

CHAPTER -7

STRUCTURAL AND ASSOCIATIONAL ASPECTS OF ISOMERS OF ANISIDINE AND TOLUIDINE UNDER A GIGAHERTZ ELECTRIC FIELD

STRUCTURAL AND ASSOCIATIONAL ASPECTS OF ISOMERS OF ANISIDINE AND TOLUIDINE UNDER A GIGAHERTZ ELECTRIC FIELD

7.1. Introduction

The dielectric relaxation of a polar liquid molecule in a nonpolar solvent under static and high frequency (hf) electric fields provides one with valuable information on various types of molecular associations [1,2] and the structural configuration of the polar molecule from relaxation parameters such as the relaxation time τ and dipole moment μ , measured by any standard method [3,4]. μ_j 's determined by concentration variation of the real part of the hf dielectric susceptibility are concerned with the orientational polarization and are further used to shed more light on the structural and associational aspects of a polar molecule [5].

Srivastava and Chandra [6] measured the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of the relative complex permittivity, ϵ^*_{ij} and the static and infinitely hf relative permittivities, ϵ_{oij} and $\epsilon_{\infty ij}$ of isomers of anisidines and toluidines in C_6H_6 under 2.02, 3.86 and 22.06 GHz electric fields at 35°C. The purpose of such study was to observe the solute-solvent and solute-solute molecular associations, besides the possible existence of either double or single relaxation behaviour of anisidines and toluidines.

Nowadays, the usual practice is to study dielectric relaxation phenomena by dimensionless complex hf dielectric orientational susceptibility χ^*_{ij} [5] rather than the relative hf permittivity ϵ^*_{ij} or hf conductivity σ^*_{ij} . The ϵ^*_{ij} includes within it all types of polarizations while σ^*_{ij} is concerned with the transport of bound charges. Hence it is better to work with χ_{ij} for its more direct link with orientational polarization. Moreover, the present system of study in the modern concept of internationally accepted symbols of dielectric terminology and

parameters in SI units is interesting because of its rationalized, coherent and unified nature.

Under such a context we derived a linear equation (7.5) in terms of the real $\chi'_{ij} = (\epsilon'_{ij} - \epsilon_{\infty ij})$ and imaginary $\chi''_{ij} = \epsilon''_{ij}$ parts of the complex $hf \chi^*_{ij}$ and low-frequency dielectric susceptibility $\chi_{0ij} = (\epsilon_{0ij} - \epsilon_{\infty ij})$, which is real as presented in Table 7.1 under 9.945 GHz electric field, to obtain τ_1 and τ_2 of the flexible parts and the whole molecules in C_6H_6 at 35°C.

The electric field frequency of $f=9.945$ GHz was claimed to be the most effective dispersive region for such molecules [7]. When χ''_{ij} 's were plotted against frequency (f) they showed a peak in the neighbourhood of 9.945 GHz, at which point the dielectric orientation processes of polar molecules [8,9] are invariably maximum. At this frequency χ'_{ij} , χ''_{ij} and χ_{0ij} were again adjusted by a careful graphical interpolation technique [7]. One could make a strong conclusion of double relaxation phenomena of a polar molecule in a nonpolar solvent based on single-frequency measurement of the relaxation parameters, provided the accurate value of χ_{0ij} involved with ϵ_{0ij} and $\epsilon_{\infty ij}$ is available. The use of n^2_{Dij} for $\epsilon_{\infty ij}$ [6] may often introduce additional error into the calculation. Nevertheless, the data are accurate up to 5% for χ''_{ij} and 2% for χ'_{ij} and χ_{0ij} . The liquid molecules at this f absorb electric energy much more strongly to exhibit reasonable τ_1 and τ_2 for all the chemical systems under identical environments. τ_1 and τ_2 are, however, measured from the intercept and slope of the derived straight-line equation (see equation (7.5) of $(\chi_{0ij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij} / χ'_{ij} of Figure 7.1 for different weight fractions w_j 's of polar solute at the single frequency $\omega (= 2\pi f)$, signifying the material property of the systems. The correlation coefficients r and minimum chisquare values to test the linearity of the curves of Figure 7.1, along with the estimated τ_1 and τ_2 , are given in Table 7.2. In absence of reliable τ , the ratio of the individual slopes of variation of χ''_{ij} and χ'_{ij} with w_j 's at $w_j \rightarrow 0$, as seen in Figures 7.2 and 7.3, were conveniently used to evaluate τ_j to compare with those of Murthy *et al* [10] of Figure 7.4 and Gopalakrishna's method [11].

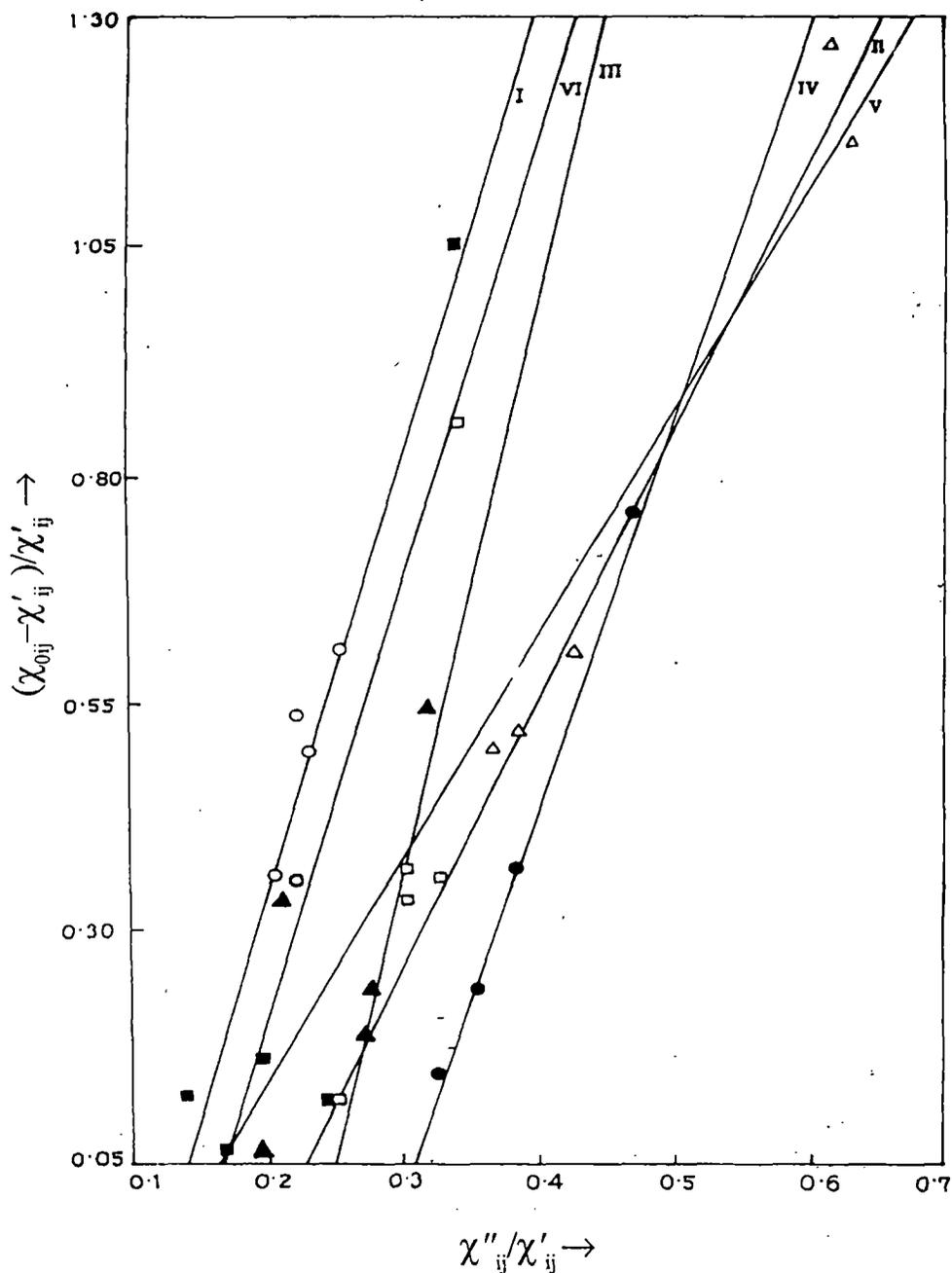


Figure 7.1. Linear variation of $(\chi_{0ij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} of isomers of anisidine and toluidine in benzene at 35°C under a 9.945 GHz electric field. ((I) o-anisidine (—○—), (II) m-anisidine (—△—), (III) p-anisidine (—□—), (IV) o-toluidine (—●—), (V) m-toluidine (—▲—) and (VI) p-toluidine (—■—)).

The theoretical weighted contributions c_1 and c_2 due to the estimated τ_1 and τ_2 presented in Table 7.3, towards dielectric dispersions, were calculated from Fröhlich's equations [12] in order to compare with the experimental contributions by the graphical extrapolation technique of Figures 7.5 and 7.6 at $w_j \rightarrow 0$. The symmetric and asymmetric distributions parameters γ and δ were, however, worked out from the variation of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} with w_j in the limit $w_j = 0$ to conclude the symmetric distribution behaviour obeyed by such molecules. The characteristic relaxation time τ_{cs} from δ and ϕ of Figure 7.7 along with the symmetric relaxation time τ_s in terms of γ are found out to compare with τ_1 , τ_2 and τ_j in Table 7.2. The dipole moments μ_1 , μ_2 , and μ_0 in Coulomb metres (C m), in terms of b_1 , b_2 and b_0 involved with τ_1 , τ_2 , and τ_0 , where τ_0 is the most probable relaxation time ($=\sqrt{\tau_1\tau_2}$) and linear coefficient β 's of χ'_{ij} against w_j curves of Figure 7.3 were determined in order to place them in Table 7.4. The comparison, however, indicates that the flexible parts of the molecules rotate under X-band gigahertz electric fields. They are compared with μ_{theo} 's obtained from available bond angles and bond moments of the substituent polar groups attached to the parent molecules, as displayed in Figure 7.8, and μ_j by freshly calculated Gopalakrishna's method of Table 7.4. The slight disagreement between the measured μ 's and μ_{theo} 's invites the existence of inductive and mesomeric effects of substituent polar groups.

7.2. Theoretical formulations for τ_1 , τ_2 and τ_0

Bergmann *et al*'s equations [13] are concerned with molecular orientational polarization processes. We therefore introduce χ_{ij} 's to avoid clumsiness of algebra as $\epsilon_{\infty ij}$ includes a fast polarization process and frequently appears as a subtracted term in the equations. Thus, with the established symbols of parameters of dielectric terminology like $\chi'_{ij} = (\epsilon'_{ij} - \epsilon_{\infty ij})$, $\chi''_{ij} = \epsilon''_{ij}$ and $\chi_{0ij} = (\epsilon_{0ij} - \epsilon_{\infty ij})$ of Table 7.1, Bergmann *et al*'s

Table 7.1 : Concentration variations of the measured real ϵ'_{ij} and imaginary ϵ''_{ij} parts of the hf complex relative permittivity under a 9.945 GHz electric field, the static and hf relative permittivities ϵ_{0ij} and $\epsilon_{\infty ij}$ along with the real χ'_{ij} and imaginary χ''_{ij} parts of the complex dimensionless dielectric orientational susceptibility χ^*_{ij} and the low-frequency susceptibility χ_{0ij} which is real for isomers of anisidine and toluidine in benzene at 35°C.

System with Serial number and molecular weight (M_i)	Weight fraction, w_p , of solute	Measured dielectric relative permittivities				Dimensionless dielectric orientational susceptibilities		
		ϵ'_{ij}	ϵ''_{ij}	ϵ_{0ij}	$\epsilon_{\infty ij}$	χ'_{ij}	χ''_{ij}	χ_{0ij}
(i) o-anisidine $M_i = 0.123$ kg.	0.0326	2.3104	0.0148	2.336	2.239	0.0714	0.0148	0.097
	0.0604	2.3520	0.0244	2.404	2.247	0.1050	0.0244	0.157
	0.0884	2.4064	0.0340	2.459	2.255	0.1514	0.0340	0.204
	0.1135	2.4416	0.0400	2.538	2.262	0.1796	0.0400	0.276
	0.1361	2.4672	0.0512	2.588	2.267	0.2002	0.0512	0.321
(ii) m-anisidine $M_i = 0.123$ kg.	0.0160	2.2720	0.0234	2.315	2.235	0.0370	0.0234	0.080
	0.0336	2.3040	0.0390	2.384	2.241	0.0630	0.0390	0.143
	0.0579	2.3904	0.0618	2.477	2.246	0.1444	0.0618	0.231
	0.0823	2.4544	0.0744	2.553	2.253	0.2014	0.0744	0.300
	0.1109	2.5344	0.1056	2.675	2.261	0.2734	0.1056	0.414
(iii) p-anisidine $M_i = 0.123$ kg.	0.0319	2.3104	0.0252	2.373	2.237	0.0734	0.0252	0.136
	0.0597	2.3904	0.0474	2.442	2.246	0.1444	0.0474	0.196
	0.0848	2.5088	0.0642	2.539	2.250	0.2588	0.0642	0.289
	0.1106	2.5376	0.0840	2.638	2.262	0.2756	0.0840	0.376
	0.1396	2.6272	0.1086	2.745	2.269	0.3582	0.1086	0.476
(iv) o-toluidine $M_i = 0.107$ kg.	0.0137	2.2752	0.0162	2.301	2.241	0.0342	0.0162	0.060
	0.0459	2.3648	0.0408	2.392	2.250	0.1148	0.0408	0.142
	0.0622	2.4032	0.0570	2.457	2.255	0.1482	0.0570	0.202
	0.1048	2.5376	0.0900	2.577	2.264	0.2736	0.0900	0.313
(v) m-toluidine $M_i = 0.107$ kg.	0.0264	2.3136	0.0150	2.337	2.243	0.0706	0.0150	0.094
	0.0538	2.3552	0.0342	2.413	2.248	0.1072	0.0342	0.165
	0.0781	2.4576	0.0402	2.470	2.252	0.2056	0.0402	0.218
	0.1015	2.4840	0.0618	2.526	2.258	0.2260	0.0618	0.268
	0.1225	2.5280	0.0732	2.591	2.262	0.2660	0.0732	0.329
(vi) p-toluidine $M_i = 0.107$ kg.	0.0213	2.3100	0.0102	2.319	2.237	0.0730	0.0102	0.082
	0.0428	2.3040	0.0204	2.367	2.244	0.0600	0.0204	0.123
	0.0616	2.3904	0.0276	2.413	2.249	0.1414	0.0276	0.164
	0.0916	2.4704	0.0384	2.483	2.254	0.2164	0.0384	0.229
	0.1048	2.4960	0.0582	2.523	2.260	0.2360	0.0582	0.263

equations become

$$\frac{\chi'_{ij}}{\chi_{0ij}} = c_1 \frac{1}{1+\omega^2\tau_1^2} + c_2 \frac{1}{1+\omega^2\tau_2^2} \quad (7.1)$$

and

$$\frac{\chi''_{ij}}{\chi_{0ij}} = c_1 \frac{\omega\tau_1}{1+\omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1+\omega^2\tau_2^2} \quad (7.2)$$

assuming the molecules possess two separate broad dispersions for which the relative weight factors c_1 and c_2 are such that $c_1 + c_2 = 1$. χ'_{ij} and χ''_{ij} are the real and imaginary parts of the hf complex susceptibility χ^*_{ij} and χ_{0ij} is the static or low-frequency susceptibility which is real.

Let $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$, Eqs (7.1) and (7.2) are solved to obtain

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{0ij}(\alpha_2 - \alpha_1)} \quad (7.3)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{0ij}(\alpha_2 - \alpha_1)} \quad (7.4)$$

provided $\alpha_2 > \alpha_1$. Now adding Eqs. (7.3) and (7.4), since $c_1 + c_2 = 1$, one obtains

$$\frac{\chi_{0ij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2\tau_1\tau_2. \quad (7.5)$$

Eq. (7.5) gives a straight line between the variables $(\chi_{0ij} - \chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} having intercept $-\omega^2\tau_1\tau_2$ and slope $\omega(\tau_1 + \tau_2)$. It was solved for different concentrations w_j 's of each of the polar molecules of Table 7.1 for a given fixed value of the angular frequency $\omega (= 2\pi f)$ of the applied electric field at 35°C, where $f = 9.945$ GHz. The values of τ_1 and τ_2 from the intercept and slope of Eq. (7.5) are found as shown in Table 7.2.

The theoretical values of c_1 and c_2 towards dielectric relaxations were obtained from Eqs. (7.3) and (7.4) using values of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} of Fröhlich's [12] following equations (7.6) and (7.7), in terms of the estimated τ_1 and τ_2 of Table 7.2 from the intercepts and slopes of Eq. (7.5):

$$\chi'_{ij}/\chi_{0ij} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right) \quad (7.6)$$

$$\chi''_{ij}/\chi_{0ij} = \frac{1}{A} [\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)] \quad (7.7)$$

The theoretical c_1 and c_2 are given in Table 7.3 in order to compare them with the experimental values obtained by graphically extrapolated values of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} in the limit $w_j = 0$ in Figures 7.5 and 7.6 and Eqs. (7.3) and (7.4). The Fröhlich's parameter A where $A = \ln(\tau_2/\tau_1)$ is given in Table 7.3 for each compound.

Table 7.2 : Slope and intercept of the linear equation of $(\chi_{0ij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} , correlation coefficient (r), minimum chisquare values, relaxation time τ_1 and τ_2 of the flexible part as well as the whole molecules, measured τ from Eq. (7.9) and (7.10), reported τ (Gopalakrishna) and most probable relaxation time τ_0 , together with symmetric τ_s and characteristic τ_{cs} from symmetric and asymmetric distribution parameters γ and δ of some monosubstituted anilines at 35°C under a 9.945 GHz (X-band microwave) electric field.

System with serial number and molecular weight (M_j)	Intercept and slope from Eq.(7.5) for $(\chi_{0ij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij}		Correlation Coefficient (r)	Chisquare Value ($\times 10^2$)	Estimated Relaxation times τ_1 and τ_2 (ps)	Most probable relaxation time $\tau_0 = \sqrt{\tau_1 \tau_2}$	Measured τ (ps) ^a	Ratio of slopes of χ''_{ij} and χ'_{ij} with w_j of Eq. (7.10)	
	Intercept (c)	Slope (m)						$(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}$	$(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}$
(i) o-anisidine $M_j = 0.123$ kg	0.6373	4.8390	0.7743	4.36	2.17	75.31	12.78	4.18	0.1560
(ii) m-anisidine $M_j = 0.123$ kg	0.6075	2.9047	0.9888	1.22	3.63	42.88	12.48	5.20	0.3033
(iii) p-anisidine $M_j = 0.123$ kg	1.4948	6.2149	0.8310	24.77	4.01	95.50	19.57	4.47	0.1824
(iv) o-toluidine $M_j = 0.107$ kg	1.2684	4.2603	0.9986	0.13	5.15	63.06	18.02	4.95	0.4025
(v) m-toluidine $M_j = 0.107$ kg	0.3501	2.4337	0.6864	30.10	2.46	36.51	9.48	4.18	0.1605
(vi) p-toluidine $M_j = 0.107$ kg	0.7348	4.7136	0.8687	-23.25	2.58	72.89	13.71	3.36	0.1755

System with serial number and molecular weight (M_j)	Relaxation times			
	τ (ps) ^b	τ (ps) ^c	τ (ps) ^d	τ (ps) ^e
(i) o-anisidine $M_j = 0.123$ kg	2.50	3.29	2.46	130.40
(ii) m-anisidine $M_j = 0.123$ kg	4.86	4.28	3.02	64.22
(iii) p-anisidine $M_j = 0.123$ kg	2.92	3.70	140.19	305.52
(iv) o-toluidine $M_j = 0.107$ kg	6.44	4.15	16.05	82.37
(v) m-toluidine $M_j = 0.107$ kg	2.57	4.01	5.85	458.51
(vi) p-toluidine $M_j = 0.107$ kg	2.81	3.34	1.38	12.07

^a Measured by the slope of χ''_{ij} against χ'_{ij} using the straight-line equation (7.9).

^b From the ratio of individual slopes. ^c By Gopalakrishna's method [11] ^d From the symmetric distribution parameter γ of Eq.(7.17).

^e From the asymmetric distribution parameter of Eq. (7.19).

7.3 Theoretical formulation for the dipole moment

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of the hf complex relative permittivity are written as

$$\epsilon'_{ij} = \epsilon_{\infty ij} + (1/\omega\tau)\epsilon''_{ij}$$

or
$$\epsilon'_{ij} - \epsilon_{\infty ij} = (1/\omega\tau)\epsilon''_{ij}$$

or
$$\chi'_{ij} = (1/\omega\tau)\chi''_{ij} \quad (7.8)$$

and
$$(d\chi''_{ij}/d\chi'_{ij}) = \omega\tau_j \quad (7.9)$$

The variation of susceptibility χ''_{ij} with χ'_{ij} Eq. (7.9) is caused by variation in concentrations, w_j 's, of the polar liquids under the fixed frequency of the electric field. As χ''_{ij} is, however, claimed to vary linearly with χ'_{ij} [10] of different concentrations and the frequency is fixed, the slope of χ''_{ij} with χ'_{ij} can conveniently be used to obtain τ_j from Eq. (7.9).

However, in case of monosubstituted anilines the variations of χ''_{ij} with χ'_{ij} , as seen in Figure 7.4, are not strictly linear. The ratio of individual slopes from the variations of χ''_{ij} and χ'_{ij} with w_j 's in Figures 7.2 and 7.3 is, however, thought to be a better representation of Eq. (7.9) to obtain τ_j where polar-polar interactions are supposed to be fully avoided.

Table 7.3 : Fröhlich's parameter A, relative contributions c_1 and c_2 due to theoretical τ_1 and τ_2 values of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} of Fröhlich's equations, (7.6) and (7.7), and those by the graphical method at $w_j \rightarrow 0$, symmetric γ and asymmetric distribution parameters δ of some monosubstituted anilines at 35°C under a 9.945 GHz (X-band microwave) electric field.

System with serial number	Fröhlich's parameter A = ln (τ_1/τ_2)	Estimated values of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} of Fröhlich's equations (7.6) and (7.7)		Weighted contributions c_1 and c_2 from Eq.(7.3) and (7.4)		Estimated values of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} from Figures 7.5 & 7.6 at $w_j \rightarrow 0$		Weighted contribution c_1 and c_2 from the graphical technique		Symmetric distribution parameter γ	Asymmetric distribution parameter δ
		c_1	c_2	c_1	c_2	c_1	c_2	γ	δ		
(i) o-anisidine	3.5469	0.5598	0.3458	0.5099	1.3664	0.7100	0.1470	0.7117	0.2570	0.5716	0.1360
(ii) m-anisidine	2.4692	0.5848	0.4011	0.4997	0.8952	0.3339	0.3094	0.2508	0.7791	0.2475	0.5671
(iii) p-anisidine	3.1703	0.4419	0.3656	0.4222	1.6317	0.2114	0.1523	0.2062	0.6360	0.4813	0.4111
(iv) o-toluidine	2.5051	0.4600	0.4035	0.4296	1.1665	0.4995	0.2638	0.5197	0.4708	0.3821	0.3524
(v) m-toluidine	2.6974	0.6661	0.3726	0.5517	0.7879	0.5894	0.1308	0.5839	0.1173	0.6650	0.1422
(vi) p-toluidine	3.3412	0.5432	0.3576	0.4818	1.3361	0.9550	0.1148	0.9889	-0.1933	0.1617	0.1853

Thus

$$\left(\frac{d\chi''_{ij}}{dw_j}\right)_{w_j \rightarrow 0} \cdot \left[\left(\frac{d\chi'_{ij}}{dw_j}\right)_{w_j \rightarrow 0}\right]^{-1} = \omega\tau_j \quad (7.10)$$

The imaginary part χ''_{ij} of χ^*_{ij} is [14,15]

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) (\varepsilon_{ij} + 2)^2 w_j \quad (7.11)$$

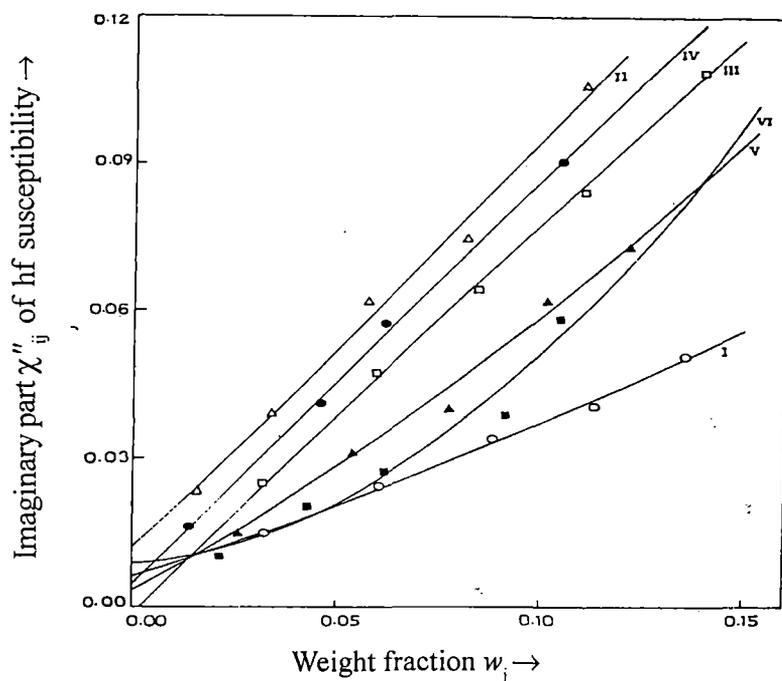


Figure 7.2. Variation of the imaginary part χ''_{ij} of the hf susceptibility against the weight fraction w_j of solute in benzene at 35°C under a 9.945 GHz electric field: (I) o-anisidine (—○—), (II) m-anisidine (—△—), (III) p-anisidine (—□—), (IV) o-toluidine (—●—), (V) m-toluidine (—▲—) and (VI) p-toluidine (—■—).

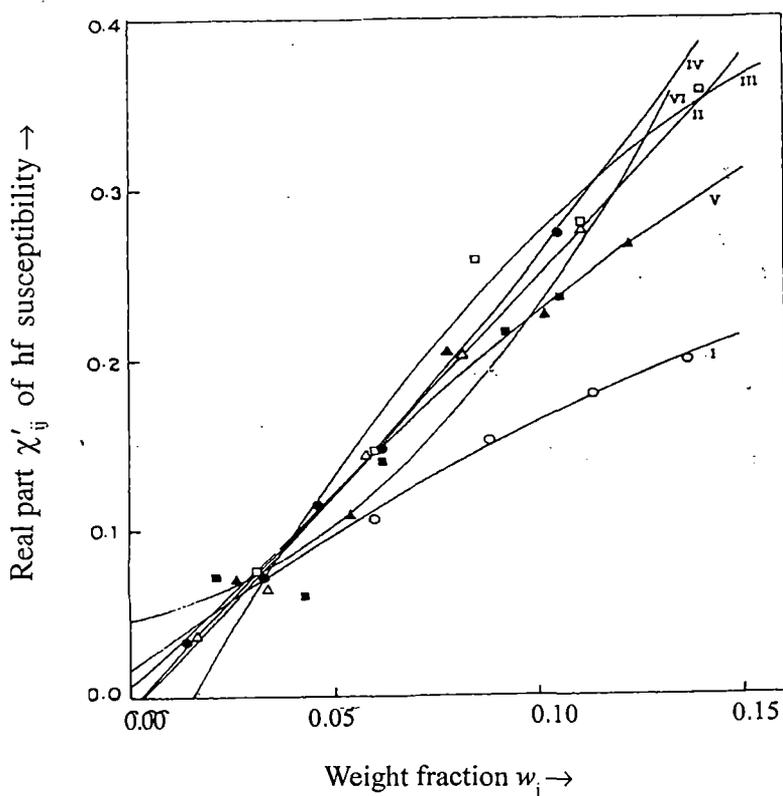


Figure 7.3. Variation of the real part χ'_{ij} of the hf susceptibility against the weight fraction w_j of solute in benzene at 35°C under a 9.945 GHz electric field: (I) o-anisidine (—○—), (II) m-anisidine (—△—), (III) p-anisidine (—□—), (IV) o-toluidine (—●—), (V) m-toluidine (—▲—) and (VI) p-toluidine (—■—).

Eq. (7.11), when differentiated with respect to w_j and at $w_j \rightarrow 0$ yields

$$\left(\frac{d\chi''_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) (\varepsilon_i + 2)^2 \quad (7.12)$$

At $w_j \rightarrow 0$, the density of solution ρ_{ij} and $(\varepsilon_{ij} + 2)^2$ tends to ρ_i and $(\varepsilon_i + 2)^2$ where ρ_i and ε_i are the density and relative permittivity of solvent i , respectively.

In comparison to earlier works presented elsewhere [15,16] the approximation that $\chi_{ij} \simeq \chi''_{ij}$, as $\sigma_{ij} \simeq \sigma''_{ij}$, is not necessary to obtain the μ_j 's from the τ_j 's where σ''_{ij} is the imaginary part of the complex hf conductivity and σ_{ij} is the total hf conductivity of the polar-nonpolar liquid mixture.

From Eqs. (7.10) and (7.12) one obtains

$$\omega\tau_j \left(\frac{d\chi'_{ij}}{dw_j}\right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) (\varepsilon_i + 2)^2$$

or

$$\mu_j = \left[\frac{27\varepsilon_0 M_j k_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 b} \right]^{1/2} \quad (7.13)$$

where τ_j and μ_j are the relaxation time and the dipole moment of the j th solute and ε_0 is the permittivity of free space, $8.854 \times 10^{-12} \text{ Fm}^{-1}$. Here N is the Avogadro number, 6.023×10^{23} ; ρ_i is the density of the solvent, 865 kg m^{-3} ; k_B is the Boltzmann constant, $1.38 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}$; ε_i is the dielectric relative permittivity of the solvent, benzene, 2.253; M_j is the molecular weight of the solute in kilogrammes; β is the linear coefficient of the $\chi'_{ij}-w_j$ curve at $w_j \rightarrow 0$; and $b = 1/(1+\omega^2\tau^2)$ is a dimensionless parameter involved with the measured τ_j .

Table 7.4 : Coefficients α, β and γ of the $\chi'_{ij}-w_j$ curve (Figure 7.3) with correlation coefficients and percentage of errors, dimensionless parameter b , estimated μ_j 's where μ is from $\mu_1 = \mu_2(c_1/c_2)^{1/2}$ and theoretical μ from bond angles and bond moments together with reported μ (Gopalakrishna [11]) of some monosubstituted anilines in benzene at 35°C under a 9.945 GHz (X-band microwave) electric field.

System with serial number and molecular weight (M_j)	Coefficients of the equation $\chi'_{ij} = \alpha + \beta w_j + \gamma w_j^2$			Correlation coefficient of $\chi'_{ij}-w_j$ equation	% of error involved in $\chi'_{ij}-w_j$ equation	Dimensionless parameters			Estimated dipole moments μ ($\times 10^{30}$ Cm)		
	α	β	γ			b_0^a	b_1^b	b_2^c	μ_0	μ_1	μ_2
(i) o-anisidine $M_j = 0.123$ kg	0.0149	1.7546	-2.8056	0.9960	0.24	0.6108	0.9820	0.0432	6.17	4.87	23.21
(ii) m-anisidine $M_j = 0.123$ kg	-0.0094	2.5108	0.4641	0.9968	0.19	0.6221	0.9511	0.1224	7.31	5.91	16.49
(iii) p-anisidine $M_j = 0.123$ kg	-0.0634	4.4003	-10.2107	0.9962	0.23	0.4010	0.9410	0.0273	12.06	7.87	46.23
(iv) o-toluidine $M_j = 0.107$ kg	0.0063	2.0495	4.7368	0.9979	0.14	0.4412	0.9062	0.0606	7.32	5.11	19.75
(v) m-toluidine $M_j = 0.107$ kg	-0.0078	2.8140	-4.6071	0.9782	1.30	0.7404	0.9769	0.1613	6.62	5.76	14.19
(vi) p-toluidine $M_j = 0.107$ kg.	0.0464	0.3863	14.5432	0.9593	2.41	0.5770	0.9747	0.0460	2.78	2.14	9.84

Systems with serial number and molecular weight (M_j)	Dipole moments		
	Estimated μ ($\times 10^{30}$ Cm) ^a	Theoretical μ ($\times 10^{30}$ Cm) ^c	μ ($\times 10^{30}$ Cm) ^f
(i) o-anisidine $M_j = 0.123$ kg	14.18	3.40	4.50
(ii) m-anisidine $M_j = 0.123$ kg	12.32	5.50	6.17
(iii) p-anisidine $M_j = 0.123$ kg	23.51	6.30	6.53
(iv) o-toluidine $M_j = 0.107$ kg	11.98	4.63	5.77
(v) m-toluidine $M_j = 0.107$ kg	11.87	3.43	5.17
(vi) p-toluidine $M_j = 0.107$ kg	5.91	5.13	5.30

$$^a b_0 = \frac{I}{1 + \omega^2 \tau_0^2}$$

^c From bond angles and bond moments.

^f From Gopalakrishna's method [11].

$$^b b_1 = \frac{I}{1 + \omega^2 \tau_1^2}$$

$$^c b_2 = \frac{I}{1 + \omega^2 \tau_2^2}$$

$$^d \text{ From } \mu_1 = \mu_2 \left(\frac{c_1}{c_2} \right)^{1/2}$$

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 of $\chi'_{ij}-w_j$ curves of Figure 7.3. The μ 's thus obtained from Eq. (7.13) are given in Table 7.4 in order to compare with those of Gopalakrishna [11] and μ_{theo} 's obtained from bond angles and bond moments of the substituent polar groups of the molecules of Figure 7.8.

7.4. Symmetric and characteristic relaxation times τ_s and τ_{cs}

The symmetric and asymmetric distribution parameters γ and δ appear in the following equations :

$$\chi_{ij}^*/\chi_{0ij} = \frac{1}{1+(j\omega\tau_s)^{1-\gamma}} \quad (7.14)$$

$$\chi_{ij}^*/\chi_{0ij} = \frac{1}{(1+j\omega\tau_{cs})^\delta} \quad (7.15)$$

Although the left-hand side of Eqs. (7.14) and (7.15) are identical, the former is associated with the symmetric relaxation time τ_s and latter with the characteristic relaxation time τ_{cs} . Separating the real and imaginary parts of Eqs.(7.14) and (7.15) and rearranging them in terms of $(\chi'_{ij}/\chi_{0ij})_{\omega j \rightarrow 0}$ and $(\chi''_{ij}/\chi_{0ij})_{\omega j \rightarrow 0}$ obtained from Figures 7.5 and 7.6 the γ and τ_s were found using.

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{0ij}}\right) \frac{\chi'_{ij}}{\chi''_{ij}} - \frac{\chi''_{ij}}{\chi_{0ij}} \right] \quad (7.16)$$

and

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{(\chi'_{ij}/\chi''_{ij}) \cos(\gamma\pi/2) - \sin(\gamma\pi/2)} \right]^{1/(1-\gamma)} \quad (7.17)$$

Again δ and τ_{cs} can be obtained from Eq. (7.15)

$$\tan(\phi\delta) = \frac{\chi''_{ij}}{\chi'_{ij}} \quad (7.18)$$

and

$$\tan \phi = \omega\tau_{cs} \quad (7.19)$$

As ϕ cannot be evaluated directly, an arbitrary theoretical curve between $(1/\phi) \log(\cos\phi)$ against ϕ in degrees was drawn in Figure 7.7, from which

$$\frac{1}{\phi} \log (\cos \phi) = \frac{\log \left[\left(\chi'_{ij} / \chi_{0ij} \right) / \cos (\phi \delta) \right]}{\phi \delta} \quad (7.20)$$

can be found. The known value of $(1/\phi) \log (\cos \phi)$ is used to obtain ϕ . With known ϕ and δ , τ_{cs} were found out from Eqs. (7.18) and (7.19). τ_s and τ_{cs} so evaluated are given in Table 7.2 in order to compare with values of τ by Murthy *et al* [10], Gopalakrishna [11] and τ_1 and τ_2 determined by double relaxation methods. The estimated values of γ and δ are however, given in Table 7.3.

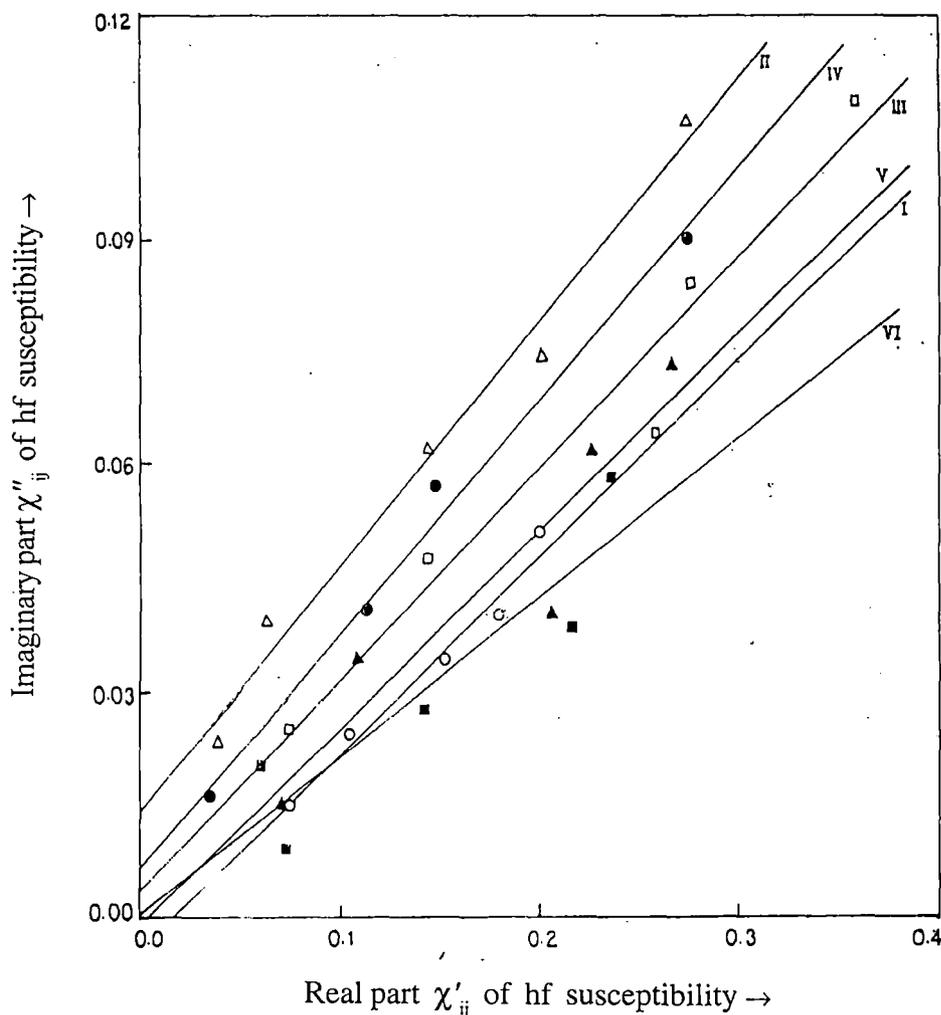


Figure 7.4. Linear plot of Imaginary part χ''_{ij} of the hf susceptibility against the real part χ'_{ij} of anisidine and toluidine in benzene at 35°C under a 9.945 GHz electric field: (I) o-anisidine (—○—), (II) m-anisidine (—△—), (III) p-anisidine (—□—), (IV) o-toluidine (—●—), (V) m-toluidine (—▲—) and (VI) p-toluidine (—■—).

7.5. Results and discussion

The least-squares fitted linear equations of $(\chi_{0ij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} for different weight fractions w_j 's of the monosubstituted anilines in benzene at 35°C under a 9.945 GHz electric field are shown graphically in Figure 7.1, with the symbols denoting the experimental points. The experimental points are found to satisfy Eq. (7.5). χ'_{ij} and χ''_{ij} are the real and imaginary parts of the complex dielectric orientational susceptibility χ^*_{ij} and χ_{0ij} is the low-frequency dielectric susceptibility which is real. They are, however, derived from the measured relative permittivities [7] ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ of Table 7.1. The linearity of all the curves of Figure 7.1 are confirmed by correlation coefficients, r 's lying in the range 0.6894-0.9986. The chisquare test of all the curves were again made to support their linearity. The slopes and intercepts of all the linear curves of Figure 7.1 are placed in the second and third columns of Table 7.2. The chisquare values are, however, large for *o*-anisidine, *p*-anisidine and *m*-toluidine probably because of the large errors introduced in the ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ measurements for the molecules. In order to find the existence of double relaxation phenomena, accurate measurements of ϵ_{0ij} and $\epsilon_{\infty ij}$ are necessary. The refractive index n^2_{Dij} measured by Abbe's refractometer yields $\epsilon_{\infty ij} = n^2_{Dij}$ [6], although Cole-Cole [3,4] plot often gives $\epsilon_{\infty ij}$ as 1-1.15 times n^2_{Dij} .

The slope and intercept of each straight-line equation (7.5), obtained from χ'_{ij} , χ''_{ij} and χ_{0ij} of different w_j 's of Table 7.1 by least-squares fitting are used to determine τ_1 and τ_2 for each compound, as seen in the sixth and seventh columns of Table 7.2. τ_2 's are found to increase gradually from the *meta* to the *ortho* and to the *para* forms for all the anisidines and toluidines, probably due to the presence of the C→NH₂ group in them. The electric field of nearly 3 cm wavelength greatly influences the C→NH₂ group. On the other hand, τ_1 increases from *ortho* to *para* for the anisidines, while the reverse is true for the toluidines. The increase in the τ_1 values indicates that the flexible parts of the molecules

are more loosely bound to the parent molecules [17,18], which signifies that the material property of the system is undergoing relaxation.

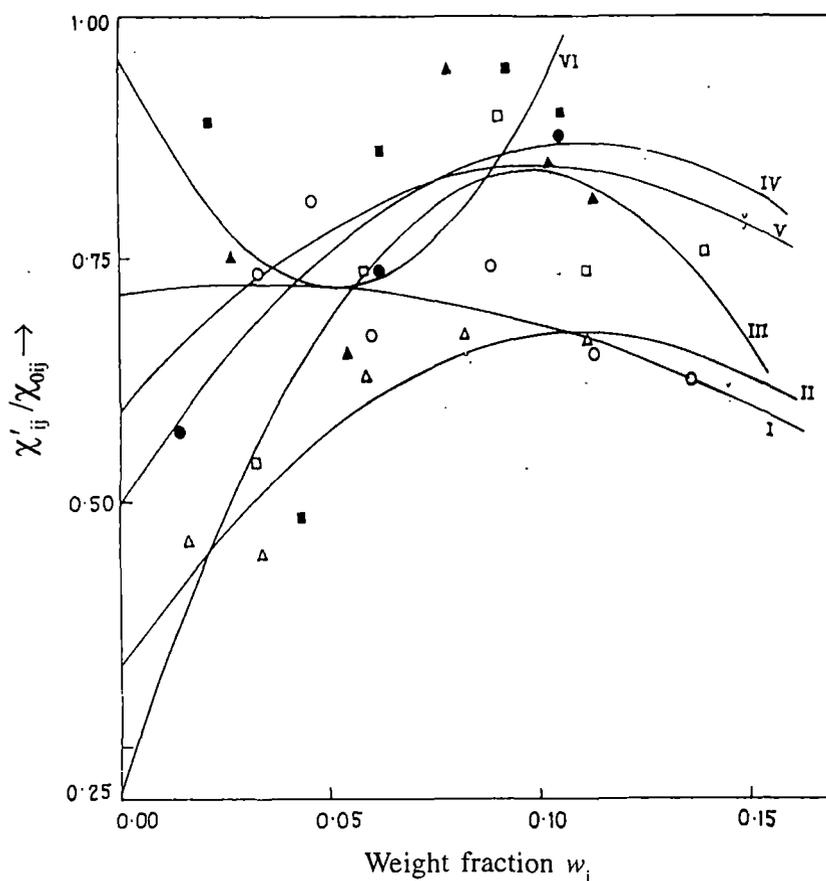


Figure 7.5. Plot of χ''_{ij}/χ'_{0ij} against the weight fraction w_j of isomers of anisidine and toluidine in benzene at 35°C under a 9.945 GHz electric field : (I) o-anisidine (—○—), (II) m-anisidine (—△—), (III) p-anisidine (—□—), (IV) o-toluidine (—●—), (V) m-toluidine (—▲—) and (VI) p-toluidine (—■—).

In the absence of a reliable τ_j under a hf electric field we tried to calculate τ_j 's from the slopes of the least-squares fitted straight-line equation of χ''_{ij} against χ'_{ij} as claimed by Murthy *et al* [10], and give them in the ninth column of Table 7.2. The available experimental points were found to deviate from linearity as illustrated in Figure 7.4. The individual plots of χ''_{ij} and χ'_{ij} against the w_j 's of the isomers of the anisidines and toluidines are not strictly linear as observed in Figures 7.2 and 7.3. This at once prompted us to use the ratio of the individual slopes of variations of χ''_{ij} and χ'_{ij} with the w_j 's at $w_j \rightarrow 0$ of Figures 7.2 and 7.3

to obtain τ_j 's. The τ_j 's thus obtained agree well with τ_1 from double relaxation and Gopalakrishna's [11] methods. This confirms the basic soundness of the latter method to determine τ_j where polar-polar interactions are fully avoided. Moreover, it shows that the hf dielectric susceptibility measurement yields a microscopic relaxation time whereas the double relaxation method gives both microscopic and macroscopic τ_1 and τ_2 , as observed elsewhere [19].

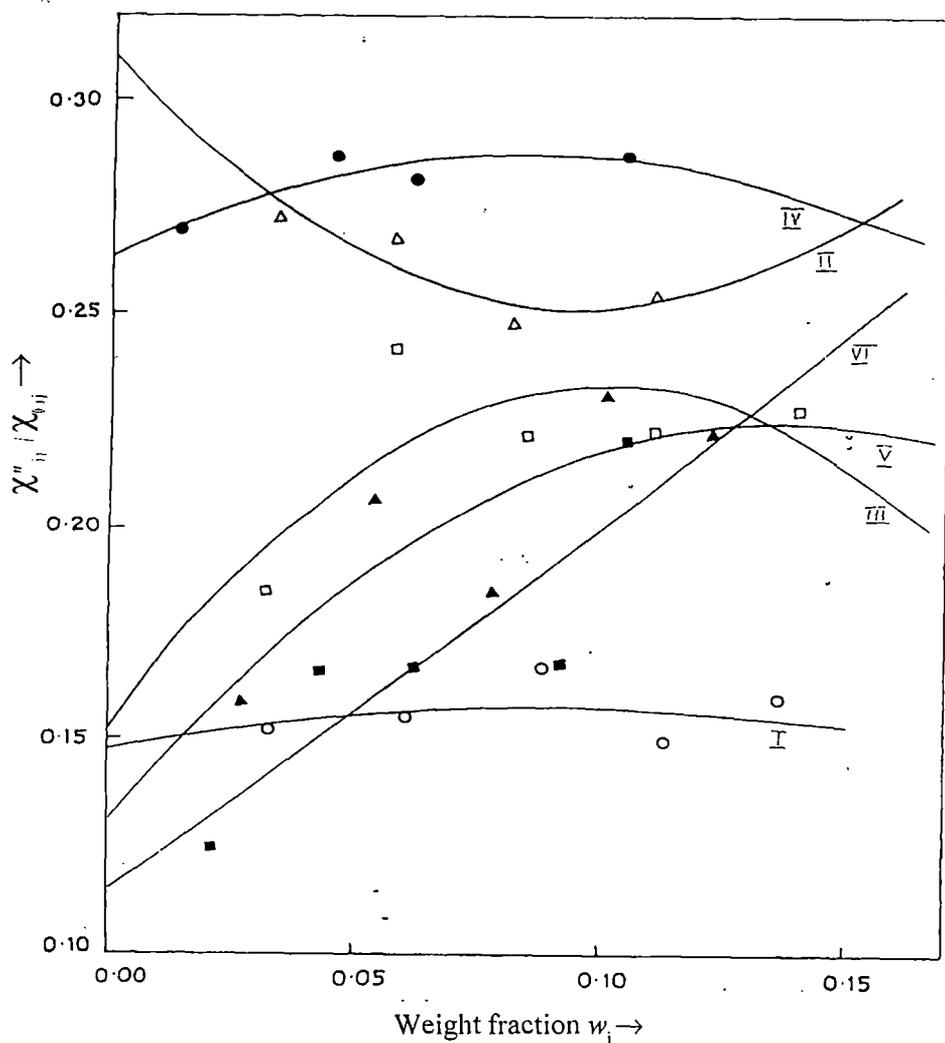


Figure 7.6. Plot of χ''_{ij}/χ'_{0ij} against the weight fraction w_j of isomers of anisidine and toluidine in benzene at 35°C under a 9.945 GHz electric field : (I) o-anisidine (—○—), (II) m-anisidine (—△—), (III) p-anisidine (—□—), (IV) o-toluidine (—●—), (V) m-toluidine (—▲—) and (VI) p-toluidine (—■—).

Large τ_2 's signify the larger sizes of the rotating units of solute-solvent, i.e. monomer formation under a hf electric field. The existence of a distribution of τ 's between τ_2 and τ_1 helps us to test the symmetric and asymmetric distribution parameters γ and δ of such compounds. These are calculated from Eqs. (7.16) and (7.18) with the values of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} at $w_j \rightarrow 0$ of Figures 7.5 and 7.6. The values of $(1/\phi) \log(\cos\phi)$ against ϕ in degrees as shown in Figure 7.7 is essential to obtain δ . Knowing ϕ from the curve of Figure 7.7, δ 's were obtained. γ and δ so obtained are seen in the 11th and 12th columns of Table 7.3. The values of γ establishes the non-rigid behaviour of the molecules in benzene in a 9.945 GHz electric field. They obey symmetric relaxation phenomena as δ 's are found to be low.

The symmetric relaxation time τ_s from Eq. (7.17) agrees with the τ_1 's and τ 's due to Gopalakrishna's method [11] indicating symmetric relaxation behaviour for such molecules; but in case of p-anisidine the agreement is poor. It may probably be due to the experimental uncertainty or the presence of two flexible polar units in a line. The characteristic relaxation time τ_{cs} obtained from δ gives high values. They thus rule out the applicability of asymmetric relaxation behaviour for such polar molecules in benzene.

We find the relative contributions c_1 and c_2 towards dielectric dispersions for each polar compound, reported in tables and figures from Eqs. (7.3) and (7.4) for fixed τ_1 and τ_2 of Eq. (7.5) and χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} of Fröhlich's equations, (7.6) and (7.7). The same could, however, be obtained by a graphical technique. The c_1 and c_2 by both the methods are given in Table 7.3. The Fröhlich's parameter, A , which predicts the temperature variation of the width of the distribution of τ . A is equal to $\ln(\tau_2/\tau_1)$. c_1 and c_2 obtained with χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} of Fröhlich's equations and the least-squares fitted graphically estimated values from Figures 7.5 and 7.6 satisfy $c_1 + c_2 \simeq 1$. The variation of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} with w_j usually do not obey Bergmann *et al's* [13] equation (7.1) and (7.2), as observed elsewhere [17, 18]. For p-toluidine c_2 becomes negative as seen in the tenth column of

Table 7.3. This arises due to the inertia of the whole molecule with respect to its flexible part under nearly 10 GHz electric field [7,19].

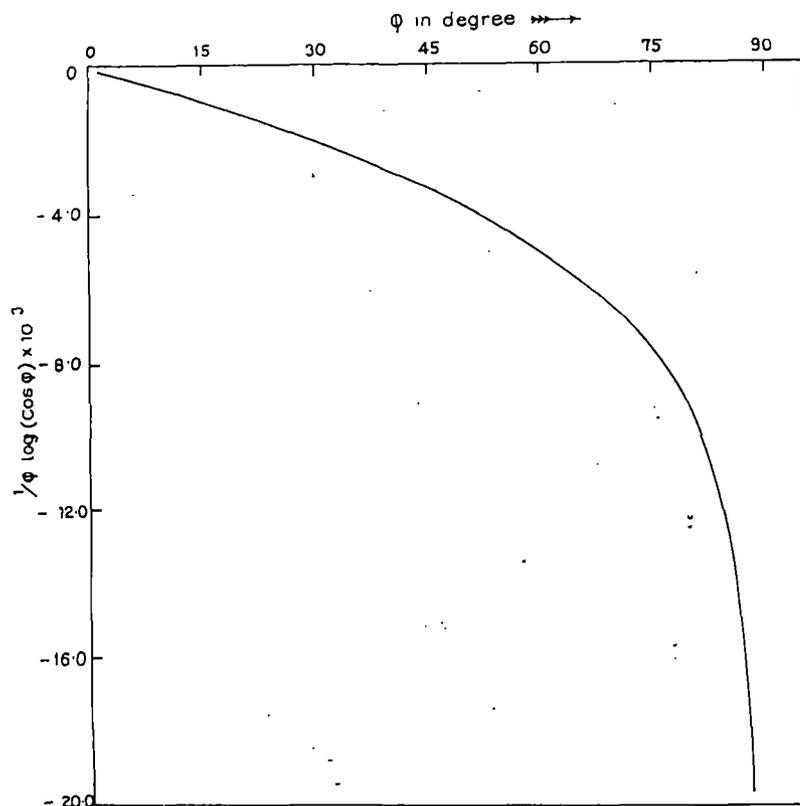


Figure 7.7. Variation of $1/\phi \log(\cos \phi) \times 10^3$ against ϕ in degree

The dipole moments μ_1 and μ_2 of the flexible parts and whole molecules of all the compounds under investigation were obtained in terms of the dimensionless parameters b_1 and b_2 related to τ_1 and τ_2 and the linear coefficient β of the $\chi'_{ij}-w_j$ curve of Figure 7.3. They are placed in the 11th and 12th columns of Table 7.4 together with μ_0 in terms of b_0 related to τ_0 , where τ_0 is the most probable relaxation time ($=\sqrt{\tau_1 \tau_2}$) for the distribution of τ 's between two fixed values. The correlation coefficients, r 's, of the $\chi'_{ij}-w_j$ curves were also estimated and are entered in the fifth column of Table 7.4, but only to show how far the χ'_{ij} 's are correlated with the w_j 's. The corresponding percentage of error in terms of r are entered in the sixth column of Table 7.4. The variation of the χ'_{ij} 's with the w_j 's gives a reliable slope of β to yield reliable μ_1 , μ_2 and μ_0 values. Almost

all $\chi'_{ij}-w_j$ curves in Figure 7.3 show a tendency to be closer in the region $0.00 \leq w_j \leq 0.03$, indicating an almost identical polarity of the solute molecules in addition to solute-solvent (monomer) and solute-solute (dimer) formations [9].

The solvent, benzene, is a cyclic compound with three double bonds and six p-electrons on six carbon atoms. Hence the $\pi - \pi$ interaction or resonance effect combined with an inductive effect, known as the mesomeric effect, is expected to play an important role in the measured hf μ_j . Special attention is therefore, paid to obtain the conformational structures of the isomers of anisidine and toluidine from the available bond angles and bond moments of the substituent polar groups. The polar groups C—NH₂ ($\angle 142^\circ$) C—OCH₃ ($\angle 57^\circ$) and C—CH₃ ($\angle 180^\circ$) having bond moments of 3.90×10^{-30} , 2.40×10^{-30} and 1.23×10^{-30} Cm, respectively, are used to obtain the theoretical μ_{theo} of Figure 7.8. In the case of the anisidines, the amino group, —NH₂, exhibits a mesomeric effect by pushing the electrons towards the C atom of the benzene ring, but the inductive effect is more prominent in the —OCH₃ group rather than mesomeric effect; so the latter pulls the electrons from the C atom of the ring. Hence the resultant μ_{theo} increases from the *para* to the *ortho* and to the *meta* forms, as seen in Table 7.4. In the case of the methyl group, —CH₃, in toluidines the inductive effect is important as the sp² hybridized C atom of benzene is more electronegative than the C atom of the —CH₃ group, which is sp³ hybridized. Thus the direction of the bond moment is towards the benzene ring. For the —NH₂ group the mesomeric and inductive effects act oppositely, but as the mesomeric effect is more pronounced so resultant bond moment is toward the C₆H₆ ring. In the *ortho*, *meta* and *para* toluidines, the angle between the —CH₃ and —NH₂ groups are 60°, 120° and 180°, respectively. Hence there is an increment in μ_{theo} from the *ortho* to the *meta* and to the *para* forms (Table 7.4).

In the absence of reliable μ_j values of these compounds Gopalakrishna's method [11] was employed to obtain hf μ_j 's (reported data). The close agreement between the reported μ_j (Gopalakrishna), μ_1 and μ_{theo} as seen in Table 7.4

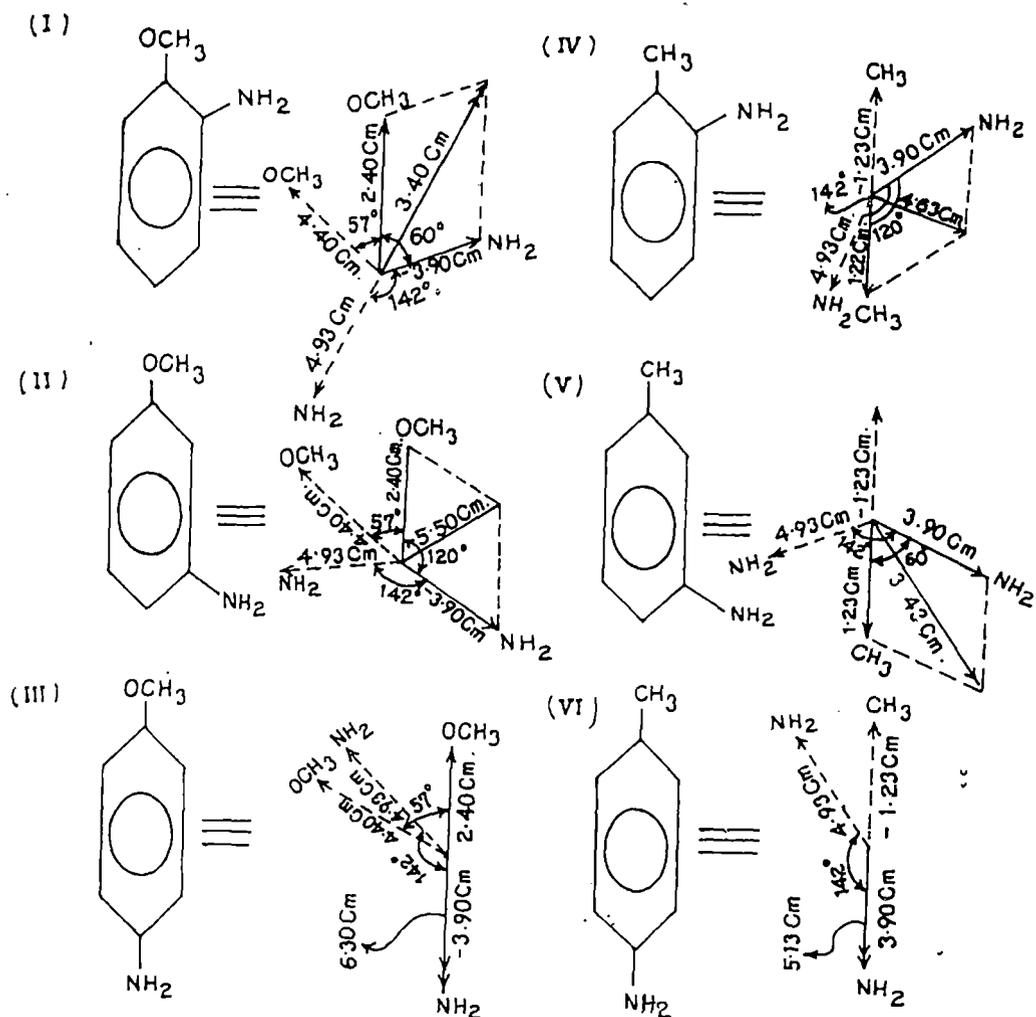


Figure 7.8: Conformational structures of isomers of anisidine and toluidine : (i) ortho anisidine, (ii) meta anisidine, (iii) para anisidine, (iv) orthotoluidine, (v) meta toluidine, (vi) para toluidine.

[Bond moment $\times 10^{30}$ Coulomb metre (C.m) given in figures]

establishes the basic soundness of the method prescribed for obtaining $hf\mu_j$. It also confirms the fact that a part of the molecule is rotating under a nearly 3 cm wavelength electric field.

7.6 Conclusions

The theoretical consideration for the effective utilization of the established symbols of the dielectric susceptibilities, χ_{ij} 's, from the dielectric relative permittivities ϵ_{ij} 's appear to be sound to study the dielectric relaxation mechanism as χ_{ij} 's are directly concerned with orientational polarization. The significant equations in terms of the χ_{ij} 's help one to grasp new physical insight into polar-polar and polar-nonpolar molecular interactions in solution. The single-frequency measurement of the relaxation parameters thus provides a unique method to obtain macroscopic and microscopic relaxation times and hence dipole moments of the whole and the flexible parts of the molecules. The estimation of τ from the linear equation (7.5) is a very simple, straightforward and significant one to obtain μ from equation (7.13) in terms of linear coefficient β of the familiar $\chi'_{ij}-w_j$ curve. The correlation coefficient r and the chisquare values signify the minimum error introduced into the desired parameters. The molecules under identical states show interesting phenomena of a double or, often, a single relaxation mechanism depending upon the solvent used. The probability of showing the double relaxation phenomena of monosubstituted anilines in benzene depends upon the electric field frequency of nearly 10 GHz. Various types of molecular associations, such as solute – solute and solute – solvent interactions, are thus inferred from the usual departure of graphically fitted plots of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} with w_j following Bergmann's equations [13]. Non-rigid characteristics of the molecules are ascertained by estimation of symmetric and asymmetric distribution parameters in benzene. The molecular associations are also supported by the conformational structures of the molecules in which the mesomeric, inductive and electromeric effects play prominent roles.

References

- [1] A Sharma and D R. Sharma *J. Phys. Soc. Japan* **61** (1992), 1049.
- [2] S K Sit, N Ghosh, U Saha and S Acharyya *Indian J. Phys.* **71B** (1997),533.
- [3] K S Cole and R H Cole *J. Chem. Phys.* **9** (1941), 341.
- [4] D W Davidson and R H Cole *J. Chem. Phys.* **19** (1951) 1484.
- [5] A K Jonscher *Physics of Dielectric Solids, Invited Papers* ed. C.H.L. Goodman (1980) Canterbury.
- [6] S C Srivastava and S Chandra *Indian J. Pure & Appl Phys.* **13** (1975) 101.
- [7] S K Sit and S Acharyya *Indian J. Pure & Appl. Phys.* **34** (1996) 255.
- [8] A K. Jonscher *Inst. Phys. Conference (Canterbury)* ed. CHL Goodman (1980).
- [9] N Ghosh, A Karmakar, S K Sit and S Acharyya *Indian J. Pure & Appl. Phys.* **38** (2000) 574.
- [10] M B R Murthy, R L Patil and D K Deshpande *Indian J.Phys.* **63B** (1989) 491.
- [11] K V Gopalakrishna *Trans. Faraday Soc.* **53** (1957) 767.
- [12] H Fröhlich *Theory of Dielectrics* (Oxford : Oxford University Press) 1949.
- [13] K Bergmann, D M Roberti and C P Smyth *J. Phys. Chem.* **64**(1960) 665.
- [14] C P Smyth *Dielectric Behaviour and Structure* (New York :McGraw-Hill).(1955)
- [15] K Dutta, S K Sit and S Acharyya *Pramana : J. Phys.* **57** (2001), 775.

- [16] N Ghosh, R C Basak, S K Sit and S Acharyya *J. Mol. Liquids* **85** (2000)375.
- [17] U Saha, S K Sit, R C Basak and S Acharyya *J. Phys. D : Appl. Phys.* **27** (1994) 596.
- [18] S K Sit, R C Basak, U Saha and S Acharyya *J. Phys. D: Appl. Phys.* **27** (1994), 2194.
- [19] S K Sit, N Ghosh and S Acharyya *Indian J. Pure. & Appl. Phys.* **35** (1997)329.