

PART A

CHAPTER 3

DOUBLE RELAXATION TIMES OF NON- SPHERICAL POLAR LIQUIDS IN NON-POLAR SOLVENT : A NEW APPROACH BASED ON SINGLE FREQUENCY MEASUREMENT

3.1. 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' , ϵ'' , ϵ_0 and ϵ_{∞} of a non-spherical pure polar liquid 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. Kasta *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 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 3.1 - 3.3. 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 3.1.) 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 3.3. 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 3.4. and table 3.3. later) in order to explore their conformations (see figure 3.5. later).

3.2. 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)

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{1}{1 + \omega^2 \tau_1^2} + c_2 \frac{1}{1 + \omega^2 \tau_2^2} \quad \dots\dots(3.1)$$

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots\dots(3.2)$$

provided that $c_1 + c_2 = 1$. The symbols used in equations (3.1) and (3.2) have their usual meanings. Let

Table 3.1 The double relaxation times τ_1 (smaller) and τ_2 (larger) estimated from intercepts and slopes of equation (3.7) with errors and correlation coefficients together with reported τ of polar liquids.

System with slope number and molecular weight M_j (g)	Intercept and slope of $(\epsilon_{0ij}-\epsilon'_{ij})/(\epsilon''_{ij}-\epsilon_{\infty ij})$ against $-\epsilon''_{ij}/(\epsilon'_{ij}-\epsilon_{\infty ij})$	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; $M_j = 141.52$	-1.4276	3.2169	0.9964	1.33	8.51	42.97	18.5
(ii) 3-chloro-4-methyl aniline in benzene; $M_j = 141.52$	-0.5605	1.8913	0.9982	0.76	5.89	24.38	13.6
(iii) 5-chloro-2-methyl aniline in benzene; $M_j = 141.52$	-0.8107	2.0749	0.9727	3.67	8.36	24.85	16.6
(iv) 3-chloro-2-methyl aniline in benzene; $M_j = 141.52$	-0.3862	1.5960	0.9918	1.09	4.76	20.78	9.9
(v) 2-chloro-6-methyl aniline in benzene; $M_j = 141.52$	-0.3132	1.3711	0.9250	2.77	4.63	17.31	7.8
(vi) o-chloronitrobenzene in benzene; $M_j = 157.5$	-0.3033	1.3129	0.8170	3.77	4.79	16.22	13.5
(vii) 4-chloro-3-nitrotoluene in benzene; $M_j = 171.5$	-0.3863	1.8623	0.8776	11.90	3.81	25.99	20.9
(viii) m-nitrobenzo-trifluoride in benzene; $M_j = 191.0$	-0.6003	1.9038	0.9929	2.44	6.38	24.09	19.7
(ix) 4-chloro-3-nitrobenzotrifluoride in carbon tetrachloride; $M_j = 225.5$	-0.0587	1.6634	0.9524	5.33	0.58	26.04	21.1
(x) o-nitrobenzotrifluoride in benzene; $M_j = 191.039$	-0.0620	1.0560	0.6992	4.17	0.99	15.90	13.7
(xi) 4-chloro-3-nitrotoluene in carbon tetrachloride; $M_j = 171.5$	-0.1335	2.2819	0.9771	7.51	0.96	35.56	35.0
(xii) 4-chloro-3-nitrobenzotrifluoride in benzene; $M_j = 225.5$	2.5194	-3.0302	-0.8599	13.07	—	10.87	10.2
(xiii) m-aminobenzo-trifluoride in benzene; $M_j = 161.05$	0.8445	0.0452	0.0088	11.38	—	15.07	14.5
(xiv) o-chloronitro-benzene in carbon tetrachloride; $M_j = 157.5$	0.0194	1.2973	0.9277	5.57	—	21.00	15.8
(xv) o-chlorobenzo-trifluoride in benzene; $M_j = 180.5$	0.2856	0.5696	0.14505	19.10	—	14.25	12.3

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

and $\omega\tau = \alpha$ Equations (3.1) and (3.2) can be written as

$$x = c_1 a_1 + c_2 a_2 \quad \dots\dots(3.3)$$

$$y = c_1 b_1 + c_2 b_2 \quad \dots\dots(3.4)$$

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 (3.3) and (3.4) for c_1 and c_2 , one gets

$$c_1 = \frac{(x \alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots\dots(3.5)$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots\dots(3.6)$$

provided that $\alpha_2 > \alpha_1$. Now adding equations (3.5) and (3.6) we get, since $c_1 + c_2 = 1$,

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

or
$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega(\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2 \quad \dots\dots(3.7)$$

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 (3.7) 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 (3.1.) together with the reported τ . The error as well as correlation coefficient were also found for each curve of equation (3.7) and placed in table (3.1.), only to see how far they are linear as shown in figure 3.1.

The Fröhlich parameters A, where $A = \ln(\tau_2/\tau_1)$ shown in table 3.2 for all the polar compounds, are used to evaluate both x and y of equations (3.3) and (3.4) in terms of ω

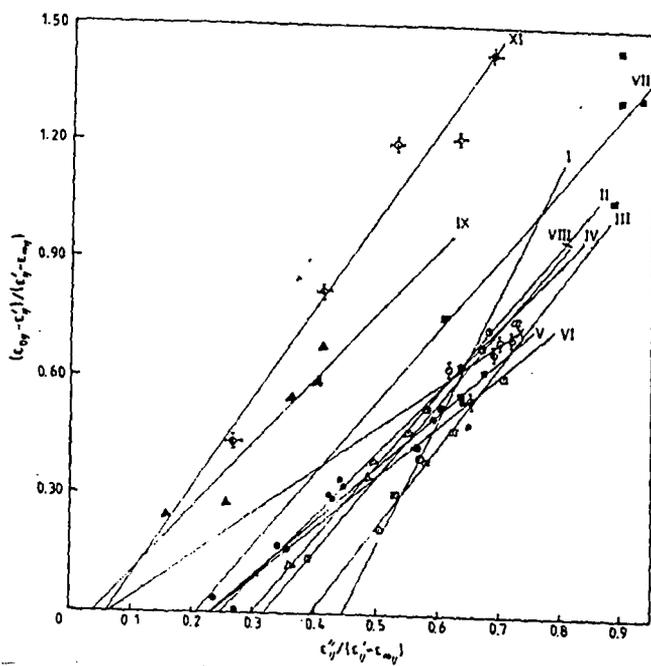


Figure 3.1 Straight line plots of $(\epsilon_{0ij} - \epsilon'_{ij})/(\epsilon'_{ij} - \epsilon_{\infty ij})$ against $\epsilon''_{ij}/(\epsilon'_{ij} - \epsilon_{\infty ij})$ for the polar-non-polar liquid mixtures : (I), (II), (III), (IV), (V), of disubstituted anilines (VI), (VII), (VIII), (IX), (X) and (XI) of disubstituted benzenes respectively at 35°C (Table 3.1)

and small limiting relaxation time τ_s , where $\tau_s = \tau_1$ by the following equations (Fröhlich 1949):

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + e^{2A} \omega^2 \tau_s^2}{1 + \omega^2 \tau_s^2} \right) \quad \dots\dots(3.8)$$

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{A} \left[\tan^{-1} (e^A \omega \tau_s) - \tan^{-1} (\omega \tau_s) \right] \quad \dots\dots (3.9)$$

The computed values of x and y from the above equations and the corresponding c_1 and c_2 from equations (3.1) and (3.2) are presented in table 3.2. Again the left hand sides of equations (3.1) and (3.2) are obviously 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 3.2 and 3.3 respectively. This at once prompted us to get the fixed values of x and y when $\omega_j \rightarrow 0$ from figures 3.2 and 3.3 to estimate c_1 and c_2 , which are shown in table 3.2 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 (3.7) for each compound when substituted on the right-hand sides of equations (3.1) and (3.2).

3.3 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

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon'_{ij}{}^2 + \epsilon''_{ij}{}^2)^{1/2} \quad \dots\dots(3.10)$$

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)

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT} \left(\frac{\omega^2 \tau_s^2}{1 + \omega^2 \tau_s^2} \right) \omega_j \quad \dots\dots(3.11)$$

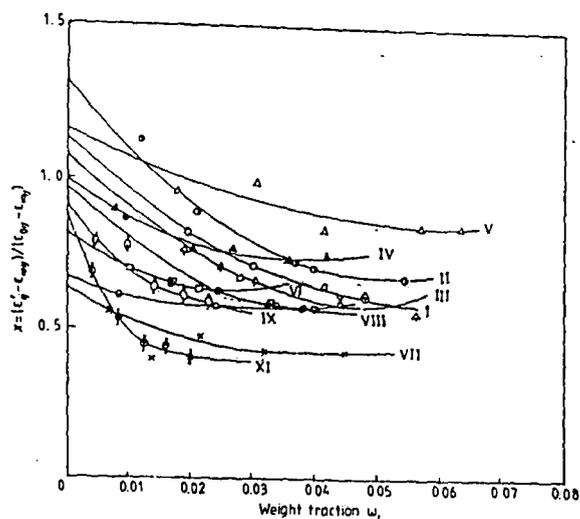


Figure 3.2 Variation of $(\epsilon'_{ij} - \epsilon_{\infty ij})/(\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction ω_j of polar solutes in dilute solutions at 35°C (Table 3.2): (I), (II), (III), (IV), (V), of disubstituted anilines, (VI), (VII), (VIII), (IX), (X) and (XI) of disubstituted benzenes respectively

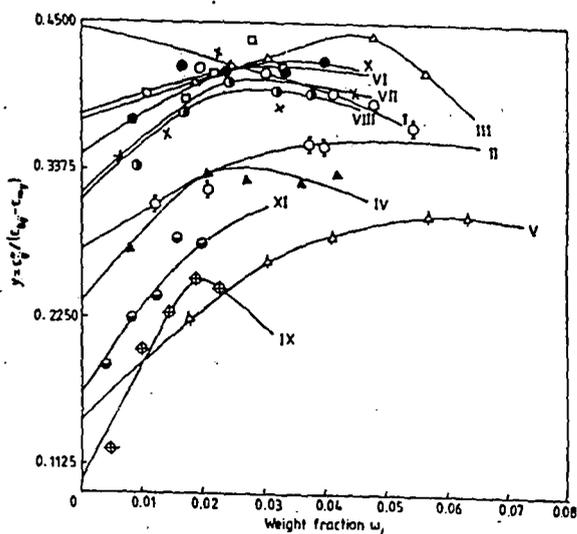


Figure 3.3 Variation of $\epsilon''_{ij}/(\epsilon_{0ij} - \epsilon_{\infty ij})$ against weight fraction ω_j of polar solutes in dilute solutions at 35°C (Table 3.2): (I), (II), (III), (IV), (V), of disubstituted anilines, (VI), (VII), (VIII), (IX), (X) and (XI) of disubstituted benzenes respectively

Table 3.2 Reported Fröhlich parameter A, relative contributions c_1 and c_2 towards dielectric relaxations with estimated values of x and y due to Fröhlich equation (3.8) and (3.9) and those by our method.

System with slope number and molecular weight M_j (g)	Fröhlich parameter A $= \ln(\tau_2/\tau_1)$	Theoretical x and y equations (3.9)	values of using (3.8) and	Theoretical c_1 and c_2	values of c_2	Estimated values of $x = \left(\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} \right)_{\omega_j \rightarrow 0}$	values of $y = \left(\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} \right)_{\omega_j \rightarrow 0}$	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) o-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) m-nitrobenzotrifluoride in benzene; $M_j = 191.0$	132.86	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) o-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

where M_j is the molecular weight of 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

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

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

$$\text{or } \left(\frac{dK'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \omega\tau \left(\frac{dK_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \omega\tau\beta \quad \dots\dots(3.12)$$

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

Equation (3.11), on being differentiated with respect to ω_j and for $\omega_j \rightarrow 0$, becomes

$$\left(\frac{dK'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad \dots\dots(3.13)$$

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 equations (3.12) and (3.13) we finally get

$$\mu_j = \left(\frac{3 M_j k T \beta}{N \rho_i F_i \omega b} \right)^{1/2} \quad \dots\dots(3.14)$$

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

$$b = \frac{1}{1 + \omega^2 \tau^2} \quad \dots\dots(3.15)$$

for τ_1 and τ_2 respectively. The values of b as well as μ_1 and μ_2 thus computed from equations (3.14) and (3.15) are placed in table 3.3.

3. 4. Results and discussion

Figure 3.1 represents the linear relationship of $(\epsilon_{0ij} - \epsilon'_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})$ to $\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$ satisfying equation (3.7) having intercepts and slopes presented in table 3.1. with the experimental points placed on each curve for 11 systems possessing double

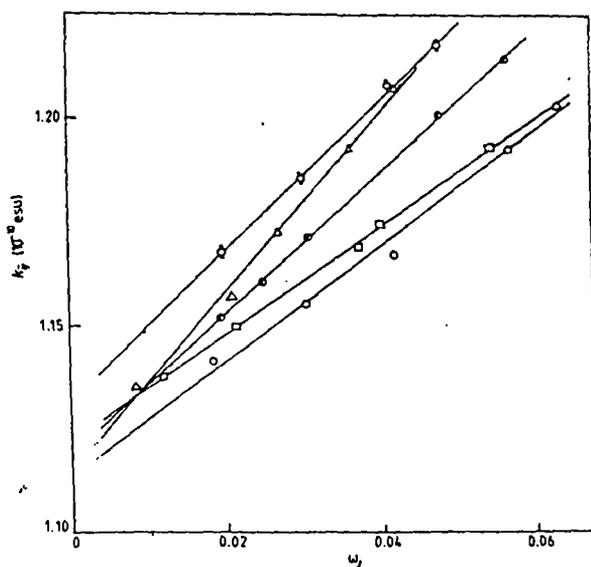


Figure 3.4 Concentration variation of microwave conductivity K_{ij} of five disubstituted anilines at 35°C

Table 3.3 Reports of the estimated intercepts and slopes of the concentration variation of UHF 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_{ij} against ω_j		Dimensionless parameters b		Estimated dipolemoment		Reported μ (D)		Theore tical μ (D)	Experimental 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)	Guggen -heim	Högasi <i>et al</i>	from bond length and bond 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) o-chloronitro benzene 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-nitroto-luene 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) m-nitrobenzotri- fluoride 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-nitroben zotriflouride in CCl_4	1.0999	1.5781	0.9987	0.2744	1.99	3.79	3.17	3.15	3.78	4.34
(x) o-nitrobenzotri- fluoride 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-nitro- benzotrifluoride in C_6H_6	1.1286	1.1894	—	0.6845	—	2.76	2.97	2.98	3.78	—
(xiii) m-aminoben zotrifluoride in C_6H_6	1.1106	2.3536	—	0.5303	—	3.73	3.51	3.60	2.48	—
(xiv) o-chloronitro- benzene in CCl_4	1.0973	5.4508	—	0.3676	—	5.08	4.19	4.13	5.28	—
(xv) o-chlorobenzo- trifluoride in C_6H_6	1.1199	2.0159	—	0.5580	—	3.57	3.38	3.49	3.98	—

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 3.1 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 3.1 -3.3 in order to calculate μ_1 and μ_2 of the flexible parts as well as the whole molecules. they are shown in tables 3.1 and 3.3 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 3.1, eight molecules, namely all the disubstituted anilines and three benzene derivatives namely *o*-chloronitrobenzene, 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 3.1). It is, however, interesting to note that the last four systems of table 3.1 show single relaxation processes, probably owing to their rigid attachment to the flexible parts. The slopes and intercepts of equation (3.7) 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 measurements are to be performed on a single polar molecule in different non-polar solvents.

Table 3.2 reports the relative contributions c_1 and c_2 due to τ_1 and τ_2 (table 3.1) towards relaxation as computed from Fröhlich's equations (3.8) and (3.9) for x and y as

well as by our graphical technique (figures 3.2 and 3.3). In total, c_2 values calculated for six polar molecules are negative although they fulfil the condition $c_1 + c_2 \simeq 1$. 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 3.4. The intercept α and slope β are placed in table 3.3 to compute μ_1 and μ_2 using relaxation times τ_1 and τ_2 of table 3.1 from equations (3.14) and (3.15). The values of b_1 and b_2 are also placed in the fourth and fifth columns of table 3.3. The corresponding μ_1 and μ_2 from equation (3.14) are shown in table 3.3. 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_{theo} from bond lengths and bond angles had also previously been studied. The same data, with those of disubstituted anilines are shown again in table 3.3 for comparison only.

In figure 3.5 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_{theo} were computed by the vector addition method and are placed in table 3.3. The close agreement of these μ_{theo} with our experimental μ_2 values suggests their correct conformational structures as shown in figure 3.5

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 3.5 and table 3.1), 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

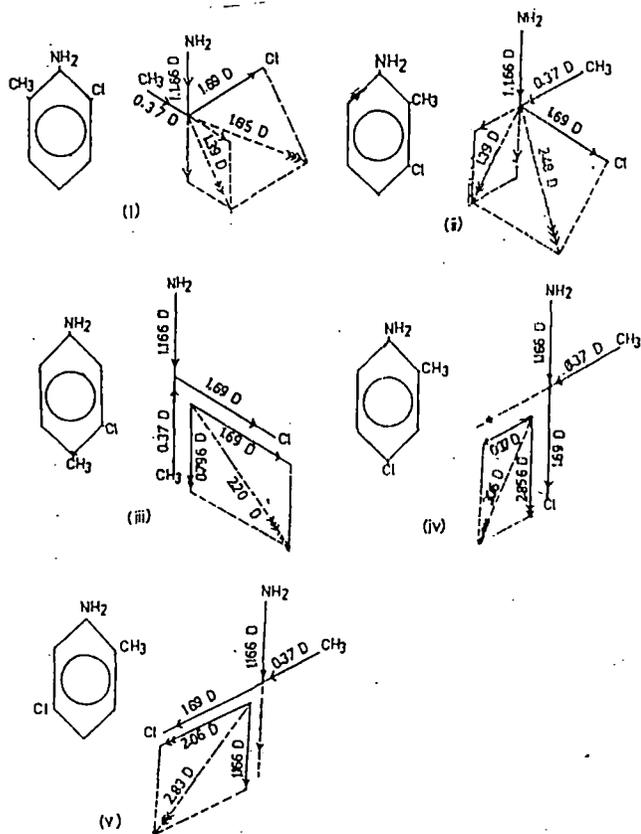


Figure 3-5 Conformations of five disubstituted anilines showing the orientation of the bond axes and bond moments and dipole moments.

probable relaxation time due to Higasi (1966) and Guggenheim (1957) also show a trend similar to ours as shown in table 3.1.

3.5 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 nonpolar liquid mixture. 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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