavelength is preferable. Saha *et al.*¹ and Sit *et al.*² recently presented an alternative approach to estimate τ_1 and τ_2 from the intercept and the slope of a derived straight line equation involved with dielectric relaxation solution data like ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$

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measured under a single frequency electric field of GHz range. One could not make a strong conclusion if ϵ_{0ij} and $\epsilon_{\infty ij}$ of a polar solute (*j*) dissolved in a nonpolar solvent (*i*) were not accurately known.

Disubstituted anilines and benzenes were found to possess the double relaxation phenomena¹ by showing considerable values of τ_1 and τ_2 in solvent benzene under the electric field of 9.945 GHz. Monosubstituted anilines, however, showed mono as well as often the double relaxation phenomena² in solvent benzene under the electric field of different frequencies of 2.02 to 22.06 GHz. We, therefore, thought to use ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ of such monosubstituted anilines for different weight fractions ω_j 's under 9.945 GHz electric field which is supposed to be the most effective dispersive region for such isomers of anisidine and toluidine. The dielectric relaxation parameters were, however, obtained at 35°C from the careful graphical interpolation made by the available data measured by Srivastava and Suresh Chandra⁸ at different frequencies.

The monosubstituted anilines are really found to exhibit the expected double relaxation phenomenon under 9.945 GHz electric field at 35°C by showing reasonable values of τ_1 and τ_2 as presented in Table 1, from the slopes and the intercepts of curves of Fig. 1 as derived from Bergmann's equations. The relative contributions c_1 and c_2 (Table 2) towards dielectric relaxations in terms of estimated τ_1 and τ_2 (Table 1) were evaluated by the graphical method^{1,2} using Figs 2 and 3 as well as by Fröhlich's equations⁹ respectively. The symmetric and the asymmetric distribution parameters of such compounds under the effective dispersive region of 9.945 GHz electric field can

also be judged to throw much light on their distribution behaviour (Table 2). In absence of the reliable τ of such isomers of anisidine and toluidine, the slope of the linear variations of the imaginary

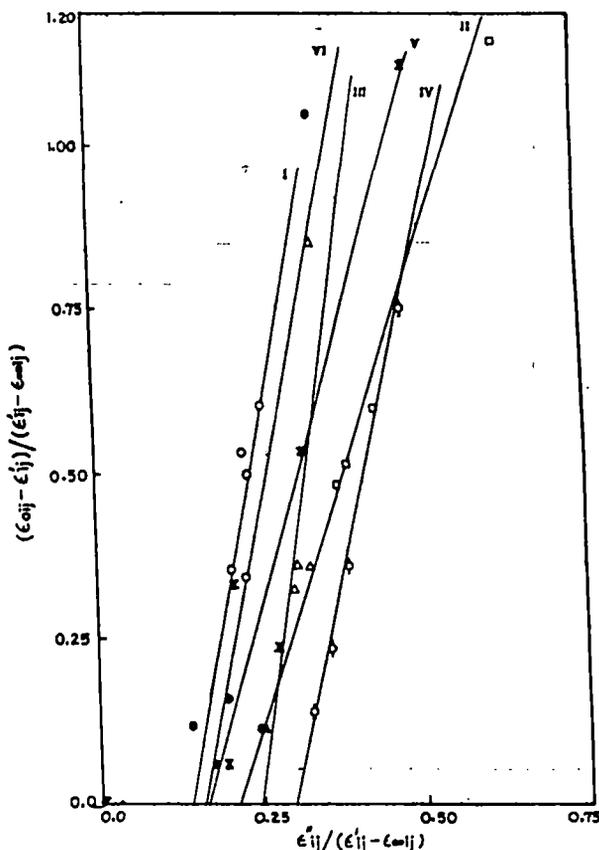


Fig. 1—Linear variation of $(\epsilon_{0ij} - \epsilon_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})$ against $\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$ of mono-substituted anilines under 9.945 GHz electric field at 35°C. (System-I: *o*-anisidine, (-○-) System-II: *m*-anisidine, (-□-) System-III: *p*-anisidine, (-△-) System-IV: *o*-toluidine, (-◇-) System-V: *m*-toluidine, (-○-) System-VI: *p*-toluidine, (-●-).

Table 1—The slope and intercept of the straight lines of $[(\epsilon_{0ij} - \epsilon_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})]$ against $[\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})]$, correlation co-efficients (*r*), % of error involved, relaxation times τ_1 and τ_2 of the flexible parts as well as the whole molecules, measured τ from $K''_{ij} - K'_{ij}$ equations and the most probable relaxation times τ_0 together with τ_s and τ_a from symmetric and asymmetric distribution parameters γ and δ of monosubstituted anilines at 35°C under 9.945 GHz electric field

System with Sl. No.	Slope and intercept of straight line Eq. (7) $\{(\epsilon_{0ij} - \epsilon_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})\}$ versus $[\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})]$	Correlation Co-efficient (<i>r</i>)	% of error involved in Eq. (7)	Estimated relaxation times τ_1 & τ_2 in p sec	Most probable relaxation time $\tau_0 = \sqrt{\tau_1 \tau_2}$ in p sec	Measured τ from $K''_{ij} - K'_{ij}$ Eq. (20) in p sec	τ_s from symmetric distribution parameter γ of Eq. (13)	τ_a from asymmetric distribution parameter δ of Eq. (15)
I <i>o</i> -anisidine	4.9294 0.6583	0.7789	11.86	2.20 76.73	12.99	3.54	0.55	61.91
II <i>m</i> -anisidine	2.9043 0.6073	0.9888	0.67	3.63 42.87	12.47	4.77	14.78	86.39
III <i>p</i> -anisidine	6.2098 1.4923	0.8308	9.34	4.01 95.42	19.56	4.20	1.41	75.33
IV <i>o</i> -toluidine	4.2660 1.2707	0.9994	0.04	5.16 63.15	18.05	4.56	4.62	41.71
V <i>m</i> -toluidine	3.3514 0.5415	0.9622	2.24	2.73 50.94	11.79	5.52	0.64	66.69
VI <i>p</i> -toluidine	4.7133 0.7348	0.8684	7.41	2.58 72.88	13.71	3.57	0.66	20.13

Table 2—The estimated values of $x = (\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$ and $y = \epsilon''_{ij} / (\epsilon_{0ij} - \epsilon_{\infty ij})$ from Fröhlich's equations and by the graphical techniques at $\omega_j \rightarrow 0$, Fröhlich's parameter A , symmetric and asymmetric distribution parameters γ and δ from x and y at $\omega_j \rightarrow 0$ along with the relative contributions c_1 and c_2 due to Fröhlich and the graphical technique under 9.945 GHz electric field

System with Sl. No	Fröhlich's parameter $A = \ln(\tau_2/\tau_1)$	Estimated values of x and y from Fröhlich's Eqs (8) and (9)	Weighted contributions c_1 & c_2 from Eqs (5) & (6)	Estimated values of x & y from Figs (2) & (3) at $\omega_j \rightarrow 0$	Weighted contributions c_1 & c_2 from the graphical technique	Symmetric & asymmetric distribution parameters γ & δ
I <i>o</i> -anisidine	3.5518	0.5555 0.3457	0.5069 1.3869	0.0875 0.106	0.8946 -0.0732	0.47 0.09
II <i>m</i> -anisidine	2.4689	0.5848 0.4009	0.4997 0.8945	0.515 0.254	0.4825 0.4574	0.40 0.33
III <i>p</i> -anisidine	3.1695	0.4420 0.3655	0.4223 1.6298	0.810 0.140	0.8725 -0.4020	0.49 0.13
IV <i>p</i> -toluidine	2.5046	0.4594 0.4033	0.4293 1.1669	0.740 0.228	1.1326 -0.0478	0.35 0.25
V <i>m</i> -toluidine	2.9263	0.5933 0.3748	0.5170 1.0107	0.870 0.106	0.9097 -0.1564	0.49 0.09
VI <i>p</i> -toluidine	3.3410	0.5432 0.3574	0.4942 1.3351	0.950 0.084	0.9908 -0.3417	0.29 0.09

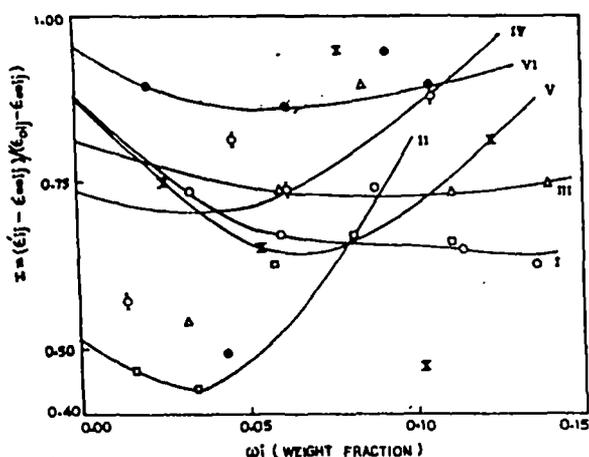


Fig. 2—Variation of $(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction ω_j 's of solutes under 9.945 GHz electric field at 35°C. (System-I: *o*-anisidine, (-○-)) System-II: *m*-anisidine, (-□-) System-III: *p*-anisidine, (-△-) System-IV: *o*-toluidine, (-◇-) System-V: *m*-toluidine, (-X-) System-VI: *p*-toluidine, (-●-).

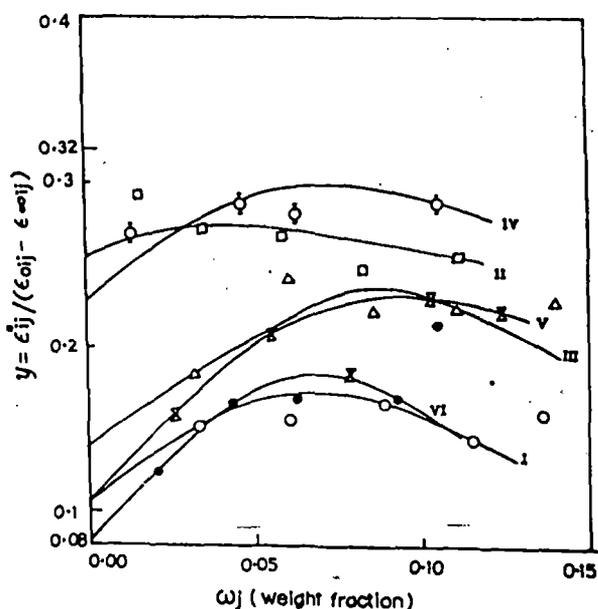


Fig. 3—Variation of $\epsilon''_{ij} / (\epsilon_{0ij} - \epsilon_{\infty ij})$ against ω_j 's of isomers of anisidines and toluidines under 9.945 GHz electric field at 35°C. (System-I: *o*-anisidine, (-○-)) System-II: *m*-anisidine, (-□-) System-III: *p*-anisidine, (-△-) System-IV: *o*-toluidine, (-◇-) System-V: *m*-toluidine, (-X-) System-VI: *p*-toluidine, (-●-).

parts K''_{ij} against the real parts K'_{ij} of the complex hf conductivities K^*_{ij} of the solutions were used to τ as shown in Table 1, together with τ_1 , get τ_s and τ_{cs} where τ_0 is the most probable relaxation time given by $\tau_0 = \sqrt{\tau_1 \tau_2}$, and τ_{cs} are called symmetric and characteristic relaxation times associated with symmetric and asymmetric distribution parameters γ and δ respectively. The respective dipole moments μ_1 , μ_2 and μ_0 in terms of τ_1 , τ_2 and τ_0 of these compounds as obtained from the slope β of the linear variations of total hf conductivities K^*_{ij} 's of the solutions against ω_j 's of mono-substituted anilines in benzene (Fig. 4) are in close agreement with the theoretical dipole moments μ_{theos} 's, (Table 3) as computed from bond angles and bond moments of several groups in anisidines and toluidines with respect to benzene ring.

2 Theory and Formulation

When the polar molecule is provided with more

than one relaxation times i.e., τ_1 and τ_2 Debye's equations of polar-nonpolar liquid mixture lead to Bergmann's equations:

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

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

such that $c_1 + c_2 = 1$.

The co-efficients c_1 and c_2 are the weight factors of the two Debye processes governed by τ_1 and

Table 3—Intercept and slope of $K_{ij} - \omega_j$ curve, dimensionless parameters b_i dipole moments μ_i in Debye (D) together with estimated μ_1 from $\mu_1 = \mu_2(c_1/c_2)^{1/2}$ and theoretical μ from bond angles and bond moments of isomers of anisidine and toluidine at 9.945 GHz electric field and at 35°C

System with Sl. No. & mol wt	Intercept & slope of $K_{ij} - \omega_j$ equation		Dimensionless parameters			Estimated dipole moments in Debye			Theoretical μ_{theo} in D from bond angles and bond moments	Estimated $\mu_{theo}\mu_1$ from $\mu_2(c_1/c_2)^{1/2}$ D
	$\alpha \times 10^{-10}$	$\beta \times 10^{-10}$	$b_0 =$	$b_1 =$	$b_2 =$	μ_0	μ_1	μ_2		
	esu	esu	$\frac{1}{1 + \omega^2 \tau_0^2}$	$\frac{1}{1 + \omega^2 \tau_1^2}$	$\frac{1}{1 + \omega^2 \tau_2^2}$	D	D	D		
I <i>o</i> -anisidine $M_1 = 123$ gm	1.1244	0.7757	0.6030	0.9815	0.0417	2.45	1.92	9.33	1.02	5.64
II <i>m</i> -anisidine	1.1039	1.4215	0.6224	0.9511	0.1224	3.27	2.264	7.37	1.65	5.51
III <i>p</i> -anisidine $M_3 = 123$ gm	1.1060	1.4663	0.4012	0.9410	0.0274	4.13	2.70	15.82	1.89	8.05
IV <i>o</i> -toluidine $M_4 = 107$ gm	1.1151	1.1932	0.4404	0.9059	0.0604	3.32	2.31	8.96	1.39	5.43
V <i>m</i> -toluidine $M_5 = 107$ gm	1.1359	0.5788	0.6484	0.9718	0.0899	1.91	1.56	5.12	1.03	3.66
VI <i>p</i> -toluidine $M_6 = 107$ gm	1.1323	0.3501	0.5770	0.9747	0.0460	1.57	1.21	5.56	1.54	3.38

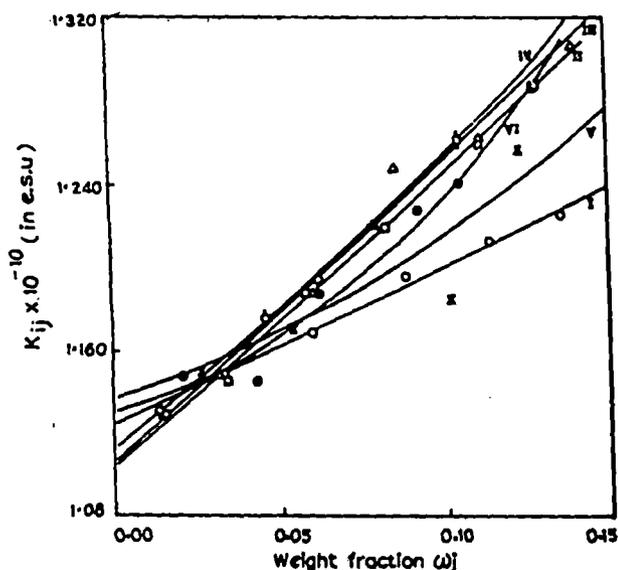


Fig. 4—Variation of hf conductivity K_{ij} with different weight fractions ω_j of solutes at 35°C and 9.945 GHz electric field. (System-I: *o*-anisidine, (-O-)) System-II: *m*-anisidine, (-□-) System-III: *p*-anisidine, (-Δ-) System-IV: *o*-toluidine, (-○-) System-V: *m*-toluidine, (-X-) System-VI: *p*-toluidine, (-●-).

τ_2 respectively. The symbols used in Eqs (1) and (2) convey the usual meanings:

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

and $\omega \tau = a$. Using the notations $a = 1/(1 + \alpha^2)$ and $b = \alpha/(1 + \alpha^2)$ the above Eqs (1) and (2) can be written as:

$$x = c_1 a_1 + c_2 a_2 \quad \dots (3)$$

$$y = c_1 b_1 + c_2 b_2 \quad \dots (4)$$

The suffices 1 and 2 with a and b are related to τ_1 and τ_2 respectively.

Evaluating c_1 and c_2 from Eqs (3) and (4) one gets:

$$c_1 = \frac{(x a_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots (5)$$

and

$$c_2 = \frac{(y - x \alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots (6)$$

provided $\alpha_2 > \alpha_1$. Now adding Eqs (5) and (6) and since $c_1 + c_2 = 1$ we get:

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

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

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2 \quad \dots (7)$$

representing a straight line of $\{(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})\}$ against $\{\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})\}$ with slope $\omega(\tau_1 + \tau_2)$

and intercept $-\omega^2\tau_1\tau_2$. The slopes and intercepts of Eq.(7) were, however, evaluated by fitting ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ for different ω_j 's of the mono-substituted anilines, referred to Tables (1-3) and Figs (1-4) at 35°C under 9.945 GHz electric field. They are finally placed in Table 1, to yield τ_1 and τ_2 respectively for them.

The weighted contributions c_1 and c_2 towards dielectric relaxation may be computed from Eqs (5) and (6) by using x and y in Fröhlich's equations (Ref. 9)

$$x = \frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + e^{2A}\omega^2\tau_1^2}{1 + \omega^2\tau_1^2} \right) \quad \dots (8)$$

and

$$y = \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} [\tan^{-1}(e^A\omega\tau_1) - \tan^{-1}(\omega\tau_1)] \quad \dots (9)$$

where $A = \text{Fröhlich parameter} = \ln(\tau_2/\tau_1)$ and $\tau_1 = \text{small limiting relaxation time} = \tau_1$. Both c_1 and c_2 may also be calculated from Eqs (5) and (6) with the graphically extrapolated fixed values of x and y when $\omega_j \rightarrow 0$ as shown in Figs (2) and (3). They are shown in Table 2.

The molecules appear to behave like nonrigid ones having either symmetric or asymmetric distribution parameters γ and δ which may be calculated from Eqs (10-11)

$$\epsilon^*_{ij} = \epsilon_{\infty ij} + \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{1 + (j\omega\tau_1)^{1-\gamma}} \quad \dots (10)$$

or

$$\epsilon^*_{ij} = \epsilon_{\infty ij} + \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{(1 + j\omega\tau_{cs})^\delta} \quad \dots (11)$$

the former and the latter ones are associated with τ_1 and τ_{cs} where τ_1 and τ_{cs} are called the symmetric as well as the characteristic relaxation times. Separating the real and the imaginary parts of Eqs (10) and (11) and rearranging them in terms of x and y as shown in Figs (2) and (3) at $\omega_j \rightarrow 0$ we have the symmetric parameter γ from:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[(1-x) \frac{x}{y} - y \right] \quad \dots (12)$$

and the symmetric relaxation time τ_1 from:

$$\tau_1 = \frac{1}{\omega} \left\{ \frac{1}{\left[\frac{x}{y} \cos\left(\frac{\gamma\pi}{2}\right) - \sin\left(\frac{\gamma\pi}{2}\right) \right]} \right\}^{1/(1-\gamma)} \quad \dots (13)$$

similarly, δ and τ_{cs} can be had from Eqs (11) as:

$$\tan(\delta\phi) = \frac{y}{x} \quad \dots (14)$$

and

$$\tan\phi = \omega\tau_{cs} \quad \dots (15)$$

As the values of ϕ cannot be estimated directly we draw a theoretical curve for $\log(\cos\phi)^{1/\phi}$ against ϕ as shown in Fig. 5 from which

$$\log(\cos\phi)^{1/\phi} = \frac{\log \frac{x}{\cos(\delta\phi)}}{\delta\phi} \quad \dots (16)$$

can be known. With the known ϕ from Fig. 5; τ_{cs} and δ can be estimated from Eqs (14) and (15) respectively. The τ_1 and τ_{cs} thus estimated are placed in Table 1 to compare with τ_1 and τ_2 from double relaxation method, but γ and δ are placed in Table 2.

The complex high frequency conductivity K^*_{ij} of a dilute polar-nonpolar liquid mixture¹² is given by:

$$K_{ij} = K'_{ij} + jK''_{ij} \quad \dots (17)$$

where

$$K'_{ij} = \frac{\omega}{4\pi} \epsilon'_{ij} \quad \text{and} \quad K''_{ij} = \frac{\omega}{4\pi} \epsilon''_{ij}$$

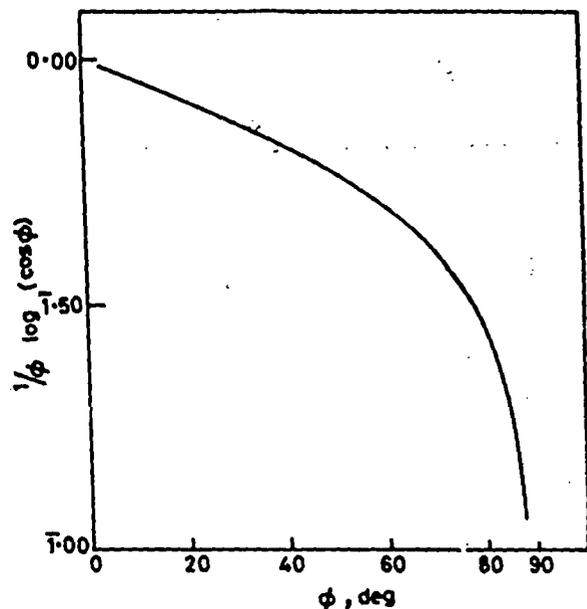


Fig. 5—Variation of $\log(\cos\phi)^{1/\phi}$ against ϕ .

The magnitude of the total hf conductivity is:

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon''_{ij}{}^2 + \epsilon'_{ij}{}^2)^{1/2} \quad \dots (18)$$

The dielectric permittivity ϵ'_{ij} of solution in hf region is very small and eventually equals the optical dielectric constant. The dielectric loss ϵ''_{ij} is responsible for the absorption of electrical energy and, therefore, offers resistance to polarisation. The K_{ij} may thus be approximated as:

$$K_{ij} = \frac{\omega}{4\pi} \epsilon'_{ij} \text{ since } \epsilon'_{ij} \gg \epsilon''_{ij}$$

The real part of the complex conductivity of a solution of weight-fraction ω_j of polar solute at TK is:

$$K'_{ij} = \frac{\mu_j^2 N \rho_j F_j}{3 M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \omega_j \quad \dots (19)$$

where the symbols have their usual significance. But for hf region it can be shown that

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

or

$$K'_{ij} = K_{\infty ij} + \frac{K'_{ij}}{\omega \tau} \quad \dots (20)$$

Since K_{ij} is a function of ω_j it can be shown at infinite dilution:

$$\left(\frac{dK'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \omega \tau \beta \quad \dots (21)$$

where β is the slope of $K_{ij} - \omega_j$ curve at $\omega_j \rightarrow 0$. Eq. (19) on being differentiated with respect to ω_j and at $\omega_j \rightarrow 0$ becomes:

$$\left(\frac{dK'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \frac{\mu_j^2 N \rho_j F_j}{3 M_j k T} \left(\frac{-\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad \dots (22)$$

because at $\omega_j \rightarrow 0$, ρ_{ij} the density of the solution becomes ρ_i , the density of the solvent and F_{ij} the local field in the solution becomes F_i , where $F_i = [(\epsilon_i + 2)/3]^2$, ϵ_i is the dielectric constant of the solvent. From Eqs (21) and (22) we finally get:

$$\mu_j = \left(\frac{3 M_j k T \beta}{N \rho_i F_i \omega b} \right)^{1/2} \quad \dots (23)$$

as the dipole moment of the polar liquid in terms of b where

$$b = \frac{1}{1 + \omega^2 \tau^2} \quad \dots (24)$$

which is a dimensionless parameter. The μ_1 , μ_2 and μ_0 in terms of b_1 , b_2 and b_0 involved with τ_1 , τ_2 and τ_0 respectively were then computed with the knowledge of β . They are finally placed in Table 3 together with μ_{theo} obtained from bond angles and bond moments for comparison.

3 Results and Discussion

The values of x and y in terms of dielectric relaxation data at 9.945 GHz are first estimated for different ω_j 's with the available data⁸ measured under 2.02, 3.86 and 22.06 GHz electric field. They are then plotted against ω_j 's as shown in Figs (2) and (3) which are found to agree well with the Bergmann Eqs (1) and (2) almost exactly. The close agreement of the curves in Figs (2) and (3) with Eqs (1) and (2) suggests that the data selected by graphical interpolations at 3 cm wavelength electric field are almost accurate. The dielectric relaxation parameters ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ thus obtained, are used to calculate the slopes and the intercepts of the fitted straight lines of Eq. (7) with the experimental points placed upon them as shown in Fig. 1. The correlation coefficient r for each straight line is, however, estimated and found to lie within the range of 0.9994 to 0.7789 together with % error involved in each case. They are shown in 4th and 5th columns of Table 1. Table 1 also shows that *o*- and *p*-anisidine like *p*-toluidine exhibit errors of larger magnitudes than the other systems. This may, perhaps, be due to the uncertainty in the estimation of dielectric relaxation data for such systems. Monosubstituted anilines often showed double as well as mono relaxation behaviour as observed earlier². *p*-anisidine, however, is an exception². It showed the mono relaxation behaviour at 2.02, 3.86 and 22.06 GHz respectively. It is again very much interesting to note that all the anisidines and toluidines as referred to Table 1, nevertheless exhibit the double relaxation behaviour by showing reasonably considerable values of τ_1 (smaller) and τ_2 (larger) to represent the relaxation times for their flexible parts attached to the parent ring and the whole molecules respectively. It signifies that 9.945 GHz (≈ 3 cm, wavelength) electric field seems to be the most effective dispersive region for such molecule to yield τ_1 and τ_2 .

The τ_2 's as observed from the slopes and the

intercepts of Eq. (7) gradually increase from *meta*- to *ortho*- and to *para*-forms of all the anisidines and toluidines probably due to $C-NH_2$ groups which is highly influenced by 9.945 GHz (≈ 3 cm wavelength) electric field for its different positions in them. The τ_{1s} ' on the other hand, increase from *ortho* to *para* for anisidines while reverse is true for toluidines. The increase in the values of τ_{1s} ' indicates the flexible parts of the molecules are more loosely bound to parent molecules^{1,2}.

The most probable relaxation time τ_0 as shown in the 8th column of Table 1, can be compared with the measured τ_s ' from the slopes⁵ of $K''_{ij} - K'_{ij}$ along with symmetric τ_s and characteristic τ_{cs} from γ and δ . The τ_s ' as shown in the 9th column of Table 1 agree excellently well with τ_1 . This fact indicates that the *hf* conductivity measurement of polar-nonpolar liquid mixture yields the microscopic relaxation time while the double relaxation method gives macroscopic as well as microscopic relaxation times as observed earlier¹³. τ_{cs} ' in Table 1 are slightly smaller than τ_s ; as obtained from *hf* conductivity for almost all systems besides *m*-anisidine and *o*-toluidine whose τ_{cs} ' agree well with τ_0 and τ respectively. The slight difference is due to different steric hindrances as a result of structural conformations. All these discussions made above, confirms τ_s to represent microscopic relaxation time. τ_{cs} 's, on the other hand, are larger in magnitude and agree with τ_2 as obtained by double relaxation method. Thus τ_{cs} under the electric field of 9.945 GHz gives τ_2 .

The relative contributions c_1 and c_2 towards dielectric relaxations were found out in the graphical method by using Figs 2 and 3 as well as Fröhlich's

$$\text{equations of } x \left[= \frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} \right] \text{ and } y \left[= \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} \right]$$

both from Bergmann's Eqs (1) and (2) in terms of τ_1 and τ_2 . The x and y in Fröhlich's Eqs (8) and (9) are related to Fröhlich parameter A which depends on the difference of the activation energies E_2 and E_1 of the rotating units and is expressed in terms of τ_2/τ_1 by $\tau_2/\tau_1 = \exp(E_2 - E_1)/RT$. The constancy of the factor $(E_2 - E_1)/RT$ at a fixed temperature may be put equal to A where $A = \ln(\tau_2/\tau_1)$. The positive values of c_1 and c_2 such that $c_2 > c_1$ and $c_1 + c_2 > 1$ in Fröhlich's method for all the systems are shown in the 5th and 6th columns of Table 2 together with the Fröhlich parameters A in the 2nd column respectively. But the graphical extrapolation technique suggested by Saha *et al.*¹ and Sit *et al.*², however, yields c_2 always negative except *m*-anisidine satisfying the condition that $c_1 + c_2 \approx 1$ as shown in the 9th and

10th columns of same Table 2. The negative sign before c_2 in the latter method signifies the lag in inertia of the whole molecules with respect to their flexible parts^{1,2} under *hf* electric field.

The double relaxation times showed by all the monosubstituted anilines under 9.945 GHz electric field at 35°C indicate the nonrigidity of the molecules. This fact at once inspired us to test the symmetric as well as asymmetric distribution parameters γ and δ for such compounds. They are calculated from Eqs (12) and (16) with the values of x and y at $\omega_j \rightarrow 0$ from Figs 2 and 3. The values of γ and δ thus obtained with the aid of the direct measurements of relaxation data seem to be accurate enough to specify the distribution parameters as placed in the last two columns of Table 2. It is observed from Table 2 that the values of γ lie in the range of $0.29 \leq \gamma \leq 0.49$ indicating thereby symmetric relaxation behaviour for such molecules under 9.945 GHz electric field. The low values of δ in the range of $0.09 \leq \delta \leq 0.33$ invariably rule out the possibility of occurrence of asymmetric dielectric distributions¹⁴.

The dipole moments μ_1 and μ_2 of the flexible parts and the whole molecules of anisidines and toluidines are obtained from Eq. (23) in terms of dimensionless parameters b_1 , b_2 from Eq. (24) involved with τ_1 and τ_2 respectively (Table 1) and the slope β of $K_{ij} - \omega_j$ curves in Fig. 4 which shows the variation of K_{ij} 's with ω_j 's. The intercepts and slopes of $K_{ij} - \omega_j$ equations are shown in the 2nd and 3rd columns of Table 3. The intercepts are of almost equal in magnitudes in all them; but the slopes β increase slowly from *ortho*- to *para*- for anisidines and reverse in toluidines. The almost same intercepts and slopes of $K_{ij} - \omega_j$ curves in Fig. 4 arise probably due to the identical polarity³ of the molecules. Some of the curves in Fig. 4 meet at a point near $\omega_j \rightarrow 0$ indicating thereby solute-solvent (monomer) or solute-solute (dimer) associations in the region $0.02 < \omega_j < 0.035$ of the concentration. Unlike toluidines the most probable dipole moments μ_0 and μ_1 gradually increase from *o*- to *p*- for anisidines as reported in 7th and 8th columns of Table 3. μ_2 's, on the other hand, increase gradually from *m*- to *o*- with a high value in *p*-anisidine while in case of toluidines μ_2 's increase from *m*- to *p*- and *o*-configurations. The above facts, however, reveal that μ_0 as obtained from $\tau_0 = \sqrt{\tau_1 \tau_2}$ depends solely upon the group moments like μ_1 of their flexible parts. The gradual increase of μ_0 from *o*- to *p*-anisidine and from *p*- to *o*-toluidine like μ_1 is probably due to their almost same polarity as supported by the slopes β 's of K_{ij} as a function of ω_j 's (Fig. 4).

The theoretical dipole moments $\mu_{\text{theo}}^{\prime}$ from the bond angles and bond moments of $\text{C} \rightarrow \text{OCH}_3$ in anisidines and $\text{C} \rightarrow \text{CH}_3$ in toluidines with $\text{C} \rightarrow \text{NH}_2$ with respect to the benzene ring were already calculated elsewhere² and placed in the 10th column of Table 3. They are compared with all the μ s' together with μ_1 from $\mu_1 = \mu_2(c_1/c_2)^{1/2}$ assuming the two relaxation processes are equally probable.

4 Conclusion

The correlation coefficients r s' and hence the % of errors introduced in Eq. (7) with the dielectric relaxation parameters like ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ of the polar-nonpolar liquid mixtures under 9.945 GHz electric field at 35°C, as presented in Table 1, are within such range that τ_1 and τ_2 as obtained from the intercepts and slopes of Eq. (7) are of considerable accuracy because τ s' are usually claimed to be accurate within $\pm 10\%$. The methodology of single frequency measurements of dielectric relaxation data at different ω_j s' seems to be much simple in comparison to the existing methods where data of pure polar liquid at two or more electric field frequencies of GHz region are, usually required. The relative contributions c_1 and c_2 in terms of τ_1 and τ_2 are, however, obtained by using Fröhlich's equations as well as graphical technique which also offers a convenient method to decide either symmetric or asymmetric distribution behaviour under the electric field of given fre-

quency. The dipole moments μ_1 , μ_2 in terms of τ_1 and τ_2 and slope β of concentration variation of K_{ij} of polar-nonpolar liquid mixture provide the valuable information of the conformation of a complex polar liquid.

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Double relaxation of straight chain alcohols under high frequency electric field

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Abstract : Alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol are long straight chain polar molecules almost like polymers. In these alcohols as well as in methanol and ethanol, there exist many possibilities of having internal rotation, bending and twisting, each with a characteristic relaxation time, under high frequency electric field of Giga hertz range. An attempt is, therefore, made to detect the double relaxation phenomena by the new approach suggested earlier. It involves single frequency measurements of the dielectric relaxation data of those compounds in solvent *n*-heptane at 25°C under three different frequencies of 24.33, 9.25 and 3.00 GHz electric field as well as those of methanol and ethanol in benzene at 9.84 GHz respectively to get τ_1 and τ_2 for their flexible parts and the whole molecules. The alcohols under investigation, always exhibit the double relaxation behaviours at all frequencies except methanol at 9.84 GHz, thus indicating separate broad dispersions in them. The relative contributions ϵ_1 and ϵ_2 towards dielectric relaxations due to τ_1 and τ_2 , are calculated from Debye's equations to compare with those as obtained by graphical technique. The dipole moments μ 's are also estimated in terms of the relaxation times τ_1 and τ_2 , obtained from the slopes β 's of the hl conductivities K_{hl} 's of the solutions against the weight fraction w_1 's of the solutes in order to support their usual conformations.

Keywords : Double relaxation, dipole moments, straight chain alcohols

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1. Introduction

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

The nomenclature of symbols used, are given in the Appendix.

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valuable information regarding sizes, shapes, structures and different thermodynamic parameters due to relaxation of the polar liquids [3].

The relaxation phenomena of pure primary alcohols are very interesting as they were found to possess three distinct low frequency Debye type processes predicting inherently the single relaxation time [4,5]. The dilution of polar alcohols with nonpolar solvents, however, increases the relative contributions towards dielectric dispersions in the hf electric field [6]. The straight chain mono-alcohols, on the other hand, are almost like polymers having $-\text{CH}_3$ and $-\text{OH}$ groups in their structures. Obviously, there exist many possibilities of internal and molecular rotations, bending, twisting *etc* each with a characteristic relaxation time. In averaging to the macroscopic condition, a distribution of relaxation time may also be possible. Mishra *et al* [7] claimed that it is not possible to resolve dielectric dispersion in three relaxation processes from the measured relaxation data under a single frequency electric field.

Again, to detect the double relaxation phenomena of a polar solute, Bergmann *et al* [8] proposed a technique based on measured relaxation parameters of pure polar liquid like real ϵ' , loss ϵ'' of the complex dielectric constant ϵ^* as well as static ϵ_0 and the high frequency dielectric constant ϵ_∞ at different frequencies of the electric field. The term $\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}$ was then plotted against $\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty}$ following Cole-Cole semi-circle equation. A suitable chord joining the two fixed points on the semi-circle consistent with all the experimental points is then chosen to yield the relaxation time τ_1 and τ_2 of the flexible part and the whole molecule itself. Bhattacharyya *et al* [9] had subsequently modified the procedure of Bergmann *et al* [8] to get τ_1 and τ_2 of a pure polar liquid in terms of the relaxation parameters measured at two different frequencies of the electric field in the GHz range.

In such a context, we have studied the double relaxation phenomena of some straight chain aliphatic alcohols, namely 1-butanol, 1-hexanol, 1-heptanol and 1-decanol dissolved in n-heptane at 24.33, 9.25 and 3.00 GHz electric field together with methanol and ethanol dissolved in benzene at 9.84 GHz electric field respectively at a temperature of 25°C by the recently developed method [10]. It is usually made with the single frequency measurements of the dielectric relaxation parameters like ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ of a polar solute (*j*) in a nonpolar solvent (*i*) for different weight fractions w_j 's of the polar solute. τ_1 and τ_2 are then obtained from the slope and the intercept of a straight line equation containing the dielectric relaxation data of which ϵ_{0ij} and $\epsilon_{\infty ij}$ should be accurately known [11]. The approach as suggested earlier [10], seems to be an effective tool to detect the double relaxation phenomena of the polar liquid in a nonpolar solvent within the framework of Debye and Smyth model. For such straight chain alcohols behaving almost like polymers, Onsager's equation may be a better choice due to the strong intermolecular force exerted by alcohols in solution owing to their high dipole moments. But the resulting expressions can not be solved so easily as has been done in [10], because of the presence of the quadratic term ϵ''_{ij} . The method [10] was already applied to mono-substituted anilines [12] in benzene in order

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

System with Sl. No. and molecular wt.	Frequency f in GHz	Intercept and slope of equation (8)		Correlation coefficient (r)	Percentage error in regression technique	Estimated values of τ_2 and τ_1 in p Sec		Measured τ_x in p Sec	Most probable relaxation time $\tau_0 = \sqrt{\tau_1 \tau_2}$ in p Sec
I) 1-Butanol in n-heptane $M_j = 74$ gm	(a) 24.33	2.6046	8.6557	0.9013	5.16	54.60	2.04	1.96	10.55
	(b) 9.25	1.2809	6.1343	0.9347	3.47	101.87	3.73	4.30	19.49
	(c) 3.00	0.6825	4.1544	0.9328	3.57	211.41	9.10	16.98	43.86
II) 1-Hexanol in n-heptane $M_j = 102$ gm	(a) 24.33	2.045	6.7079	0.6195	18.58	41.81	2.10	2.74	9.37
	(b) 9.25	1.0803	5.1697	0.9163	4.42	85.24	3.76	5.86	17.90
	(c) 3.00	0.6651	4.0210	0.9308	3.67	204.26	9.17	13.14	43.28
III) 1-Heptanol in n-heptane $M_j = 116$ gm	(a) 24.33	2.8273	7.9933	0.6752	14.98	49.89	2.43	2.11	11.01
	(b) 9.25	0.9233	5.0147	0.9433	3.03	83.03	3.30	5.78	16.55
	(c) 3.00	0.6823	4.1075	0.9638	1.95	208.81	9.20	13.49	43.83
IV) 1-Decanol in n-heptane $M_j = 158$ gm	(a) 24.33	2.4813	5.4316	0.8153	9.23	32.25	3.30	2.69	10.32
	(b) 9.25	1.5735	5.1553	0.9463	2.87	83.14	5.61	5.71 ^o	21.60
	(c) 3.00	0.3316	2.6855	0.9228	4.08	135.66	6.89	14.37	30.57
V) Ethanol in benzene $M_j = 46$ gm	9.84	4.5211	288.7386	0.9416	3.42	4672.26	0.25	3.9	34.18
VI) Methanol in benzene $M_j = 32$ gm	9.84	-5.4003	198.2809	0.8952	5.99	3209.12	—	4.3	—

Table 2. Fröhlich parameter A , relative contributions c_1 and c_2 due to τ_1 and τ_2 , theoretical values of x and y due to Fröhlich eqs. (9) and (10) and those by our method at infinite dilution for monoalcohols under different uhf electric field at 25°C.

System with Sl. No. and molecular wt.	Frequency f in GHz	Fröhlich parameter $A = \ln(\tau_2/\tau_1)$	Theoretical values of x and y from eq. no. (9) and (10)		Theoretical values of c_1 and c_2 from eq. no. (4) and (5)		Estimated values of x and y at $w_j \rightarrow 0$ from Figs. (2) and (3)		Estimated values of c_1 and c_2 from graphical technique	
I) 1-Butanol in n-heptane $M_j = 74$ gm	(a) 24.33	3.2871	0.3666	0.3495	0.3701	2.0678	0.83	0.218	0.9162	-0.3579
	(b) 9.25	3.3073	0.4651	0.3596	0.4394	1.6354	0.99	0.15	1.0483	-0.4076
	(c) 3.00	3.1455	0.5556	0.3670	0.4985	1.2024	1.11	0.13	1.1589	-0.2668
II) 1-Hexanol in n-heptane $M_j = 102$ gm	(a) 24.33	2.9912	0.3924	0.3692	0.3885	1.6769	0.79	0.264	0.8694	0.0725
	(b) 9.25	3.1211	0.4885	0.3704	0.4535	1.4215	0.70	0.130	0.7385	-0.1234
	(c) 3.00	3.1035	0.5600	0.3689	0.5004	1.1707	1.005	0.078	1.0618	-0.4113
III) 1-Heptanol in n-heptane $M_j = 116$ gm	(a) 24.33	3.0219	0.3464	0.3588	0.3580	1.8763	0.655	0.236	0.7464	-0.0586
	(b) 9.25	3.2253	0.5112	0.3647	0.4703	1.3973	0.835	0.130	0.8724	-0.1575
	(c) 3.00	3.1222	0.5560	0.3682	0.4983	1.1910	1.045	0.116	1.0942	-0.2853
IV) 1-Decanol in n-heptane $M_j = 158$ gm	(a) 24.33	2.2796	0.3412	0.3962	0.3644	1.2809	1.11	0.29	1.4687	-1.5413
	(b) 9.25	2.6960	0.4268	0.3899	0.4105	1.3544	0.955	0.17	1.0911	-0.7627
	(c) 3.00	2.9801	0.6640	0.3585	0.5611	0.8453	1.005	0.012	1.0716	-0.3678
V) Ethanol in benzene $M_j = 46$ gm	9.84	9.8357	0.4240	0.1577	0.4236	43.6436	0.24	0.0099	0.2400	1.7937

to get the frequency dependence of τ_1 and τ_2 under three different electric fields of 22.06, 3.86 and 2.02 GHz respectively, showing either the double or the mono-relaxation behaviours. *p*-anisidine alone shows the mono-relaxation behaviour at all frequencies. When the data are extended to 9.945 GHz electric field, all of them, on the other hand, show the double relaxation phenomena [13]. No such rigorous study on monohydric alcohols has been made so far. So it seems worthwhile to make an extensive study on the available data of aliphatic alcohols [14] as well as ethanol and methanol [15,16] with special emphasis on possible occurrence of τ_1 and τ_2 in the hf electric field [6].

It is evident from Table 1 and Figure 1 that all the alcohols show the double relaxation phenomena in all the frequencies of GHz range except methanol at 9.84 GHz, indicating separate broad dispersions in them. Ethanol is a system with $\tau_2 \gg \tau_1$ while methanol shows very high value of τ_2 only. τ_1 and τ_2 are compared with most probable relaxation time τ_0 where $\tau_0 = \sqrt{\tau_1 \tau_2}$ as shown in the last column of Table 1. In absence of accurate τ for such alcohols, τ 's are estimated from the slope of the imaginary part K''_{ij} and the real part K'_{ij} of the total uhf conductivity K^*_{ij} and placed in the 9th column of Table 1 for comparison with τ_1 , τ_2 and τ_0 respectively.

The relative contributions towards the dielectric relaxation i.e. c_1 and c_2 due to τ_1 and τ_2 are estimated by using Fröhlich's equations [17] as well as graphical method (Figures 2 and 3). They are also shown in Table 2.

The dipole moments μ_1 and μ_2 of the flexible part as well as of the whole molecule are then estimated in terms of τ and slope β of the linear plot of K_{ij} against w_j (Figure 4). They are shown in Table 3 in order to compare with μ_0 due to τ_0 and μ_{theo} from bond angles and bond moments (Figure 5) respectively. The μ_1 's in terms of c_1 , c_2 and μ_2 are also calculated by assuming that the two relaxation processes are equally probable; and they are placed in the last column of Table 3 only to compare with μ_1 due to τ_1 .

2. Theoretical formulations to estimate τ_1 , τ_2 ; c_1, c_2 and μ_1, μ_2

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

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

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

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

and

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2}, \quad (3)$$

such that $c_1 + c_2 = 1$, where c_1 and c_2 are the relative contributions towards dielectric relaxations due to intra-molecular relaxation time τ_1 and molecular relaxation time τ_2 .

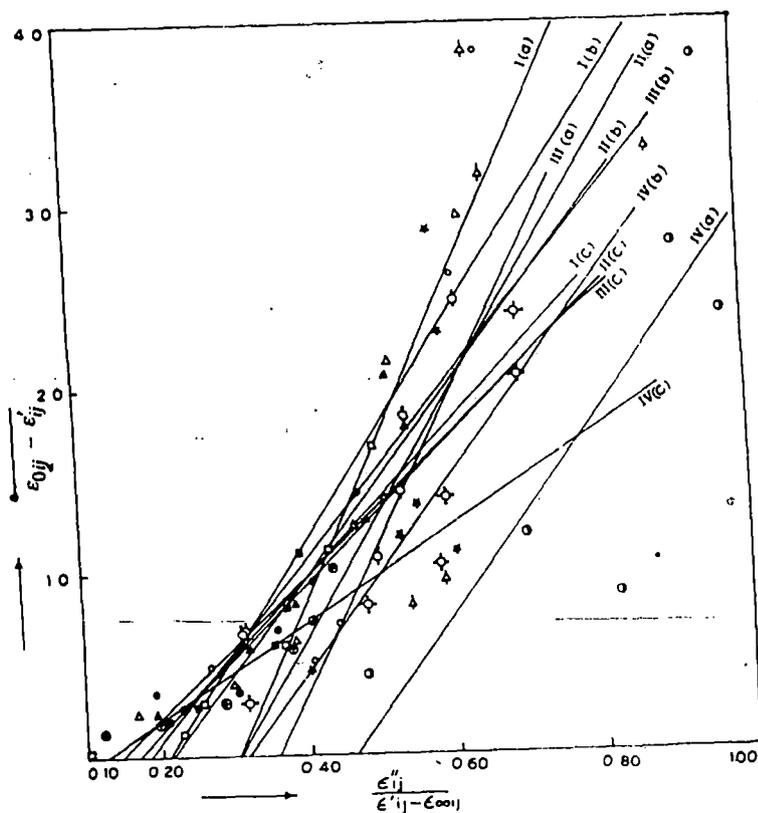


Figure 1. Straight line plots of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ against $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ of monoalcohols at 25°C under different uhf electric field.

- | | | |
|----------------|-------|------------------------------|
| System I (a) | —○—○— | for 1-Butanol at 24.33 GHz. |
| I (b) | —△—△— | for 1-Butanol at 9.25 GHz. |
| I (c) | —□—□— | for 1-Butanol at 3.00 GHz. |
| System II (a) | —▽—▽— | for 1-Hexanol at 24.33 GHz. |
| II (b) | —○—○— | for 1-Hexanol at 9.25 GHz. |
| II (c) | —●—●— | for 1-Hexanol at 3.00 GHz. |
| System III (a) | —*—*— | for 1-Heptanol at 24.33 GHz. |
| III (b) | —▲—▲— | for 1-Heptanol at 9.25 GHz. |
| III (c) | —■—■— | for 1-Heptanol at 3.00 GHz. |
| System IV (a) | —⊙—⊙— | for 1-Decanol at 24.33 GHz. |
| IV (b) | —⊗—⊗— | for 1-Decanol at 9.25 GHz. |
| IV (c) | —⊕—⊕— | for 1-Decanol at 3.00 GHz. |

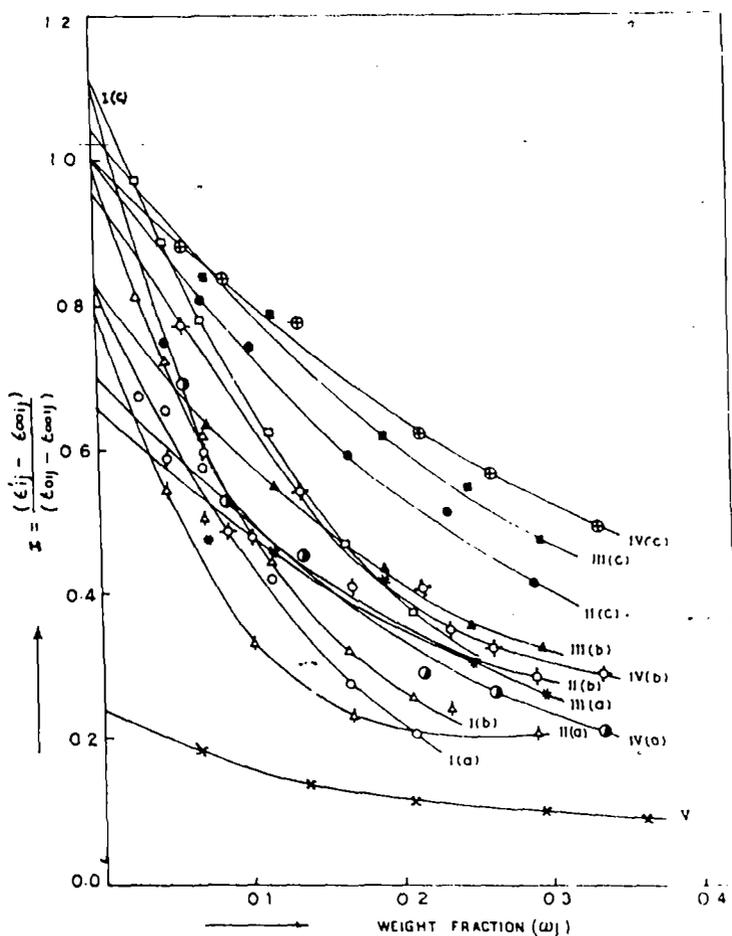


Figure 2. Variation of $(\epsilon'_{ij} - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction w_j for monoalcohols at different uhf electric field.

- | | | |
|----------------|-------|------------------------------|
| System I (a) | —○—○— | for 1-Butanol at 24.33 GHz. |
| I (b) | —△—△— | for 1-Butanol at 9.25 GHz. |
| I (c) | —□—□— | for 1-Butanol at 3.00 GHz. |
| System II (a) | —△—△— | for 1-Hexanol at 24.33 GHz. |
| II (b) | —○—○— | for 1-Hexanol at 9.25 GHz. |
| II (c) | —●—●— | for 1-Hexanol at 3.00 GHz. |
| System III (a) | —*—*— | for 1-Heptanol at 24.33 GHz. |
| III (b) | —▲—▲— | for 1-Heptanol at 9.25 GHz. |
| III (c) | —■—■— | for 1-Heptanol at 3.00 GHz. |
| System IV (a) | —●—●— | for 1-Decanol at 24.33 GHz. |
| IV (b) | —○—○— | for 1-Decanol at 9.25 GHz. |
| IV (c) | —⊕—⊕— | for 1-Decanol at 3.00 GHz. |
| System V | —x—x— | for 1-Ethanol at 9.84 GHz. |

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

$a = \frac{1}{1 + \alpha^2}$ and $b = \frac{\alpha}{1 + \alpha^2}$, the above eqs. (2) and (3) can be written as

$$x = c_1 a_1 + c_2 a_2, \quad (4)$$

$$y = c_1 b_1 + c_2 b_2, \quad (5)$$

where suffices 1 and 2 with a and b are related to τ_1 and τ_2 respectively. From eqs. (4) and (5), since $\alpha_2 - \alpha_1 \neq 0$ and $\alpha_2 > \alpha_1$ we have

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad (6)$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad (7)$$

Now, using $c_1 + c_2 = 1$, one gets the following equation with the help of eqs. (6) and (7):

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

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

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2. \quad (8)$$

Equation (8) is a straight line between $\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}}$ and $\frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}}$ with slope $\omega(\tau_1 + \tau_2)$

and intercept $-\omega^2 \tau_1 \tau_2$ respectively. Here, ω = angular frequency of the applied electric field of frequency f in GHz. When the eq. (8) is fitted with the measured dielectric relaxation data $\epsilon'_{ij}, \epsilon''_{ij}, \epsilon_{0ij}$ and $\epsilon_{\infty ij}$ for different weight fractions w_j 's of each alcohol in n-heptane (at 25°C under 24.33, 9.25 and 3.00 GHz electric fields) as well as of methanol and ethanol in benzene (at 9.84 GHz), we get the slopes and intercepts as shown in Table 1, to yield τ_1 and τ_2 .

The relative contributions c_1 and c_2 towards the dielectric relaxations in terms of x, y and τ_1, τ_2 for each alcohol are found out and shown in Table 2. The theoretical values of x and y are, however, calculated from Fröhlich's equations [17] as

$$x = \frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left(\frac{e^{2A} \omega^2 \tau_s^2 + 1}{1 + \omega^2 \tau_s^2} \right), \quad (9)$$

$$\text{and } y = \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} \left[\tan^{-1}(e^A \omega \tau_s) - \tan^{-1}(\omega \tau_s) \right]. \quad (10)$$

Table 3. The estimated intercept (α) and slope (β) of $K_{ij} - w_j$ equation with correlation coefficient (r) and percentage of error, dimensionless parameters β 's and dipole moments μ_j 's with theoretical μ 's and μ calculated by using the relation $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$ at 25°C of monoalcohols under different hf electric field

System with Sl no. and Mol. wt. of solute	Frequency f in GHz	Intercept and slope of $K_{ij} - w_j$ eqn.		Correlation coeff. (r)	% of error in regre. tech.	Dimensionless parameters			Estimated dipole moments in Debye				
		$\alpha \times 10^{-10}$ in e.s.u.	$\beta \times 10^{-10}$ in e.s.u.			$b_0 = \frac{1}{1 + \omega^2 \tau_0^2}$	$b_2 = \frac{1}{1 + \omega^2 \tau_2^2}$	$b_1 = \frac{1}{1 + \omega^2 \tau_1^2}$	μ_0	μ_2	μ_1	μ_{theor}	$\mu_1 = \mu_2 \left(\frac{c_1}{c_2} \right)^{1/2}$
I) 1-Butanol in n-heptane $M_j = 74$ gm	(a) 24.33	2.3523	1.2679	0.9978	0.12	0.2777	0.0142	0.9115	1.97	8.75	1.09		3.70
	(b) 9.25	0.8941	0.5400	0.9997	0.01	0.4382	0.0278	0.9552	1.66	6.62	1.13	1.49	3.43
	(c) 3.00	0.2887	0.2338	0.9999	0.00	0.5942	0.0593	0.9715	1.65	5.23	1.29		3.37
II) 1-Hexanol in n-heptane $M_j = 102$ gm	(a) 24.33	2.3522	0.8192	0.9961	0.21	0.3279	0.0239	0.9066	1.72	6.36	1.03		3.06
	(b) 9.25	0.8929	0.4005	0.9997	0.01	0.4804	0.0392	0.9545	1.61	5.63	1.14	1.31	3.18
	(c) 3.00	0.2889	0.1695	0.9999	0.00	0.6006	0.0633	0.9710	1.64	5.06	1.29		3.31
III) 1-Heptanol in n-heptane $M_j = 116$ gm	(a) 24.33	2.3169	0.8276	0.9927	0.40	0.2611	0.0169	0.8788	2.06	8.10	1.12		3.54
	(b) 9.25	0.8973	0.3555	0.9993	0.04	0.5196	0.0412	0.9646	1.55	5.52	1.14	1.22	3.20
	(c) 3.00	0.2891	0.1519	0.9997	0.01	0.5946	0.0607	0.9708	1.67	5.22	1.30		3.38
IV) 1-Decanol in n-heptane $M_j = 158$ gm	(a) 24.33	2.3575	0.5787	1.0002	0.01	0.2870	0.0396	0.7973	1.92	5.17	1.15		2.76
	(b) 9.25	0.8949	0.2609	0.9966	0.18	0.3885	0.0411	0.9040	1.79	5.52	1.18	0.95	3.04
	(c) 3.00	0.2894	0.1151	0.9997	0.01	0.7509	0.1327	0.9834	1.51	3.58	1.32		2.92
V) Ethanol in benzene $M_j = 46$ gm	9.84	1.1925	0.1977	0.9927	0.44	0.1831	0.00001	0.9997	1.19	147.19	0.51	1.57	14.50
VI) Methanol in benzene $M_j = 32$ gm	9.84	1.2058	0.2161	0.9928	0.43	—	0.00002	—	—	88.17	—	1.76	—

Double relaxation of straight chain alcohols etc

where $A = \text{Fröhlich parameter} = \ln(\tau_2/\tau_1)$ and τ_s is called the small limiting relaxation time being given by $\tau_s = \tau_1$. A simple graphical extrapolation technique, on the other hand, has been adopted here to get the values of x and y at $w_j \rightarrow 0$, as illustrated graphically in Figures 2 and 3 respectively. This is really in accord with Bergmann's eqs. (2) and (3) when the once estimated τ_1 and τ_2 from eq. (8) are substituted in the right hand sides of the above eqs. (2) and (3).

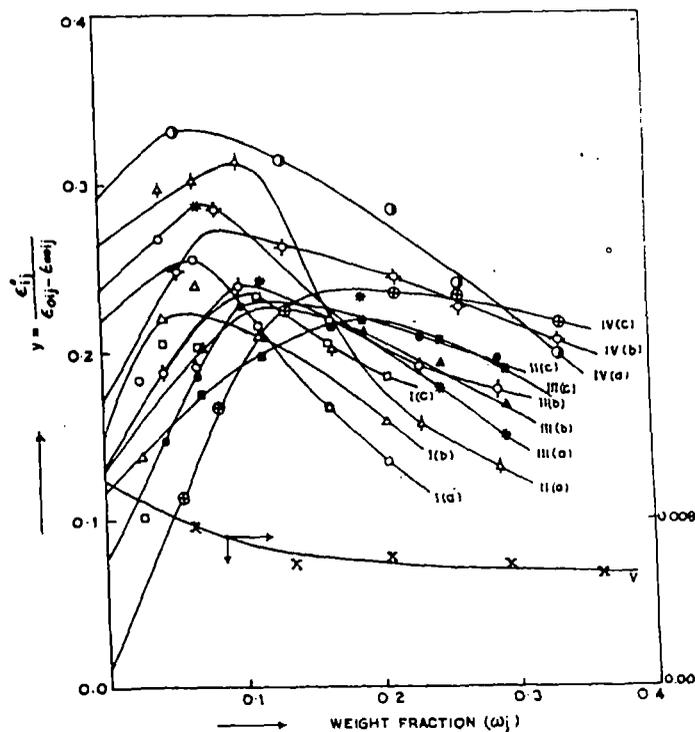


Figure 3. Variation of $\epsilon''_{ij}/(\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction w_j for monoalcohols at different uhf electric field.

System I (a)	—○—○—	for 1-Butanol at 24.33 GHz.
I (b)	-Δ-Δ-	for 1-Butanol at 9.25 GHz.
I (c)	—()—()—	for 1-Butanol at 3.00 GHz.
System II (a)	—△—△—	for 1-Hexanol at 24.33 GHz.
II (b)	—○—○—	for 1-Hexanol at 9.25 GHz.
II (c)	—●—●—	for 1-Hexanol at 3.00 GHz.
System III (a)	—*—*—	for 1-Heptanol at 24.33 GHz.
III (b)	—▲—▲—	for 1-Heptanol at 9.25 GHz.
III (c)	—■—■—	for 1-Heptanol at 3.00 GHz.
System IV (a)	—⊙—⊙—	for 1-Decanol at 24.33 GHz.
IV (b)	—⊕—⊕—	for 1-Decanol at 9.25 GHz.
IV (c)	—⊗—⊗—	for 1-Decanol at 3.00 GHz.
System V	—x—x—	for 1-Ethanol at 9.84 GHz.

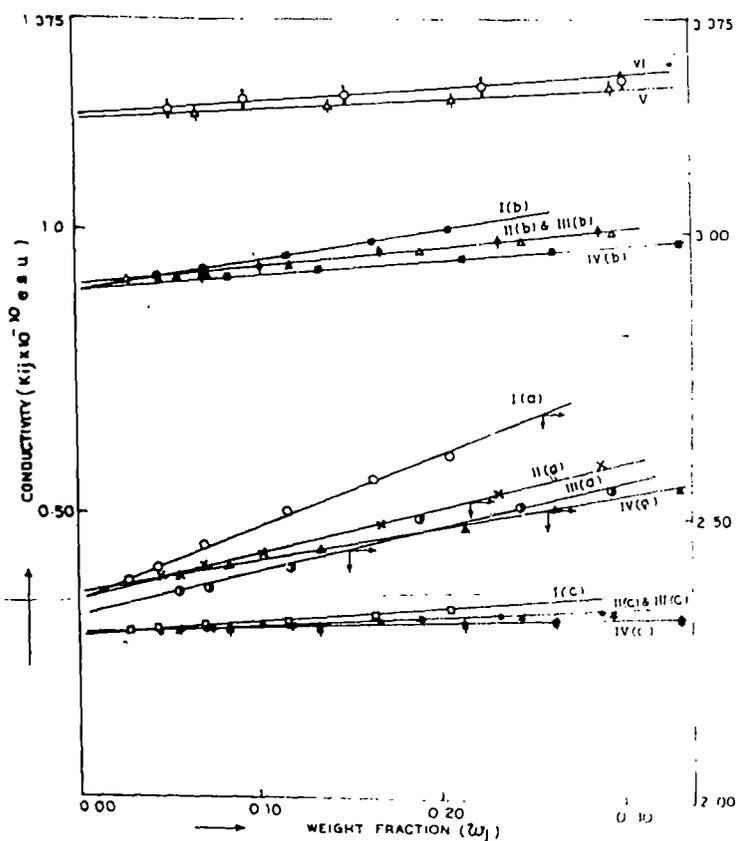


Figure 4. Straight line plots of K_j against w_1 under different ω_j electric field at 25°C

System I (a)	—○—○—	for 1-Butanol at 24.33 GHz
I (b)	—●—●—	for 1-Butanol at 9.25 GHz
I (c)	—△—△—	for 1-Butanol at 3.00 GHz
System II (a)	—×—×—	for 1-Hexanol at 24.33 GHz
II (b)	—●—●—	for 1-Hexanol at 9.25 GHz
II (c)	—●—●—	for 1-Hexanol at 3.00 GHz
System III (a)	—○—○—	for 1-Heptanol at 24.33 GHz
III (b)	—△—△—	for 1-Heptanol at 9.25 GHz
III (c)	—*—*—	for 1-Heptanol at 3.00 GHz
System IV (a)	—▲—▲—	for 1-Decanol at 24.33 GHz
IV (b)	—■—■—	for 1-Decanol at 9.25 GHz
IV (c)	—■—■—	for 1-Decanol at 3.00 GHz
System V	—△—△—	for Ethanol at 9.84 GHz
System VI	—○—○—	for Methanol at 9.84 GHz

The dipole moments μ_1 and μ_2 of polar solutes in terms of τ_1 and τ_2 as obtained from the double relaxation method and slope β of the concentration variation of the experimental

uhf conductivity K_{ij} are then estimated. The uhf conductivity K_{ij} is, however, given by Murphy and Morgan [19] as

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon_{ij}''^2 + \epsilon_{ij}'^2)^{1/2}, \quad (11)$$

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

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) w_j. \quad (12)$$

Differentiating the above eq. (12) with respect to w_j and for $w_j \rightarrow 0$, the eq. (12) reduces to

$$\left(\frac{dK'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right), \quad (13)$$

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 $F_{ij} = \frac{1}{3}(\epsilon_{ij} + 2)^2$ becomes $F_i = \frac{1}{3}(\epsilon_i + 2)^2$ and the density $\rho_{ij} \rightarrow \rho_i$ the density of solvent at $w_j \rightarrow 0$.

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

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

$$\text{or,} \quad \left(\frac{dK'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega \tau \left(\frac{dK_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \omega \tau \beta, \quad (14)$$

where β is the slope of $K_{ij} - w_j$ curve at infinite dilution. From eqs. (13) and (14) we thus get

$$\mu_j = \left(\frac{3M_j k T \beta}{N \rho_i F_i \omega b} \right)^{1/2} \quad (15)$$

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

$$b = \frac{1}{1 + \omega^2 \tau^2}. \quad (16)$$

The computed μ_1, μ_2 and μ_0 together with b_1, b_2 and b_0 and β 's of $K_{ij} - w_j$ equations for all the alcohols are given in Table 3.

3. Results and discussions

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

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

and

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

The experimental data of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{0ij})$ for methanol and ethanol are so high that they can not be plotted in Figure 1. In absence of reliable values of ϵ_{0ij} and $\epsilon_{\infty ij}$ for methanol, it is not possible to show the applicability of simple mixing rule in determining relaxation data for this system. But the method has been applied to ethanol and it is found that the τ value is 3207.57 p Sec which is in good agreement with the measured data as presented in Table 1. The weight fractions w_j 's of the respective solutes have been obtained from mole fractions x_i and x_j of the solvent and solute of molecular weights M_i and M_j respectively by a relation [21]

$$w_j = \frac{x_j M_j}{x_i M_i + x_j M_j} \quad (17)$$

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

τ_2 and τ_1 for each alcohol are estimated from the slope and the intercept of straight line eq. (8) and are placed in the 7-th and the 8-th columns of Table 1 respectively. All the monoalcohols show τ_2 and τ_1 at all the frequencies with an exception for methanol which exhibits the monorelaxation behaviour [12].

The monorelaxation behaviour [12] can easily be evaluated on the basis of the relaxation parameters by putting $c_1 = 0$ in eqs. (2) and (3). The resulting equation becomes :

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega \tau_2 \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} \quad (18)$$

τ_2 for methanol is found to be 5254.3 p Sec in approximate agreement with τ_2 as obtained by double relaxation method (Table 1). τ_2 's and τ_1 's as obtained from the double relaxation method are then compared with the most probable relaxation time τ_0 where $\tau_0 = \sqrt{\tau_1 \tau_2}$ and the measured relaxation time τ_s 's from the slope of the given relation :

$$K''_{ij} = K_{\infty ij} + \frac{1}{\omega \tau_s} K'_{ij}, \quad (19)$$

where $K_{\infty ij}$ is the constant conductivity at infinite dilution. Both τ_0 and τ_s are shown in the 10-th and the 9-th columns of Table 1, respectively. τ_2 and τ_1 for the double relaxation processes show low values at 24.33 GHz and increase gradually at the lower frequencies of

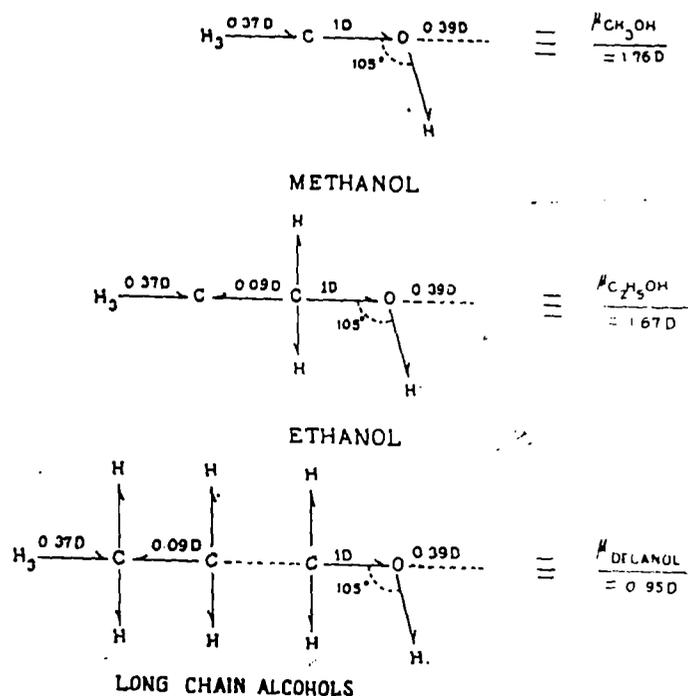


Figure 5. Conformational structures of methanol, ethanol and decanol.

9.25 and 3.00 GHz respectively. This is explained on the basis of the fact that at higher frequency, the rate of hydrogen bond rupture in long chain alcohols may be maximum to reduce τ for each rotating unit. This sort of behaviour is also observed in the estimated τ_s and τ_0 respectively. Although, the measured τ_s and τ_0 are smaller in magnitudes, τ_1 agrees excellently with τ_s (Table 1). This is perhaps due to the fact that the hf conductivity measurement always yields the average microscopic relaxation time whereas the double relaxation phenomena offers a better understanding of microscopic as well as macroscopic molecular relaxation times.

The relative contributions c_1 and c_2 towards dielectric relaxations for each alcohol have been evaluated from Bergmann's eqs. (2) and (3) for fixed values of τ_1 and τ_2 as predicted by eq. (8), with the estimated x and y from graphical technique as well as from Fröhlich's eqs. (9) and (10) respectively. c_1 and c_2 thus obtained by Fröhlich's method are placed in the 6-th and 7-th columns of Table 2. In the 10-th and the 11-th columns of the same Table 2 are shown c_1 and c_2 values with the fixed values of x and y at infinite dilutions of Figures 2 and 3. The variations of x and y with w_j are concave and convex in nature as illustrated graphically in Figures 2 and 3 in accordance with Bergmann's eqs. (2) and (3) respectively. Ethanol is an exception whose y value changes in a similar way as x . This anomaly is perhaps due to nonavailability of the accurate ϵ_{0ij} and $\epsilon_{\infty ij}$ [11], and it thereby yields abnormally high τ value like methanol, although the latter one exhibits monorelaxation behaviours as shown in Table 1. However, the estimated value of c_2 is greater than c_1 for each alcohol, under investigation, in Fröhlich's method, while the reverse is true for the graphical method. Eventually, c_2 is -ve for most of the cases except 1-hexanol at 24.33 GHz and ethanol at 9.84 GHz respectively in the latter case. This -ve value of c_2 is due to inertia of the flexible part [10]. This type of behaviour may be explained on the basis of the fact that the latter one ascertains the nature of the flexible part in comparison to Fröhlich's method. It is also interesting to note that unlike Fröhlich's method, the latter method yields $c_1 + c_2 < 1$ except for 1-decanol at 24.33 GHz where $c_1 + c_2 < 0$, although $|c_1 + c_2| > 1$ signifying more than two relaxation processes may be possible in them [14].

The dipole moments μ_1 and μ_2 of all the alcohols, as enlisted in Table 3, were estimated in terms of dimensionless parameters b_1 and b_2 and slopes β of K_{ij} versus w_j equations by using eq. (15). The linear variation of uhf conductivities K_{ij} of all the alcohols as a function of w_j 's are shown in Figure 4. The correlation coefficient r and the corresponding percentage of error in the estimation of the slope β and hence all the μ 's together with b 's are shown in Table 3. From Table 3, μ_2 's are, however, found to be large at 24.33 GHz while in comparatively lower frequencies like 9.25 and 3.00 GHz, they are gradually smaller for each polar alcohol under our investigation. But μ_1 's, on the other hand, show the opposite trend. It is also interesting to note that the values of μ_2 's for all the alcohols decrease with the increase of C-atoms in them. This type of behaviour may be explained by the fact that the long chain polymer type molecules having a large number of carbon atoms, in a nonpolar solvent, tend to break up in the hf electric field in order to reduce or even eliminate the absorption attributable to them. The proportion of smaller molecular species, on the other hand, have comparatively smaller number of C-atoms and the corresponding absorption will increase [14]. This is also confirmed by the fact that as τ decreases with increasing ω , the term $\omega^2\tau^2$ is higher and therefore, eq. (16) yields smaller b values to increase μ 's according to eq. (15).

μ_1 , μ_2 and μ_0 are finally compared with μ_{theo} for the orientational polarisation of all the associated liquids containing a large number of dipolar groups like $\text{H}_3\rightarrow\text{C}$, $\text{C}\leftarrow\text{O}$ and $\text{O}\leftarrow\text{H}$ when their individual monomeric moments are added vectorially as shown in Figure 5. μ_{theo} may also be inferred from Fröhlich's equation having correlation factor which bears structural information for such liquids. But to a fair approximation, the structural conformation of such liquids, as shown diagrammatically in Figure 5 and placed in Table 3, from the bond moments of $\text{H}_3\rightarrow\text{C}$, $\text{C}\leftarrow\text{O}$ and $\text{O}\leftarrow\text{H}$ and the bond angle of 105° made by $-\text{OH}$ groups with the main bond axis, have the major contributions in yielding the theoretical dipole moment, μ_{theo} . All the μ 's are displayed in Table 3 with those of μ_1 , where $\mu_1 = \mu_2 \left(\frac{c_1}{c_2} \right)^{1/2}$, assuming the two relaxation processes are equally probable. These μ_1 's are slightly larger in magnitudes in comparison to μ_{theo} , μ_1 and μ_0 which are in close agreement among themselves.

4. Conclusion

The methodology so far advanced for double and single broad dispersions of the polar-nonpolar liquid mixtures seems to be much simpler, straightforward and significant one to detect the existence of double and monorelaxation behaviours of polar liquids in nonpolar solvents. The correlation coefficients between the desired parameters as given in eqs. (8) and (18) could, however, be estimated to find out the percentage of errors entered in the dielectric relaxation data, to yield τ_1 and τ_2 of the polar liquids, because the relaxation times τ 's are claimed to be accurate within $\pm 10\%$. The monohydric alcohols so far studied always yield, both τ_1 and τ_2 at all frequencies of the electric field. The corresponding dipole moments μ_1 and μ_2 can then be estimated from eq. (15) in terms of b_1 and b_2 (which are, however, related to τ_1 and τ_2 as estimated) to arrive at their conformations as shown in Figure 5.

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Appendix

List of nomenclature used :

- $\epsilon'_{ij}, \epsilon''_{ij}$ real and imaginary parts of the complex dielectric constant ϵ_{ij}^* of a solution,
- $\epsilon_{ij}^* = \epsilon'_{ij} - j\epsilon''_{ij}$ where $j = \sqrt{-1}$ is a complex number,
- $\epsilon_{0ij}, \epsilon_{\infty ij}$ static and optical dielectric constants of the solution,
- $\omega = 2\pi f$ angular frequency of the applied electric field, f being the frequency in Hertz,
- K'_{ij}, K''_{ij} real and imaginary parts of the complex electrical conductivity K_{ij}^* of a solution,
- $K_{ij}^* = K'_{ij} + jK''_{ij}$ where $j = \sqrt{-1}$ is a complex number,
- $K_{\infty ij}$ constant conductivity of the solution at $\omega \rightarrow 0$,
- μ_j dipole moment of the j -th type of solute,
- μ_1, μ_2 dipole moments of the flexible part and the whole molecule,
- τ_j relaxation time of the solute,
- τ_1, τ_2 relaxation times of the flexible part and the whole molecule,

τ_0	most probable relaxation time of the solute,
$A = \ln(\tau_2/\tau_1)$	the Fröhlich parameter,
w_j	weight fraction of the solute,
c_1, c_2	relative contributions due to τ_1 and τ_2 respectively,
M_j	molecular weight of the j -th type of solute,
β	slope of the $K_{ij} - w_j$ curve.

Double relaxations of some isomeric octyl alcohols by high frequency absorption in non-polar solvent

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The double relaxation behaviour of some isomeric octyl alcohols in n-heptane at 25°C under the electric field frequencies of 24.33, 9.25 and 3.00 GHz is studied to get the relaxation times τ_1 and τ_2 for their flexible parts of whole molecules by a method of single frequency measurements of dielectric relaxation parameters. The isomers are long, straight chain, hydrogen bonded, polymer type molecules having methyl and hydroxyl groups attached to their C-atoms which may bend, twist or rotate internally under HF electric field each with a characteristic τ . The relative contributions c_1 and c_2 towards dielectric relaxations due to τ_1 and τ_2 are also estimated by using Fröhlich's equations and the graphical technique. The dipole moments μ_1 and μ_2 in terms of τ_1 and τ_2 of flexible part and the whole molecules are again found out from slope β of the total HF conductivity K''_1 as a function of weight fractions w_1 's of the solute indicating μ_1 for the rotation of their -OH groups about C-C bonds only. μ_1 and μ_2 are finally compared with the theoretical dipole moments μ_{theor} arising out of the structures with bond-angles and bond-moments of their substituent groups to establish the conformations of these isomers are justified like normal alcohols observed earlier.

Table 1—The estimated relaxation times τ_2 and τ_1 from the slope and the intercept of straight line Eq. 8 with errors and correlation coefficient (r) together with measured τ_1 from $K''_1 - K''_0$ curve and most probable relaxation time $\tau_0 = \tau_1 \tau_2$ for six isomeric octyl alcohols at 25°C under different frequencies of electric fields

System with Sl. No. & Mol. wt M_1	Frequency in GHz	Intercept & slope of Eq. (8)	Correlation coefficient (r)	% Error in regression technique	Estimated values of τ_2 & τ_1 in p. Sec.	Measured τ_1 in p. Sec.	Most probable relaxation time $\tau_0 = \tau_1 \tau_2$ in p. Sec.
I) 1/2-methyl-3-heptanol in n-heptane $M_1 = 130$ gm.	(a) 24.33	2.3718	0.9011	25.86	29.96	3.39	1.84
	(b) 9.25	0.6871	0.9700	1.90	49.61	4.10	3.58
	(c) 3.00	0.1408	0.9771	1.50	73.31	5.41	6.74
II) 3-methyl-3-heptanol in n-heptane $M_1 = 130$ gm.	(a) 24.33	0.9087	0.9294	4.59	14.52	2.68	2.19
	(b) 9.25	0.6389	0.9709	1.93	43.34	4.37	3.70
	(c) 3.00	0.1611	0.9985	0.10	73.55	6.17	5.58
III) 4-methyl-3-heptanol in n-heptane $M_1 = 130$ gm.	(a) 24.33	1.9653	0.8851	7.30	25.40	3.51	1.90
	(b) 9.25	0.6411	0.9682	2.11	43.08	4.21	1.13
	(c) 3.00	0.2008	0.9206	5.14	84.34	6.71	11.98
IV) 5-methyl-3-heptanol in n-heptane $M_1 = 130$ gm.	(a) 24.33	0.6929	0.5684	26.36	17.83	1.67	1.71
	(b) 9.25	0.7445	0.9846	1.19	52.16	4.21	5.39
	(c) 3.00	0.2362	0.9371	4.74	101.22	6.58	13.11
V) 4-Octanol in n-heptane $M_1 = 130$ gm.	(a) 24.33	0.9572	0.8569	10.34	20.77	1.97	1.83
	(b) 9.25	0.3810	0.9470	4.02	42.74	2.64	5.46
	(c) 3.00	0.1428	0.9846	1.18	85.13	4.72	12.76
VI) 2-Octanol in n-heptane $M_1 = 130$ gm.	(a) 24.33	1.3664	0.6336	23.60	30.30	1.89	1.83
	(b) 9.25	1.5853	0.9888	0.66	92.00	5.11	6.26
	(c) 3.00	0.4458	0.9780	1.69	160.41	7.83	18.70

Table 2—Fröhlich parameter A, relative contributions c_1 and c_2 due to τ_1 and τ_2 , theoretical values of α and β from Fröhlich's Eqs. 9 and 10 and from graphical extrapolation technique at $\omega \rightarrow 0$

System with Sl. No.	Frequency, GHz	Fröhlich parameter A in τ_1, τ_2	Theoretical values of α & β from Eqs. (9) and (10)	Theoretical values of c_1 & c_2	Estimated values of α & β at $\omega \rightarrow 0$	Estimated values of c_1 and c_2				
I) 1/2-methyl-3-heptanol in n-heptane	(a) 24.33	2.1790	0.3457	0.4028	0.3686	1.2101	0.765	0.366	1.0226	0.2476
	(b) 9.25	2.4932	0.5637	0.4023	0.4886	0.9434	1.075	0.39	0.673	0.2324
	(c) 3.00	2.6063	0.7973	0.3232	0.6144	0.5800	1.075	0.074	1.1133	0.0808
II) 3-methyl-3-heptanol in n-heptane	(a) 24.33	1.0797	0.5195	0.4490	0.4542	0.1733	0.885	0.52	0.33	0.3320
	(b) 9.25	2.2943	0.5792	0.4115	0.4922	0.8853	0.75	0.256	0.486	0.0810
	(c) 3.00	2.4781	0.7865	0.349	0.6028	0.5600	1.023	0.034	1.055	0.0579
III) 4-methyl-3-heptanol in n-heptane	(a) 24.33	2.0378	0.3747	0.4173	0.3857	1.0832	0.75	0.37	0.41	0.371

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n-heptane	(a) 24.33	2.3710	0.5775	0.4075	0.4932	0.8812	0.95	0.208	1.0177	-0.0805
	(b) 9.25	2.313	0.7543	0.3490	0.5902	0.6112	1.015	0.094	1.1753	-0.0577
	(c) 3.00	2.313	0.7543	0.3490	0.5902	0.6112	1.015	0.094	1.1753	-0.0577
2-methyl-3-heptanol	(a) 24.33	1.741	0.5644	0.4088	0.4862	0.9057	0.645	0.274	0.6389	0.3763
n-heptane	(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	1.1376	-0.2341
4-octanol in n-heptane	(a) 24.33	2.3555	0.6020	0.4731	0.4553	1.0030	0.72	0.22	0.7840	0.0126
	(b) 9.25	2.3555	0.6020	0.4731	0.4553	1.0030	0.72	0.22	0.7840	0.0126
	(c) 3.00	2.8924	0.7813	0.3197	0.6210	0.5900	0.99	0.052	1.0218	-0.0850
1) V/2-octanol in n-heptane	(a) 24.33	2.7964	0.4507	0.3967	0.4257	1.3507	0.67	0.208	0.7223	0.0764
	(b) 9.25	2.7925	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

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Table 3—Estimated intercept and slope of $K_{ij} - \omega$ equation, dimensionless parameters b_2, b_1 (eq. (16)), estimated dipole moments μ_1, μ_2 (eq. (15)), $\mu_{D_{max}}$ from bond angles and bond moments together with μ_1 from $\mu_1 = \mu_1(c_1/c_2)^{1/2}$ in Debye

System with SI. No. Mol. Wt.	Frequency GHz	Intercept & slope of $K_{ij} - \omega$ equation		Dimensionless parameter		Estimated dipole moments (in Debye)		Estimated μ_1 in D from $\mu_1 = \mu_1(c_1/c_2)^{1/2}$
		$\alpha \times 10^{-10}$	$\beta \times 10^{-10}$	b_2	b_1	μ_2	μ_1	
1) 1/2-methyl-3-heptanol in n-heptane $M_1 = 130$ gm	(a) 24.33	2.3632	0.6974	0.0455	0.7885	4.80	1.15	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
2) II/3-methyl-3-heptanol in n-heptane $M_1 = 130$ gm	(a) 24.33	2.3630	0.7490	0.1689	0.8564	2.58	1.15	1.98
	(b) 9.25	0.8959	0.3554	0.1363	0.9395	3.21	1.22	1.76
	(c) 3.00	0.2910	0.1310	0.1425	0.9897	2.18	1.24	2.20
3) III/4-methyl-3-heptanol in n-heptane $M_1 = 130$ gm	(a) 24.33	2.3635	0.7213	0.123	0.7963	4.17	1.17	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
4) IV/5-methyl-3-heptanol in n-heptane $M_1 = 130$ gm	(a) 24.33	2.3646	0.6415	0.1187	0.9396	2.85	1.01	2.09
	(b) 9.25	0.9021	0.2771	0.0975	0.9436	3.35	1.08	1.76
	(c) 3.00	0.2922	0.1138	0.2157	0.9849	2.54	1.19	2.34
5) V/4-octanol in n-heptane $M_1 = 130$ gm	(a) 24.33	2.3561	0.6492	0.0903	0.9169	3.29	1.03	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
6) VI/2-octanol in heptane $M_1 = 130$ gm	(a) 24.33	2.3533	0.6572	0.0912	0.9230	4.80	1.03	2.69
	(b) 9.25	0.8980	0.2753	0.138	0.9190	5.67	1.09	1.08
	(c) 3.00	0.2897	0.1221	0.0977	0.9787	3.88	1.23	2.89

PL. write 4.80

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PL. Print 1.08

Fig. 1—Plot of $(\epsilon_{ij} - \epsilon_{ij}) / (\epsilon_{ij} - \epsilon_{ij})$ against $c_1 / (c_1 - c_2)$ of some isomeric octyl alcohols in n-heptane at 25°C. Curves of I (a), I (b), I (c) for 2-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (O, Δ, □). Curves of II (a), II (b), II (c) for 3-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (●, ▲, ■). Curves of III (a), III (b), III (c) for 4-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (○, ⊙, ⊚). Curves of IV(a), IV (b), IV (c) for 5-methyl-3-heptanol at 24.33, 9.25, 3.00 GHz (⊕, ⊙, ⊚). Curves of V (a), V (b), V (c) for 4-octanol at 24.33, 9.25 and 3.00 GHz (⊖, ⊙, ⊚). Curves of VI (a), VI (b), VI (c) for 2-octanol at 24.33, 9.25 and 3.00 GHz (⊗, ⊙, ⊚).

Fig. 2—Plot of $(\epsilon_{ij} - \epsilon_{ij}) / (\epsilon_{ij} - \epsilon_{ij})$ against weight fraction w_1 of some isomeric octyl alcohols in n-heptane at 25°C. Curves of I (a), I (b), I (c) for 2-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (O, Δ, □). Curves of II (a), II (b), II (c) for 3-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (●, ▲, ■). Curves of III (a), III (b), III (c) for 4-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (○, ⊙, ⊚). Curves of IV(a), IV (b), IV (c) for 5-methyl-3-heptanol at 24.33, 9.25, 3.00 GHz (⊕, ⊙, ⊚). Curves of V (a), V (b), V (c) for 4-octanol at 24.33, 9.25 and 3.00 GHz (⊖, ⊙, ⊚). Curves of VI (a), VI (b), VI (c) for 2-octanol at 24.33, 9.25 and 3.00 GHz (⊗, ⊙, ⊚).

Fig. 3—Plot of $\epsilon_{ij} / (\epsilon_{ij} - \epsilon_{ij})$ against weight fraction w_1 of some isomeric octyl alcohols in n-heptane at 25°C. Curves of I (a), I (b), I (c) for 2-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (O, Δ, □). Curves of II (a), II (b), II (c) for 3-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (●, ▲, ■). Curves of III (a), III (b), III (c) for 4-methyl-3-heptanol at 24.33, 9.25 and 3.00 GHz (○, ⊙, ⊚). Curves of IV(a), IV (b), IV (c) for 5-methyl-3-heptanol at 24.33, 9.25, 3.00 GHz (⊕, ⊙, ⊚). Curves of V (a), V (b), V (c) for 4-octanol at 24.33, 9.25 and 3.00 GHz (⊖, ⊙, ⊚). Curves of VI (a), VI (b), VI (c) for 2-octanol at 24.33, 9.25 and 3.00 GHz (⊗, ⊙, ⊚).

Fig. 4—Conformations of some isomeric octyl alcohols

1 Introduction

The dielectric relaxation of a polar-nonpolar liquid mixture is a very convenient and useful tool in ascertaining the shape, size and structure of a polar molecule¹. 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 non-polar solvent under different high frequency (hf) electric field of Giga hertz (GHz) range at a fixed or different temperature. There exist several methods² to estimate τ of a polar liquid in a non-polar 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. Budo³, 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 hand drawn through the points on the curve (with 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_1 , c_2 at different frequencies of the electric field.

A procedure was devised⁶ 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 $\epsilon_{\omega ij}$, $\epsilon_{\omega ij}$, ϵ''_{ij} and ϵ''_{ij} for different weight fractions ω_j of a polar solute (j) in a non-polar solvent (i) at a given temperature. The technique had already been applied on disubstituted benzenes and anilines⁶ at 9.945 GHz electric field as well as mono-substituted anilines⁷ 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 hf 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 τ^2 . 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 frequen-

cy dependence of double relaxation behaviour of four long chain normal aliphatic alcohols like 1-butanol, 1-hexanol, 1-decanol in solvent n-heptane¹⁰ including methanol and ethanol at 9.84 GHz in benzene^{11,12} at 25°C was already made¹³. 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 method⁶ 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} , $\epsilon_{\omega ij}$ and $\epsilon_{\omega ij}$ measured by Crossley *et al.*¹⁴ in n-heptane at 25°C. The straight line equations between $(\epsilon_{\omega ij} - \epsilon''_{ij})/(\epsilon''_{ij} - \epsilon_{\omega ij})$ and $(\epsilon''_{ij} - \epsilon_{\omega ij})/(\epsilon''_{ij} - \epsilon_{\omega ij})$ for all the octyl alcohols at different ω_j 's are linear as shown in Fig. 1 only to establish the applicability of Debye model in such isomeric alcohols like normal alcohols¹³ once again. Moreover, all the long chain octyl alcohols are structural isomers with the molecular formulae $C_{11}H_{24}O$ 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 state¹⁵.

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 alcohols¹³. The measured τ_1 from the slope of the linear equation (equation of imaginary ϵ''_{ij} parts 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 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 (Figs 2 and 3). The estimated c_1 and c_2 are placed in Table 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 ω_j are shown in Table 3. The slopes β and the intercepts α of the linear variation of K_{ij} with ω_j , as placed in Table 3, at each frequency for all the isomers in n-heptane are almost the same probably due to their same polarity¹⁶. This fact is also supported by their conformations as shown in Fig. 4. It was, therefore, very difficult to plot K_{ij} against ω_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_{theor} , a special attention is to be paid on the conformational structure of each isomer from the available bond angles and bond moments. They are shown in Fig. 4. Using the usual C-C bond moment of 0.09 D from methanol and ethanol¹⁷ μ_{theor} for four methyl substituted octanols are found to show slightly larger values (see Fig. 4 and Table 3) than 1-heptanol¹¹ except the desired values for 2-octanol and 4-octanol perhaps due to bond moments of C-CH₃ and -O-H groups in their structures. The calculated value of μ_1 from $\mu_1 = \mu_2 c_1 / c_2$ ¹⁸ assuming two relaxation processes are equally probable, are also placed in the last column of Table 3 with all the estimated μ 's for comparison.

n-heptane

give space

$\epsilon''_{ij}/(\epsilon''_{ij} - \epsilon_{\omega ij})$

plotting of K_{ij}

of τ_1 and τ_2

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's¹ relation.

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

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 processes. When the ϵ_{ij}^* consists of two Debye type dispersions, Budo's relation reduces to Bergmann's equations²:

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

and

$$\frac{\epsilon_{ij}^*}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (3)$$

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

$$\frac{\epsilon_{ij}^* - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = x, \quad \frac{\epsilon_{ij}^*}{\epsilon_{0ij} - \epsilon_{\infty ij}} = y \rightarrow \epsilon_{ij}^* - \epsilon_{\infty ij}$$

$\omega\tau = a$ and using $a = 1/1 + a^2$ and $b = a/1 + a^2$ Eqs (2) and (3) can be written as

$$x = c_1 a^2 + c_2 a_2 \quad \dots (4)$$

$$y = c_1 b_1 + c_2 b_2 \quad \dots (5)$$

where suffixes 1 and 2 with a and b are related to τ_1 and τ_2 respectively. From Eqs (4) and (5), since $a_2 = a_1 \neq 0$ and $a_2 > a_1$, we have

$$c_1 = \frac{(x a_2 - y)(1 + a_1^2)}{a_2 - a_1} \quad \dots (6)$$

$$c_2 = \frac{(y - x a_1)(1 + a_2^2)}{a_2 - a_1} \quad \dots (7)$$

Since $c_1 + c_2 = 1$, we get the following equation with the help of Eqs (6) and (7):

$$\frac{1-x}{y} = (a_1 + a_2) - \frac{x}{y} a_1 a_2$$

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

$$\frac{\epsilon_{0ij} - \epsilon_{ij}^*}{\epsilon_{ij}^* - \epsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\epsilon_{ij}^*}{\epsilon_{ij}^* - \epsilon_{\infty ij}} - \omega^2\tau_1\tau_2 \quad (8)$$

Eq. (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 $-\omega\tau_1\tau_2$ respectively. 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_{0ij}^* , and $\epsilon_{\infty ij}$ 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 fields¹⁴ we get slope and intercept of Eq. (8) to yield τ_1 and τ_2 as shown in Table 1.

Pl. Print Table 1

The relative contributions c_1 and c_2 towards the dielectric relaxation in terms of x , y and τ_1 , τ_2 for each octyl alcohol are found out and placed in Table 2. The theoretical values¹⁵ of x and y are, however, calculated from Fröhlich's Eqs:

$$x = \frac{\epsilon_{ij}^* - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{A} \ln \left(\frac{e^{A\omega^2\tau_1^2} + 1}{1 + \omega^2\tau_1^2} \right) \quad (9)$$

$$y = \frac{\epsilon_{ij}^*}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} [\tan^{-1}(e^{A\omega\tau_1}) - \tan^{-1}(A\omega\tau_1)] \quad (10)$$

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 $\omega \rightarrow 0$ from Figs 2 and 3 respectively. This is really in accordance with Bergmann's Eqs (2) and (3) when the once estimated τ_1 and τ_2 from Eq. (8) are substituted in the right hand sides of above Eqs (2) and (3).

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 Morgan¹⁶:

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon_{ij}'' + \epsilon_{ij}''') \quad (11)$$

as a function of ω , of polar solute. Since $\tau_1 \ll \tau_2$ in the hf electric field, the term ϵ_{ij}'' offers resistance of polarisation. Thus the real part K_{ij}' of the hf K_{ij} of a polar-nonpolar liquid mixture at TK can be written according to Smyth¹⁷ as

$$K_{ij}' = \frac{\mu_j^2 N \rho_j F_j}{3M_j kT} \left(\frac{\omega^2\tau_j}{1 + \omega^2\tau_j^2} \right) \omega \quad (12)$$

which at $\omega \rightarrow 0$ yields that:

$$\left(\frac{dK_{ij}'}{d\omega} \right)_{\omega \rightarrow 0} = \frac{\mu_j^2 N \rho_j F_j}{3M_j kT} \left(\frac{\omega^2\tau_j}{1 + \omega^2\tau_j^2} \right) \quad (13)$$

where M_j is the molecular weight of a polar solute, N the Avogadro number, k the Boltzmann constant, the local field $F_j = 1/9 (\epsilon_{ij} + 2)^2$ (between $F_j = 1/9 (\epsilon_{ij} + 2)^2$ and the density $\rho_j = \rho$, the density of solvent at $\omega_j \rightarrow 0$).

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

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

or

$$\left(\frac{dK_{ij}'}{d\omega} \right)_{\omega \rightarrow 0} = \omega\tau \left(\frac{dK_{ij}''}{d\omega} \right)_{\omega \rightarrow 0} = \omega\tau\beta \quad (14)$$

where β is the slope of $K_{ij}'' = \omega$ curve at infinite dilution. From Eqs (13) and (14) we get:

$$\mu_j = \left[\frac{27M_j kT}{N\rho_j (\epsilon_{ij} + 2)^2} \cdot \beta \right]^{1/2} \quad (15)$$

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

$$b = \frac{1}{1 + \omega^2 \tau^2} \quad (16)$$

The computed μ_1 and μ_2 together with b_1 , b_2 and β of $K''_i - \omega_i$ equations for all the octyl alcohols are placed in Table 3.

3 Results and Discussion

The least square fitted straight line equations of $(\epsilon_{\infty i} - \epsilon''_i)/(\epsilon''_i - \epsilon_{\infty i})$ against $\epsilon''_i/(\epsilon''_i - \epsilon_{\infty i})$ 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 ω_i 's of polar solutes are shown in Fig. 1 together with the experimental points on them. ω_i '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 relation¹²:

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

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 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.

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 unit¹³. τ_2 and τ_1 are then compared with the measured τ_i from the relation:

$$K''_i = K_{i\infty} + \frac{1}{\omega \tau_i} K'_i$$

and τ_0 where $\tau_0 = \sqrt{\tau_1 \tau_2}$. As evident from Table 1 although $\tau_0 > \tau_1$; τ_1 agrees well with τ_i 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 earlier¹³. Unlike normal aliphatic alcohols, -OH groups are screened by the substituted -CH₃ group, broad dispersion characterised by relatively short relaxation times were thus observed¹⁴. 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 $\epsilon''_i/(\epsilon''_i - \epsilon_{\infty i})/(\epsilon_{\infty i} - \epsilon_{\infty i})$, $\epsilon''_i/(\epsilon_{\infty i} - \epsilon_{\infty i})$ with the estimated τ_1 , τ_2 as shown in Table 2 by Fröhlich and graphical methods. $x = (\epsilon''_i - \epsilon_{\infty i})/(\epsilon_{\infty i} - \epsilon_{\infty i})$ and $y = \epsilon''_i/(\epsilon_{\infty i} - \epsilon_{\infty i})$ were, however, evaluated from Fröhlich's Eqs (9) and (10) in the first case. The usual variations of $(\epsilon''_i - \epsilon_{\infty i})/(\epsilon_{\infty i} - \epsilon_{\infty i})$ and $\epsilon''_i/(\epsilon_{\infty i} - \epsilon_{\infty i})$ with ω_i are concave and convex as found in Figs. 2 and 3 in accordance with Bergmann Eqs (2) and (3), except 5-methyl-3-heptanol at 24.33 GHz whose $\{(\epsilon''_i - \epsilon_{\infty i})/(\epsilon_{\infty i} - \epsilon_{\infty i})\}$ curve is convex in nature due to its non-accurate $\epsilon_{\infty i}$ and $\epsilon_{\infty i}$ values like ethanol as observed earlier¹⁵. x and y were also obtained graphically from Figs (2) and (3) in the limit $\omega_i = 0$.

In Fröhlich method c_1 and c_2 are all positive as evident from 6th and 7th columns of Table 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 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 $|c_1 + c_2| > 1$, signifying thus the possibility of occurrence of more than two relaxation processes in them¹⁶.

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 $K''_i - \omega_i$ curves by using Eq. (15). The variations of K''_i with ω_i are all linear having almost the same intercepts a and slopes β at each frequency of electric field. It was, therefore, difficult to plot them as they almost coincide. The values of a and β of K''_i 's are little different and comparatively large at 24.33 GHz (Table 3). This sort of behaviour is perhaps due to same dipole moments¹⁶ possessed by the polar molecules under investigation as evident from μ_2 and μ_1 placed in 7th and 8th columns of Table 3. μ_2 for most of the polar molecules shows 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 polymer molecules have long chain of C-atoms and tend to break up in a non-polar 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 thereby¹⁶. 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 1.5D of -O-H group (making an angle 105° with the -C-C- bond axis according to the preferred conformations of all the isomers as sketched in Fig. 4. This confirms that μ_1 arises due to the rotation of -OH group around C-O bond in the long chain alcohols studied so far¹⁷. The slight difference is due to difference in steric hindrances as a result of structural configurations at different frequencies. μ_1 also estimated from $\mu_1 = a_1 c_1 + c_2^{1/2}$ assuming two relaxation processes are equally probable as shown in the last column of Table 3. The other bond moments 0.7, 0.3, 1.0 and 0.09 D for C-H₃, C-H, C-O and C-C bonds are also involved to justify them

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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-heptanol¹³. But for μ_{theo} in Fig. 4 three isomer are only displayed due to typical positions of $\equiv C-H$, and $-OH$ groups. This may probably be the reason of having slightly larger values of μ_{theo} from 1-heptanol as observed earlier¹³.

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, 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. (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. (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 Fig. 4.

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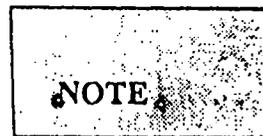
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Structural and associational aspects of binary and single polar liquids in non polar solvent under high frequency electric field

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Abstract : The structural and associational aspects of binary (J_k) polar mixtures of N,N dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) together with a single (J or k) N, N diethyl formamide (DEF) and DMSO in nonpolar solvents (i) are studied in terms of their high frequency (hf) conductivities. The relaxation times τ_k and dipole moments μ 's of the solutes under Giga hertz electric field at various temperatures are estimated from the measured real and imaginary parts of hf dielectric constants at different weight fractions of polar solutes. The variation of τ_k 's with mole fractions x_k 's of DMSO in DMF and C_6H_6 reveals the probable solute-solute molecular association around $x_k = 0.5$ of DMSO. The solute-solvent molecular association begins at and around 50 mole% DMSO in DMF and continues upto 100 mole% DMSO. The concentration and temperature variations of τ_k of these protic liquids are in accord with the information of variation of τ_k of J_k polar mixtures with x_k 's of DMSO. Thermodynamic energy parameters are also obtained from Eyring's rate process equation with the estimated τ_k to support the molecular associations. The slight disagreement between the theoretical dipole moments μ_{theo} 's from the bond angles and bond moments is noticed with the measured μ 's in terms of slopes of concentration variation of hf conductivity curves at infinite dilutions and τ_k . This indicates the temperature dependence of mesomeric and inductive moments of different substituent groups of the molecules.

Keywords : Dipole moment, relaxation time, associational aspects

PACS Nos. : 31.70.Dk, 33.15.Kr

The dielectric relaxation mechanism of a polar-nonpolar liquid mixture under the microwave electric field is of special interest [1,2] for its inherent ability to predict the associational aspects of polar solutes in nonpolar solvents. An investigation was, however, made on ternary solution of binary polar liquids in which both or even one of them are protic [2,3] to study various types of weak molecular associations by polar liquids in

nonpolar solvents. We are, therefore, tempted further to consider more mixtures of binary protic polar liquids like N,N dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) together with a single protic polar liquid like N,N diethyl formamide (DEF) and DMSO in C_6H_6 and CCl_4 [4-6] respectively. DMSO, DMF and DEF are very interesting liquids for their wide application in medicine and industry. They also act as building blocks of proteins and enzymes. The concentration variation of the measured real ϵ'_{jk} , ϵ'_{ij} or ϵ'_{ik} and imaginary ϵ''_{jk} , ϵ''_{ij} or ϵ''_{ik} parts of hf complex dielectric constants ϵ'_{jk} , ϵ'_{ij} or ϵ'_{ik} of jk , j or k polar solutes in nonpolar solvents are used to detect the weak molecular interactions among the molecules [7] at a single or different temperatures under nearly 3 cm wavelength electric field. The t_{jk} of jk polar mixtures as well as τ_j 's or τ_k 's of j or k polar solutes in a nonpolar solvent were estimated from :

$$K''_{ijk} = K_{-ijk} + \frac{1}{\omega\tau_{jk}} K'_{ijk} \quad (1)$$

where $K''_{ijk} = \frac{\omega}{4\pi} \epsilon''_{ijk}$ and $K'_{ijk} = \frac{\omega}{4\pi} \epsilon'_{ijk}$ are the imaginary and real parts of complex hf conductivity K'_{ijk} [8]. The other terms carry usual significance as presented elsewhere [2]. The τ_j 's are estimated from the slopes of the linear variations of K''_{ijk} against K'_{ijk} of eq. (1). The linearity of eq. (1) is tested by the correlation coefficients and the errors involved in the measurement of τ 's are within 5%. τ_j 's are then plotted with different mole fractions x_k 's of DMSO at various experimental temperatures as shown in Figure 1.

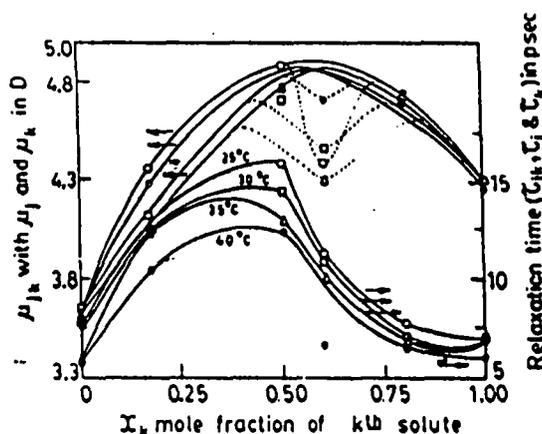


Figure 1. Variation of t_{jk} and μ_{jk} of DMF-DMSO mixture in C_6H_6 against mole fraction x_k of DMSO with t_j and t_k and μ_j and μ_k of DMF and DMSO respectively at different temperatures : (○) at 25°C, (□) at 30°C, (Δ) at 35°C and (◊) at 40°C.

The formation of dimer is responsible for the gradual rise of τ_k from τ_j of DMF at $x_k = 0$ to $x_k = 0.5$ and then its rapid fall to τ_k due to rupture of dimerisation and self association [4]. The estimated τ 's are slightly larger than those of Gopalakrishna's method [9]. But τ 's from conductivity measurement are much more reliable as they provide microscopic relaxation times [10].

The energy parameters due to dielectric relaxation process were then obtained in terms of measured τ from the rate process equation of Eyring *et al* [11]:

$$\tau_s = \frac{A}{T} e^{-\Delta F_r/RT},$$

$$\text{or } \ln(\tau_s T) = \ln A' + \frac{\Delta H_r}{RT}, \quad (2)$$

where $A' = A e^{-\Delta S_r/R}$.

Eq. (2) is a straight line of $\ln(\tau_s T)$ against $\frac{1}{T}$ as seen in Figure 2 having intercepts and slopes to yield the entropy of activation ΔS_r , enthalpy of activation ΔH_r , and free energy of activation ΔF_r , due to dielectric relaxation. The values of $\gamma \left(= \frac{\Delta H_r}{\Delta H_\eta} \right)$ for all the liquids

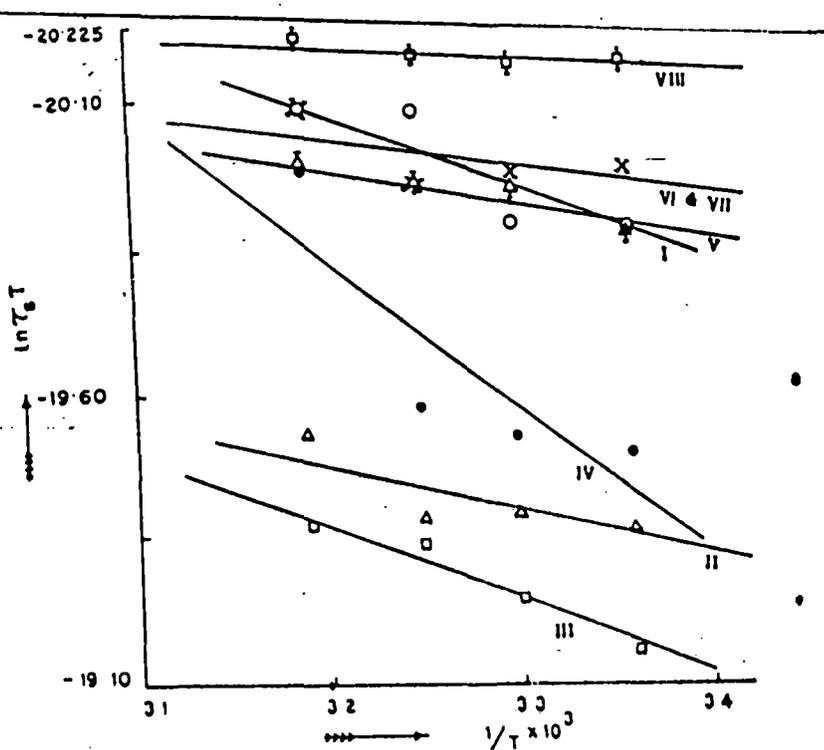


Figure 2. Variation of $\ln(\tau_s T)$ against $\frac{1}{T}$ of binary and single polar solutes in nonpolar solvent. I-DMF + 0 mole% DMSO in C_6H_6 (O), II-DMF + 17 mole% DMSO in C_6H_6 (Δ), III-DMF + 50 mole% DMSO in C_6H_6 (\square), IV-DMF + 60 mole% DMSO in C_6H_6 (\bullet), V-DMF + 80 mole% DMSO in C_6H_6 (Δ), VI-DMF + 100 mole% DMSO in C_6H_6 (X), VII-DMF + 100 mole% DMSO in CCl_4 (O).

except DMSO in CCl_4 are greater than 0.55, as obtained from the slope of the linear relation of $\ln(\tau_s T)$ with $\ln h$ indicating them as solid phase rotators in solvent environment. h is the

coefficient of viscosity of solvent. ΔH_h due to viscous flow of the solvent is obtained from slope of $\ln(\tau_i T)$ against $\frac{1}{T}$ and known g . Again, ΔH_h are greater than ΔH_f for all the mixtures except 0, 50 and 60 mole% DMSO in DMF and C_6H_6 . The difference in ΔH_f and ΔH_h is due to the involvement of various types of bondings which are either formed or broken to some extent, depending on the temperature and concentration of the system. The negative values of ΔS_f 's for all the systems except 0 and 60 mole% DMSO in DMF and C_6H_6 indicate the existence of cooperative orientation of the molecules arising out of steric forces to yield more ordered states while the reverse is true for positive ΔS_f 's. Although, ΔF_f 's in all cases are almost constant at all temperatures, they increase with x_1 of DMSO from $x_1 = 0.0$ to $x_1 = 0.5$ and then decrease gradually to $x_1 = 1.0$ signifying the maximum dimerisation of DMF-DMSO mixture around $x_1 = 0.5$. The formation of dimer causes larger molecular size and hence, the energy needed for rotation in the relaxation process is higher.

The hf conductivity K_{ijk} as a function of weight fraction W_{jk} is given by

$$K_{ijk} = \frac{\omega}{4\pi} (\epsilon'_{ijk} + \epsilon''_{ijk})^{\frac{1}{2}} \quad (3)$$

Since $\epsilon'_{ijk} \gg \epsilon''_{ijk}$ eq. (1) can be written as

$$K_{ijk} = K_{\infty ij k} + \frac{1}{\omega \tau_{jk}} K'_{ijk} \quad (4)$$

$$\left(\frac{dK'_{ijk}}{dW_{jk}} \right)_{W_{jk} \rightarrow 0} = \omega \tau_{jk} \beta$$

Here, β 's are the slopes of $K_{ijk} - W_{jk}$, $K_{ij} - W_j$ of $K_{ik} - W_k$ curves respectively, which are linear with almost identical intercepts probably due to same polarity of the molecules [2]. The real part of hf conductivity, K'_{ijk} is again related to W_{jk} of jk polar solute dissolved in a nonpolar solvent (i) at temperature $T^\circ K$ [12] as

$$K'_{ijk} = \frac{\mu_{jk}^2 NP_{ijk} F_{ijk}}{3M_{jk} kT} \left(\frac{\omega^2 \tau_{jk}}{1 + \omega^2 \tau_{jk}^2} \right) W_{jk} \quad (5)$$

Differentiating eq. (5) with respect to W_{jk} and comparing the result at $W_{jk} \rightarrow 0$ to eq. (4), one obtains the following relation

$$\mu_{jk} = \left[\frac{27M_{jk} kT}{NP_i (\epsilon_i + 2)^2} \cdot \frac{\beta}{\omega b} \right]^{1/2} \quad (6)$$

to estimate μ_{jk} , μ_j or μ_k of the respective solutes. b is a dimensionless parameter in terms of estimated τ_{jk} , τ_j or τ_k given by :

$$b = \frac{1}{1 + \omega^2 \tau_{jk}^2} \quad (7)$$

The other terms in eq. (6) carry usual significance [2]. All the μ 's are then plotted against different x_k 's of DMSO at each temperature as shown in Figure 1. It shows the gradual rise of μ_{jk} in the range $0 < x_k \leq 0.5$. It then decreases slowly in order to exhibit the convex nature of each curve with an abnormally low value of μ_{jk} around $x_k = 0.6$. This sort of behaviours of $\mu_{jk} - x_k$ curves (Figure 1) is explained by the fact that dimers are being formed from $x_k \geq 0$ to $x_k = 0.6$ causing increase of μ . The rupture of dimerisation *i.e.* self association occurs in higher concentrations in the range $0.6 \leq x_k < 1.0$ to yield lower values of μ 's. But around $x_k = 0.6$, all μ_{jk} 's are minimum indicating the possible occurrence of double relaxation phenomena in such mixtures to be studied later on. μ_{jk} together with μ_j and μ_k for each mixture of a fixed concentration are shown graphically only to observe their temperature dependence like $\mu_{jk} = a + bt + ct^2$ with coefficients a , b and c as seen in Figure 3. The variation is concave with maximum depression at 17 mole% DMSO in DMF mixture. The depression gradually decreases upto $x_k = 0.6$ of DMSO in DMF and C_6H_6 probably due to solute-solute molecular association in the range $0 < x_k < 0.6$. The maximum

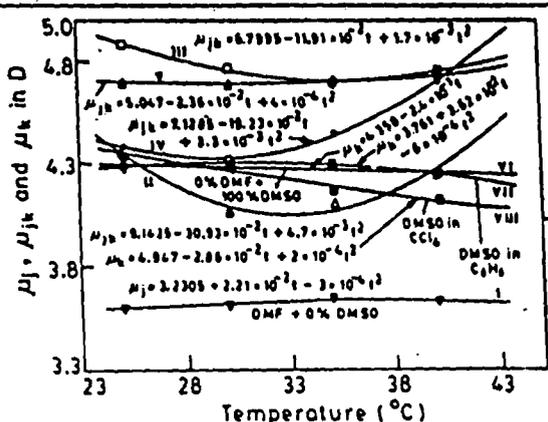


Figure 3. Variation of μ_j , μ_{jk} and μ_k of binary and single polar solutes in nonpolar solvent with temperature t in $^{\circ}\text{C}$.

I-DMF + 0 mole% DMSO in C_6H_6 (∇).
 II-DMF + 17 mole% DMSO in C_6H_6 (Δ).
 III-DMF + 50 mole% DMSO in C_6H_6 (\square).
 IV-DMF + 60 mole% DMSO in C_6H_6 (\circ).
 V-DMF + 80 mole% DMSO in C_6H_6 (∇).
 VI-DMF + 100 mole% DMSO in C_6H_6 (∇). VII-DMSO in C_6H_6 (\times). VIII-DMSO in CCl_4 (\blacksquare).

dimerisation is however, inferred from low μ 's because of the larger molecular sizes as confirmed by high values of $\tau_r T / \eta \gamma$ (being proportional to volume of the rotating unit) for 60 mole% DMSO in DMF and C_6H_6 . As temperature increases the dipole-dipole interaction is weakened and the absorption of hf electric energy increases resulting in the rupture of dimer to yield high μ 's for smaller molecular species [10]. The slight convex nature of curves for 0 mole% DMSO in DMF and C_6H_6 and DMSO in C_6H_6 , along with almost straight line variation of 100 mole% DMSO in DMF and C_6H_6 and DMSO in CCl_4 (Figure 3) is probably due to solute-solvent molecular interaction of either DMF with C_6H_6 or DMSO with C_6H_6 and CCl_4 respectively as illustrated in Figure 4. The associations of DMF, DEF and DMSO in C_6H_6 can arise due to interactions of fractional positive charges of N and S atoms of the molecules with the π delocalised electron cloud of C_6H_6 ring as seen in Figure 4(i), (iii) and (ii) respectively. Again, one of C-Cl dipoles of CCl_4 , owing to more -ve charge on Cl atom, interacts with the fractional

+ve charge of S-atom of DMSO (Figure 4 (iib)). The $\mu_{theo} = 4.55$ D of DMSO is however, computed from available bond moments of 2.350 D and 1.55 D for $S \leftarrow CH_3$ and $O \leftarrow S$ respectively, assuming the molecule to be planar one. The major contributions to μ_{theo} for DMF and DEF are due to 0.64 D and 0.78 D for $N \leftarrow CH_3$ and $N \leftarrow C_2H_5$, since the other common bond moments in them are the same with values of 0.3 D, 0.45 D and 3.10 D for $C \leftarrow H$, $C \leftarrow N$ and $C \leftarrow O$ respectively. Figure 4 (iv) however, shows a certain angle $\phi (= 106^\circ)$ between monomeric μ 's of DMF and DMSO to have $\mu_{theo} = 4.77$ D of dimer below $x_1 = 0.6$.

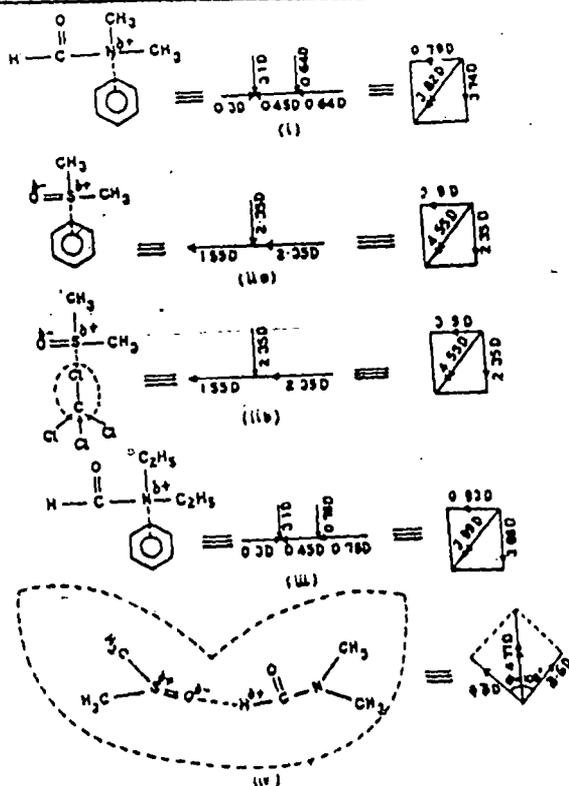


Figure 4. Conformational structures along with solute-solvent and solute-solute interaction of molecules. (i) -DMF in C_6H_6 , (ii) -DMSO in C_6H_6 , (iii) -DMSO in CCl_4 (iii) -DEF in C_6H_6 , (iv) -DMSO-DMF dimer.

The slight deviations of the μ 's from the μ_{theo} 's occur probably due to the presence of inductive and mesomeric moments of such molecules. This is also observed elsewhere [13]. The corrected μ 's obtained from the reduced bond moments of the substituent groups by factors μ_{ca}/μ_{theo} establish the above facts at different temperatures, too. Thus the dielectric relaxation parameters from *hf* conductivity measurements offer a useful tool to arrive at the structural and associational aspects of the nonspherical polar liquids.

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